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Synthesis and properties of magnetite-dispersed carbon by pressure pyrolysis of divinylbenzene–vinylferrocene with water

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Magnetite-dispersed carbon was synthesized by pressure pyrolysis of the divinylbenzene–vinylferrocene system in the presence of water at 125 MPa below 700° C. Supercritical water influenced the phase separation of oligomers formed during the pyrolysis to give carbons with various morphologies, such as spherulitic, coalescing spherulitic and polyhedral carbon, depending upon the concentration of water. Carbon spherulites from 5 to 10 μm diameter dispersed with magnetite particles (<100 nm) were synthesized by pyrolysis of divinylbenzene–5.1 mol% vinylferrocene and 20.0 wt% water at 550° C and 125 MPa. The specific area of magnetite-dispersed carbon synthesized at 600° C and 125 MPa was 92 $m^2 g^{-1}$ after heat treatment at 800° C for 1 h. The specific area of the carbon specimen increased with decreasing pyrolysis temperature of the parent copolymers from 700 to 550° C. The Curie temperature of magnetite-dispersed carbon was 585° C. Magnetite dispersed in the carbon matrix was reduced to wüstite during the further heat treatment in vacuum. The saturation magnetization of magnetite-dispersed carbon was 79% of the theoretical value, and changed in proportion to the concentration of iron in the carbon matrix.

1. Introduction

The pressure pyrolysis of organic compounds has been utilized for the synthesis of carbon because of its high carbon yield and the control of morphology of resultant carbons.

Metal-dispersed carbon of controlled morphology constitutes many kinds of applications such as magnetic materials and catalysts.

Organometallic polymers are versatile starting materials for the synthesis of carbons dispersed finely with metal particles via the pyrolysis method. Marsh *et al.* [1] described the mesophase structure obtained by the carbonization of a mixture of anthracene and ferrocene under pressure. Hirano *et al.* [2, 3] synthesized iron-dispersed carbons with various morphologies by the pressure pyrolysis of divinylbenzene copolymerized with vinylferrocene. Several ferromagnetic and alloy particles can also be dispersed uniformly in the carbon matrix by the pressure pyrolysis of organometallic polymers [4–6].

The crystallinity and particle size of metals in the carbon matrix have been found to depend strongly upon the properties of both the carbon–metal bond of organometallic compounds and the carbon–carbon bond of the polymer matrix [4, 7, 8]. The morphology of as-prepared carbon is affected by the concentration of metals in a starting polymer as well as pyrolysis conditions [3].

The present paper describes the synthesis and properties of magnetite-dispersed carbon by pressure pyrolysis of divinylbenzene–vinylferrocene in the presence of supercritical water. Spherulitic carbon dispersed with magnetite particles was synthesized by the selection of pyrolysis conditions of the parent organoiron copolymer. The specific surface area and magnetic properties of magnetite-dispersed carbon were also investigated.

2. Experimental procedure

Vinylferrocene (VF) was prepared according to Arimoto and Haven [9]. Commercially available divinylbenzene (a mixture of 55% *m*- and *p*-divinylbenzene and 45% ethylbenzene) was employed as the organic copolymer for the carbon matrix.

Pressure pyrolyses were carried out in a hydrothermal apparatus of the cold-seal type. The mixture solution of vinylferrocene (VF), divinylbenzene (DVB) and water was sealed into a thin-walled gold capsule of 3.0 or 5.0 mm diameter and 50 mm length.

Various solutions of DVB containing VF and water were polymerized at 300° C and 100 MPa for 2 h and then pyrolysed at temperatures from 550 to 700° C and 125 MPa for 3 h. The heating rate was 10° C min^{-1} at 125 MPa. The pressure was kept constant by releasing water as the pressure-transporting medium during heating. The pressure was measured with a calibrated Heise gauge and the temperature was measured with a calibrated sheathed thermocouple set inside the pressure vessel. The sample was quenched after an experimental run.

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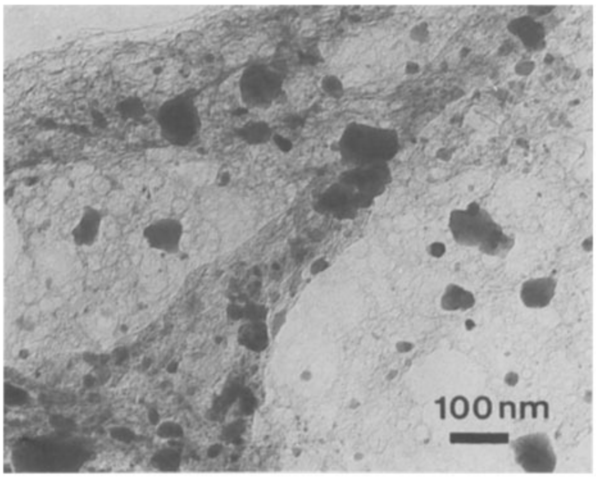


Figure 1 Microstructure of magnetite-dispersed carbon formed from DVB–5.1 mol % VF by pyrolysis at 550° C and 125 MPa.

The yield of carbon was as high as about 75% of the starting polymer in weight. The carbonized product was analysed by X-ray diffraction (XRD) analysis. The synthesized magnetite-dispersed carbon was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron diffraction analysis.

Magnetite-dispersed carbon set in a graphite crucible was heat-treated at temperatures from 700 to 850° C in a flow of nitrogen. Then, the specific surface area was measured by an analyser utilizing the continuous flow method. As-prepared magnetite-dispersed carbon was extracted with tetrahydrofuran (THF) at room temperature and then the THF insoluble solid was collected by centrifuging.

The thermomagnetization curve of magnetite-dispersed carbon was measured with a magnetic balance from room temperature to 700° C. The specimen was outgassed under vacuum for several hours at 250° C and then sealed into a quartz capsule (7 mm diameter and about 25 mm length) under vacuum prior to the magnetic susceptibility measurement. A vibrating sample magnetometer (VSM) was employed for the evaluation of the saturation magnetization of magnetite-dispersed carbons at room temperature.

3. Results and discussion

3.1. Synthesis of magnetite-dispersed carbon

DVB–5.1 mol % VF containing 17.6 wt % water (molar ratio of water: VF = 54.3) was polymerized at 300° C and 100 MPa for 2 h and successively pyrolysed at 550° C and 125 MPa for 3 h. The carbon thus formed had the morphology of coalescing spherulites, and showed ferromagnetism.

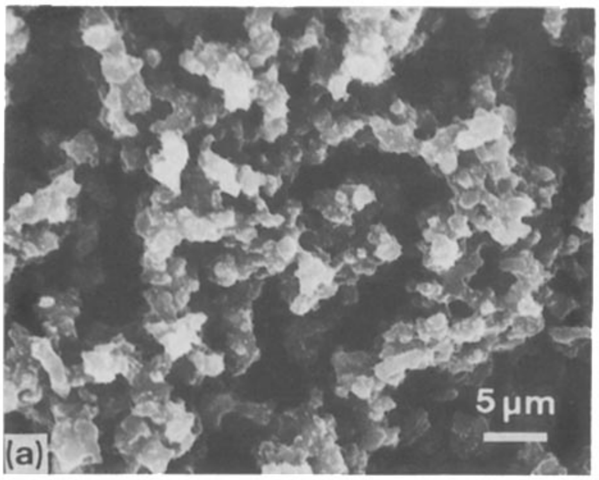
The XRD profile of the product was composed of the diffraction lines at $2\theta = 25.5, 30.1, 35.4, 43.1, 57.0$ and 62.5° (Cu$K\alpha$). The broad diffraction line centred at $2\theta = 25.5°$ is attributed to the turbostratic carbon. The other sharp diffraction lines are ascribed to those of magnetite (Fe_3O_4).

Iron as a pyrolysed product was oxidized readily with supercritical water to yield magnetite during the pyrolysis of DVB–VF copolymer, whereas cementite (Fe_3C) was formed from the DVB–VF copolymer under the same conditions without the addition of water [3, 7].

The microstructure of the pyrolysis product is shown in Fig. 1. The black particles less than 100 nm in the carbon matrix were confirmed to be magnetite by electron diffraction.

3.2. Morphology of magnetite-dispersed carbon

DVB–5.1 mol % VF was pyrolysed in the presence of



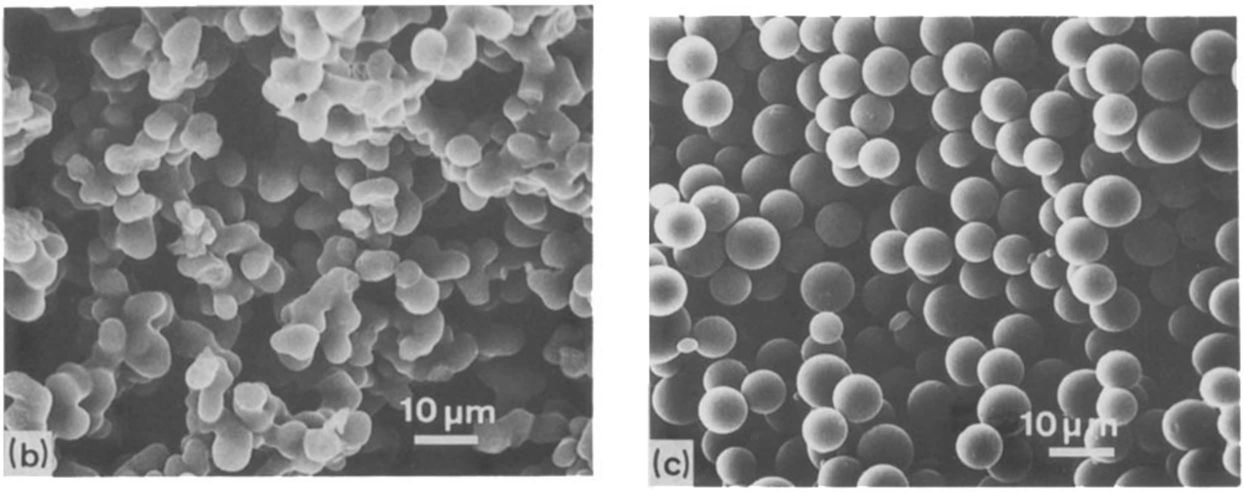


Figure 2 Morphologies of carbons prepared from DVB–5.1 mol % VF containing various concentrations of water by pyrolysis at 550° C and 125 MPa. (a) Polyhedral carbons (5.5 wt % water), (b) coalescing spherulitic carbons (10.9 wt % water), (c) spherulitic carbons (20.0 wt % water).

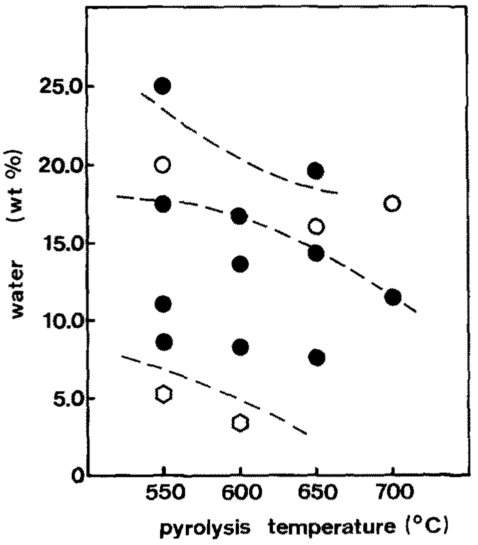


Figure 3 Morphologies of carbons formed from DVB–5.1 mol % VF at various concentrations of water and temperatures under 125 MPa. (○) spherulite, (●) coalescing spherulite, (⬡) polyhedron.

3.4 to 27.5 wt % water at temperatures between 550 and 700° C under 125 MPa.

Figs 2a, b and c show the representative morphologies of magnetite-dispersed carbons formed at 550° C at water concentrations of 5.5, 10.9 and 20.0 wt %, respectively. As the concentration of water in the starting materials increased at 550° C, the morphology of carbon tended to change from coalescing polyhedra (Fig. 2a) to spherulites (Fig. 2c) via coalescing spherulitic carbon of interconnected structure (Fig. 2b).

The morphology of carbon formed under these conditions is summarized in Fig. 3. The change of morphology with the concentration of water at temperatures from 600 to 700° C was similar to that at 550° C. Spherulites of uniform diameter from 5 to 10 μm were also formed by pyrolysis at temperatures above 550° C when the concentration of water was about 17 wt %. However, spherulites coalesced again to give the interconnected structure when the concentration of water was higher than about 20 wt %.

The morphology of resultant carbon evidently reflects the coexistent supercritical water. A similar effect of the coexistence of supercritical water was confirmed by the phase separation in the system of *p*-terphenyl and water [10].

Heat-treatment temperature influences the solubility of iron particles, the viscosity, density and the resultant phase separation of liquid phases during pyrolysis. The liquid–liquid phase separation between the oligomers having different molecular weight is responsible for the morphology of carbon [11]. When the concentration of water is low, iron particles have an effect on the phase separation of fluid phase of oligomers, affording a polyhedral carbon of irregular shape similar to that formed in the absence of water [3]. At a suitable pyrolysis temperature and concentration of water, spherulitic carbon is considered to be formed by the phase separation between the fluid phase of iron-containing oligomers of higher molecular weight and supercritical water as a lower molecular weight component.

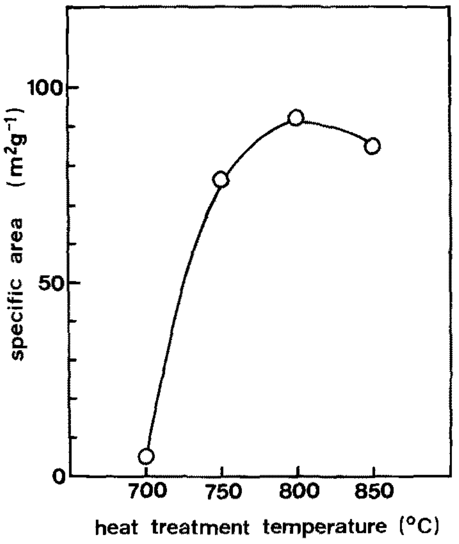


Figure 4 Specific area of magnetite-dispersed carbon heat treated at various temperatures for 1 h in a flow of nitrogen.

3.3. Specific areas of magnetite-dispersed carbon

3.3.1. Changes of specific area by heat treatment

Magnetite-dispersed carbon was synthesized from DVB–5.1 mol % VF including 12.0 wt % water at 600° C and 125 MPa for 3 h. The surface area of the as-prepared magnetite-dispersed carbon was less than 1.0 $m^2 g^{-1}$.

Variation of specific area with heat-treatment temperature is shown in Fig. 4. The specific area was about 5.0 $m^2 g^{-1}$ after heat treatment at 700° C for 1 h in a flow of nitrogen. However, the surface area increased abruptly from 5.0 to 77.0 $m^2 g^{-1}$ by heat treatment at 750° C, and reached the maximum value of 92 $m^2 g^{-1}$ by heat treatment at 800° C.

The XRD profile of magnetite in the carbon matrix treated at 700° C was almost unchanged from that of magnetite in as-prepared carbon. However, the reaction of magnetite with the matrix carbon proceeded significantly after heat treatment at 750° C, as indicated by the fact that the intensity of the diffraction lines of magnetite decreased markedly. Therefore, the increase in surface area is attributable not only to the removal of carbonaceous layers on the surface by heat treatment but also to the increase of micropores in the carbon matrix by the reaction of magnetite with carbon to release carbon oxide.

3.3.2. Effect of pyrolysis temperature of organoiron copolymer on specific area

Magnetite-dispersed carbon was synthesized from DVB–5.1 mol % VF and 12.0 wt % water by pressure pyrolysis at temperatures from 550 to 700° C and 125 MPa. As-prepared magnetite-dispersed carbon was heat-treated at 800° C for 10 min and then the specific area was measured. The specific area and the weight per cent of THF soluble component are correlated to the pyrolysis temperature in Fig. 5.

The specific area of the heat-treated specimen was dependent upon the pyrolysis temperature of the parent DVB–VF copolymer. As the pyrolysis temperature of the parent copolymer decreased from 700

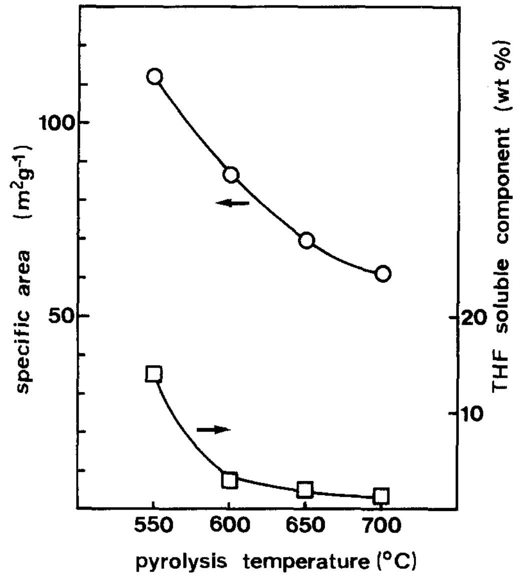


Figure 5 Specific area and THF soluble components of magnetite-dispersed carbon. (○) Specific area after heat treatment at 800° C for 10 min, (□) weight percentage of THF soluble components.

to 550° C, the specific area increased from 63 to 112 m^2 g^{-1}. The lower pyrolysis temperature resulted in the higher content of uncarbonized THF soluble component, which led to the larger specific area after heat treatment at 800° C. THF-soluble components undergo carbonization during heat treatment up to 800° C to increase the area of the active surface.

3.4. Magnetic properties of magnetite-dispersed carbon

3.4.1. Thermomagnetic behaviour

The magnetization of magnetite-dispersed carbon formed from DVB-7.8 mol % VF at 650° C and 125 MPa decreased on heating as shown in Fig. 6. The Curie point was 585° C, which was in good agreement with that of pure magnetite itself. The thermomagnetization curve on heating showed no Curie points of iron compounds except magnetite. This lends support to the specimen containing only magnetite, no other magnetic iron compounds being dispersed in the carbon matrix.

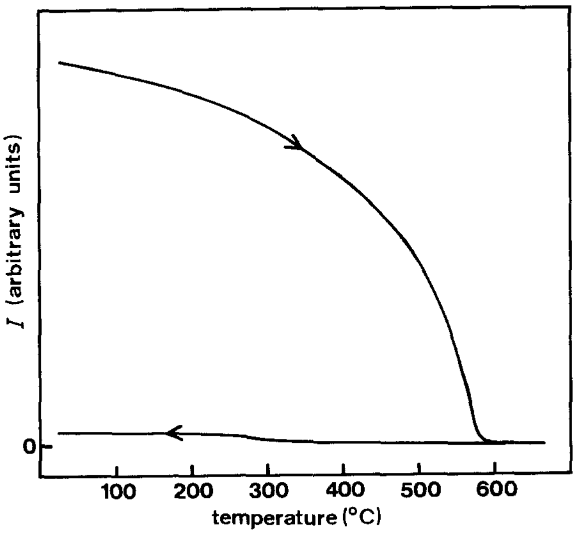


Figure 6 Thermomagnetization curve of magnetite-dispersed carbon formed from DVB-7.8 mol % VF at 650° C and 125 MPa.

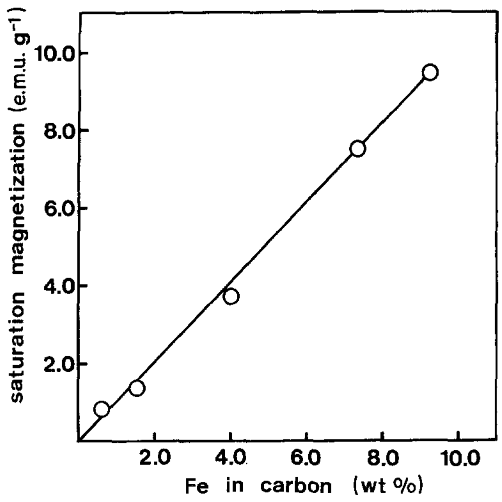


Figure 7 Saturation magnetization of magnetite-dispersed carbon synthesized from DVB–VF by pyrolysis at 550° C and 125 MPa.

On cooling, the specimen did not recover the magnetization, and the magnetization of the specimen at room temperature was almost zero after the thermomagnetic measurement. The XRD analysis showed that wüstite was dispersed in such a carbon matrix. Magnetite was reduced with excess carbon as the matrix producing wüstite during the magnetic susceptibility measurement.

3.4.2. Saturation magnetization

Fig. 7 summarizes the saturation magnetization of magnetite-dispersed carbon synthesized from DVB–VF copolymers at 550° C and 125 MPa. The saturation magnetization of magnetite-dispersed carbon had linear relation to the iron concentration in the carbon. The saturation magnetization of magnetite-dispersed carbon revealed 79% of the theoretically calculated value based upon pure magnetite itself. These results indicate that magnetite particles with comparable crystallinity were uniformly dispersed in the carbon matrix.

4. Conclusions

The copolymer of divinylbenzene and vinylferrocene was pyrolysed under pressure in the presence of water to synthesize carbons with finely dispersed magnetite. The results are summarized as follows.

1. Carbons with finely dispersed magnetite were synthesized by pressure pyrolysis of divinylbenzene–vinylferrocene and supercritical water.
2. Supercritical water had an effect on the liquid–liquid phase separation of oligomers to give spherulitic carbon with finely dispersed magnetite.
3. Magnetite-dispersed carbon synthesized at 550° C and 125 MPa increased its specific area from several to 112 m^2 g^{-1} after heat treatment at 800° C for 10 min under nitrogen.
4. Magnetite dispersed in a carbon matrix was easily reduced to wüstite by heat treatment up to 750° C.
5. The saturation magnetization of magnetite-dispersed carbon revealed 79% of the theoretically calculated value, and was proportional to the iron content in carbon.

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