JOURNAL OF MATERIALS SCIENCE 18 (1983) 2811–2816

Synthesis of iron-dispersed carbons by pressure pyrolysis of divinylbenzene–vinylferrocene copolymer

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Versatile carbons with finely dispersed iron were synthesized by pressure pyrolysis of a copolymer prepared from divinylbenzene and vinylferrocene at temperatures below 680° C and pressures of 125 MPa. The pyrolysis conditions of the copolymer were found to influence the final morphology of carbons to give fibrils, spheres and polyhedra. The resulting carbons contained uniformly fine particles of cementite (Fe_3C) which were less than 30 nm in size, whereas the magnetite was dispersed in the carbon matrix by pressure pyrolysis in the presence of water. Highly dispersed cementite in carbon was found to decompose into metallic iron by further heat treatment above 850° C. Porous spherulitic carbons were also synthesized by heat treatment of magnetite containing carbon spherulites.

1. Introduction

In a carbonization process, the reactivity of carbon–carbon bonds of original organic molecules was found to effect the character and morphology of the carbons formed [1–5]. Many kinds of organic compounds were pyrolysed to produce amorphous glassy carbons. The pressure pyrolysis of organic compounds revealed the feasibility of control of the morphology of formed carbons with high carbon yield.

Hirano *et al.* [5, 6] first reported the synthesis of isotropic, non-graphitizable carbons by the pressure pyrolysis of polydivinylbenzene. In addition, polydivinylbenzene mixed with vinylferrocene (2 wt%) was pyrolysed under pressure to give spherulites having properties different from those of the divinylbenzene polymer without any addition of vinylferrocene [5].

The present paper deals with the formation of finely dispersed iron by the pressure carbonization of the copolymer of divinylbenzene with vinylferrocene. Higher contents of vinylferrocene in the copolymer gave carbons in the form of fibrils and polyhedra. The behaviour of the carbons containing finely dispersed iron was followed by thermomagnetic analysis. It is desirable that the carbons with the new morphology and high dispersion of iron compounds have characteristics of catalysts and interesting magnetic properties.

2. Experimental procedures

Commercially available divinylbenzene (a mixture of 55% m- and p-divinylbenzene and 45% ethylbenzene) was employed as the starting organic compound. The vinylferrocene used in the formation of the copolymer was prepared by the method described in the literature [7].

All pressure work was carried out in a hydrothermal apparatus of the cold-seal type. The mixture solution of vinylferrocene (VF) and divinylbenzene (DVB) 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.

Vinylferrocene was found to dissolve in divinylbenzene up to 65 mol% at room temperature to give a solution with an orange colour. The various mixture solutions of divinylbenzene containing vinylferrocene from 1.4 to 25.5 mol% were poly-

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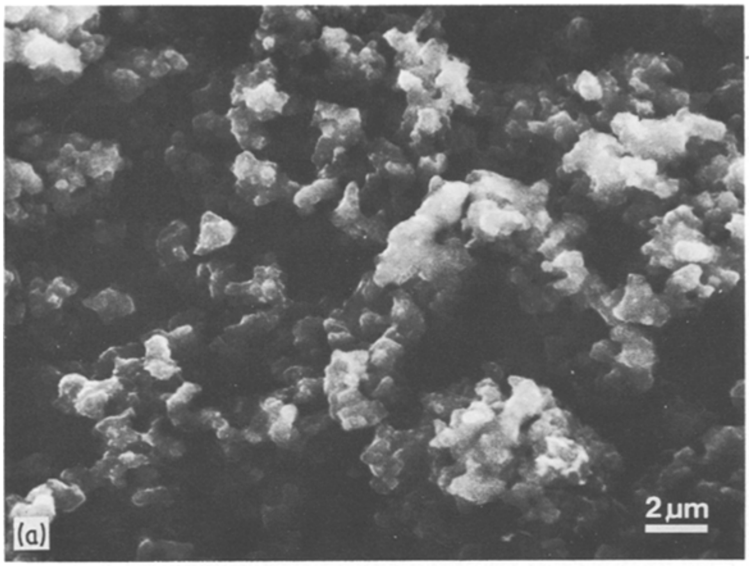

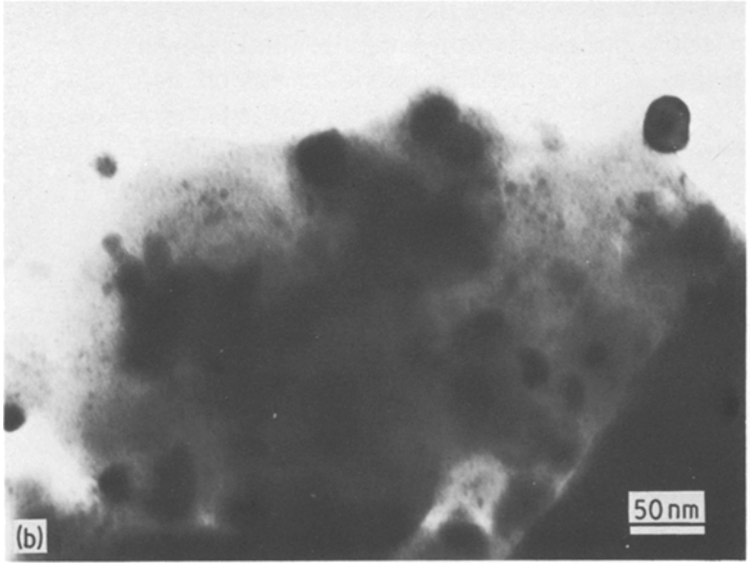

Figure 1 Morphology of carbon formed by pressure pyrolysis of DVB–14.0 mol % VF copolymer. (a) Coalescing polyhedral carbon formed by pyrolysis at 550° C and 125 MPa of a copolymer prepared at 100 MPa. (b) Microstructure of coalescing polyhedral carbon containing cementite identified as black particles.

merized at 300° C for 2 h under 100 MPa pressure and then pyrolysed at 550, 650 or 680° 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 of the pressure vessel. The temperature was raised at a heating rate of 10° C min^{-1} and quenched after an experimental run.

The carbons produced were characterized by X-ray diffraction analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The magnetic properties of the iron-containing carbons were measured with a magnetic balance. The specimen was outgassed under vacuum for several hours at 280° C and then sealed into a quartz capsule (7 mm in diameter and about 25 mm in length) under vacuum prior to the magnetic susceptibility measurements.

3. Results and discussion

3.1. Morphology of carbon formed by pressure pyrolysis

Hirano *et al.* [5] used a ferrocene as the iron-source to prepare the carbon–iron mixed materials.

In the present work, the use of vinylferrocene to copolymerize with divinylbenzene improved the dispersion of iron in the carbon matrix formed. Pressure copolymerization proceeded very rapidly

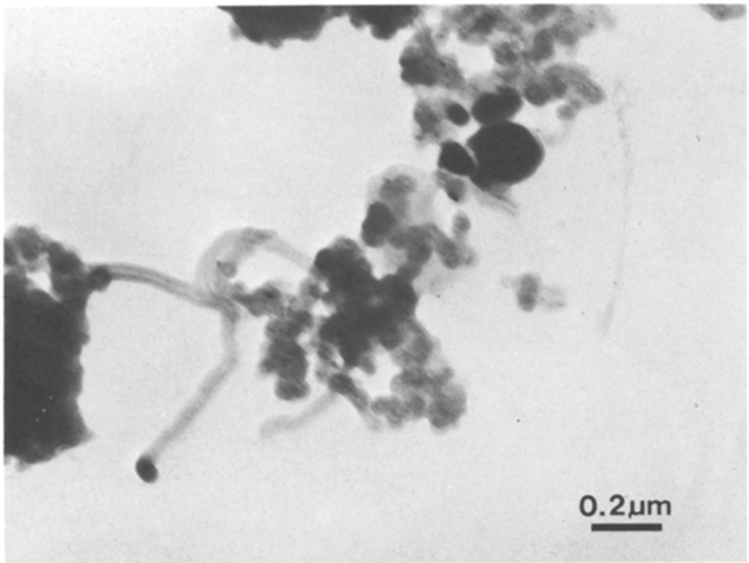

Figure 2 Microstructure of fibrous carbon dispersed with particles of cementite prepared from DVB–14.4 mol%VF by pressure pyrolysis.

at 300° C for 2 h under 100 MPa pressure (1000 kg cm^{-2}) to yield dark orange copolymers. The resulting copolymer was insoluble in the usual organic solvents and had no vinyl group ascribed to vinylferrocene in the infrared spectrum. Various copolymers containing vinylferrocene from 2.0 to 24.0 mol% were successively pyrolysed in a sealed gold capsule at 550° C for 3 h under 125 MPa pressure (1250 kg cm^{-2}) to give carbons of the polyhedral morphology with the yield of 80%. The grain size of polyhedral carbons is less than 2 μm and its representative SEM photograph is shown in Fig. 1a. A TEM photograph of the same sample (Fig. 1b) shows that small iron-compound particles of about 25 nm are mixed in the carbon matrix. The compound dispersed in carbon was identified to be cementite by the X-ray diffraction method. Electron diffraction also confirmed this particle to be cementite.

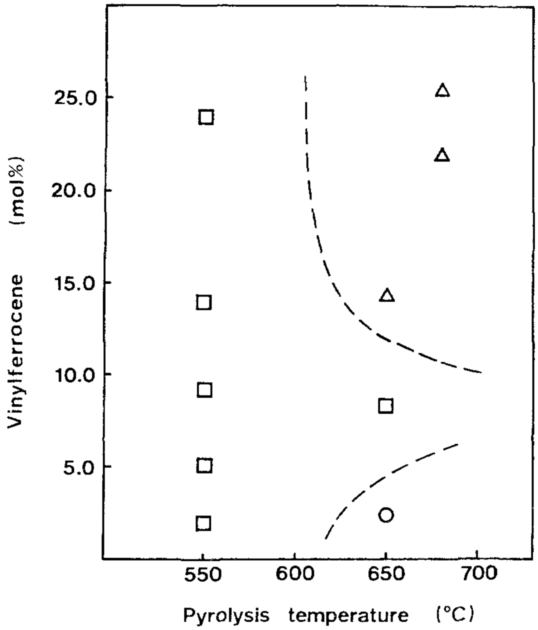

Figure 3 Morphological changes of carbon synthesized with different temperatures and compositions of DVB–VF copolymers at 125 MPa for 3 h. □, coalescing polyhedral carbon; △, fibrous carbon; ○, spherulitic carbon.

In contrast, the pressure pyrolysis at 650° C gave various morphologies of carbons which differed significantly from those obtained at 550° C. An assemblage of fibrils of carbons formed when the copolymer (14.4 mol% of vinylferrocene) was pyrolysed at 650° C for 3 h under 125 MPa pressure. TEM photographs of such fibrous carbons are shown in Fig. 2. The TEM photograph shows the fibrous carbons to have diameters of about 50 nm, in which particles of cementite less than 15 nm are finely dispersed. The reduction of the amount of vinylferrocene to 2.4 mol% in the copolymer resulted in the formation of carbon spherulites of 3 to 5 μm in diameter under the same conditions. The results obtained at various temperatures and under 125 MPa pressure are summarized in Fig. 3. Iron was found to be dispersed in the form of cementite in these cases.

In contrast, carbon spherulites with dispersed magnetite formed from the copolymer containing 7.8 mol% vinylferrocene by pressure pyrolysis in the presence of water. These spherulitic carbons containing magnetite (Fig. 4a) were found to be

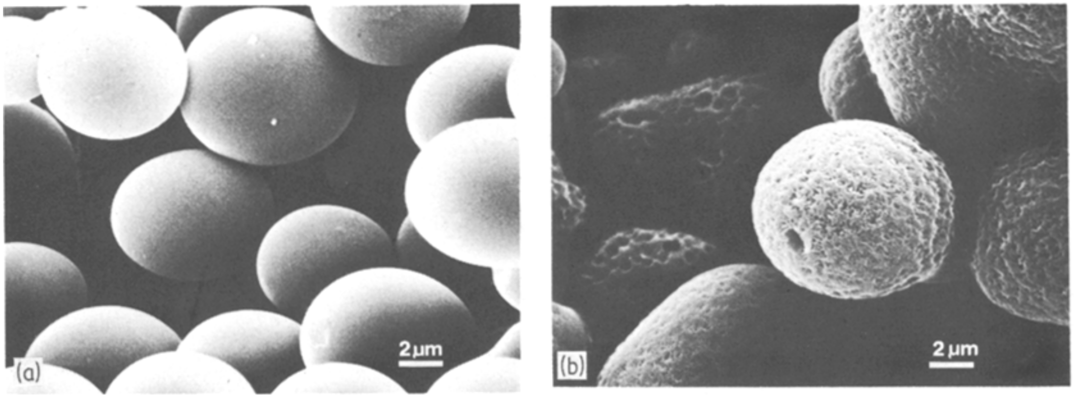

Figure 4 Photograph of Fe_3O_4-dispersed carbon spherulites. (a) Spherulitic carbon formed by pyrolysis at 650° C and 125 MPa of DVB–7.8 mol %VF copolymer in the presence of water. (b) Porous carbon obtained by further heat treatment of (a).

converted into porous carbon spherulites (Fig. 4b) by the subsequent heat treatment to 800° C. The uniformly distributed pores on the spherulite reflect the uniform dispersion of magnetite in the original carbon spherulites. The pores in the spherulitic carbons were found to form by the evolution of carbon dioxide gas during the reaction of magnetite with carbons constituting the matrix. After heat treatment up to 800° C, the magnetite-dispersed carbon had a lattice constant of 0.685 nm measured on the 002 X-ray diffraction profile. The lattice constant of 0.685 nm is comparable with that for the non-graphitizable carbon obtained by the pressure pyrolysis of polydivinylbenzene and the subsequent heat treatment at 2000° C [6]. The increase in the graphitizability is considered to be due to the presence of magnetite, which promotes the graphitization of hardly graphitizable carbons, as is the case with some metal oxides in accelerating graphitization [5]. No similar behaviour was observed on the cementite dispersed polyhedral carbons when heat treated. This fact illustrates that the formation of such new carbon spherulites is attributable to the reduction of magnetite and the concurrent graphitization of the amorphous non-graphitizable carbon.

Recently, Mulay *et al.* [8] have reported the pyrolysis of polymer obtainable from furfuryl alcohol and ferrocene derivatives. However, water generated during the condensation of furfuryl alcohol and ferrocene dicarboxylic acid inevitably caused the cementite formed to be contaminated with the magnetite. In contrast, the iron-containing carbons synthesized in this work have been always accompanied by highly dispersed pure cementite, which can be performed by excluding the presence of oxygen gas. When selective formation of magnetite has been required, the controlled addition of water during the pressure pyrolysis of the copolymers has resulted in the synthesis of magnetite-containing carbons with controllable morphology.

The process of pressure pyrolysis involves decomposition of the copolymer to oligomers, which leads to the formation of an embryo followed by its growth in the liquid phase during the phase separation suggested previously [6]. In the present case, the relative feasibility of bond scission during pyrolysis was observed in the copolymer with ferrocene and compared with the pure polydivinylbenzene, reflecting the allocation of the finely distributed ferrocene units in the copolymer. The precise mechanism of the formation of such new carbons has not yet been clarified. However, the presence of the bond between the carbon and iron atoms seems to influence the viscosity and the density of the liquid phases formed, leading to the resultant liquid–liquid microphase separation.

3.2. Magnetic properties of carbon with finely dispersed iron compounds

The thermomagnetization curves shown in Fig. 5 illustrate the features observed for the synthesized carbon specimens with dispersed cementite and iron.

On heating, the magnetization of the cementite-dispersed carbon specimen decreases with increase of temperature through curve (a) (Fig. 5) towards the Curie point of cementite at 220° C. Further heating up to 780° C showed that no iron compound except cementite had formed in the carbon

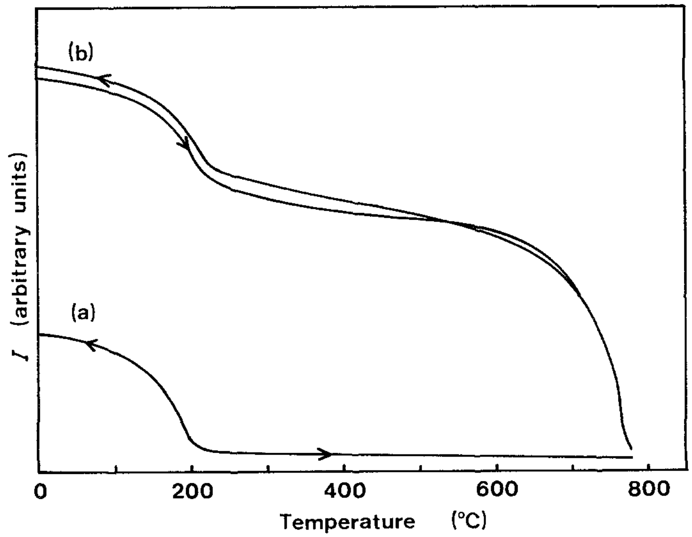

Figure 5 Magnetic susceptibility against temperature curves for glass-like carbons containing iron compounds. (a) Thermomagnetization curves of original cementite dispersed carbon after heat treatment of (a) at 850° C for 6 h.

matrix. The repeated magnetization measurements of the specimen gave curves the same curve (a).

After the cementite-dispersed carbon was heat treated at 850° C for 6 h, the magnetization of the specimen at room temperature increased to the value about three times that of the original specimen (curve (b) in Fig. 5). Both the Curie points of cementite and α-iron (780° C) can be seen in curve (b). The decomposition of cementite into metallic iron and its growth to α-iron particles of adequate size during heat treatment are responsible for the increase of the magnetization. The X-ray diffraction analysis of the specimen showed that cementite was found to be decomposed to precipitate α-iron in the carbon matrix, as shown in Fig. 6b. By prolonging the heat-treatment time in an atmosphere free of oxygen, the fine carbon particles with finely dispersed α-iron can be synthesized from the carbon spherulites or fibrils with the cementite dispersion.

Further studies are in progress toward the applications of these new carbon spherulites and fibrils with finely dispersed iron compounds in the carrier in the printing agents, the ferrofluid and the catalyst.

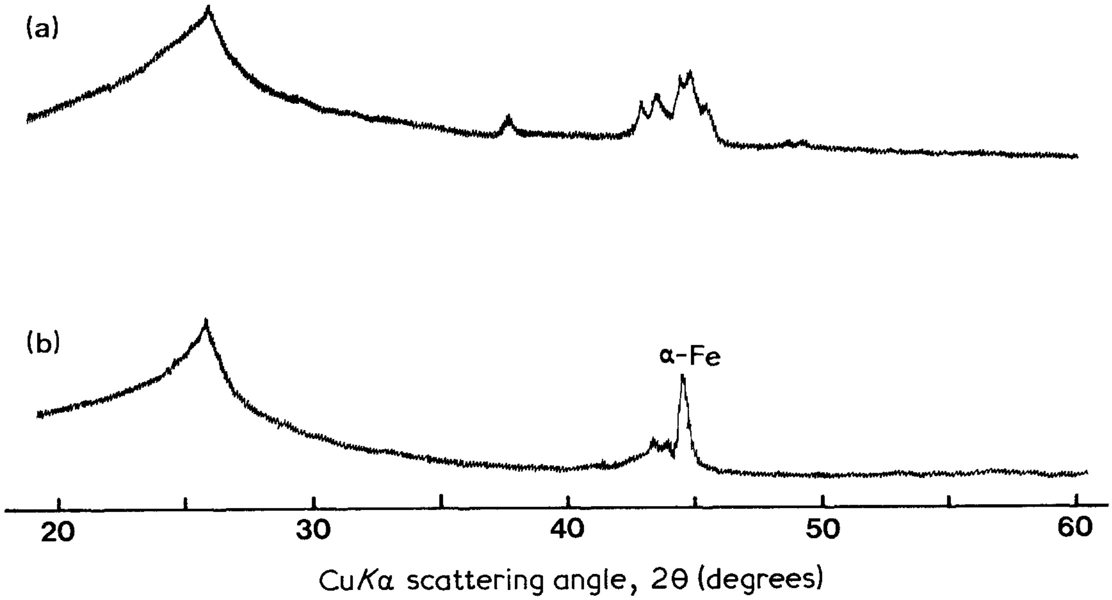

Figure 6 X-ray diffraction profiles of polyhedral carbons before and after heat treatment. (a) Original coalescing polyhedral carbons containing cementite. (b) Iron-dispersed carbon after heat treatment at 850° C for 6 h.

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Received 14 September 1982
and accepted 18 February 1983