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Synthesis of boron-dispersed carbon by pressure pyrolysis of organoborane copolymer

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Boron-dispersed carbon was synthesized by pressure pyrolysis of divinylbenzene–tris(allyl)-borane and styrene–tris(allyl)borane at 125 MPa below 650° C. Amorphous boron dispersed in a carbon matrix was oxidized easily to yield boric acid by heat treatment under air at 300° C. The B$K\alpha$ image of the product showed that boron was dispersed uniformly in a carbon matrix. Boron-dispersed carbon had the morphology of coalescing spherulite and polyhedra depending upon the concentration of boron in the parent copolymer. The grain size of carbon polyhedra decreased from 2.0 μm to 0.2 μm with an increase in the boron concentration from 1.3 to 5.7 wt%. The presence of 0.5 wt% boron in a carbon matrix enhanced the graphitization at 4.0 GPa and 1200° C, decreasing the lattice spacing with an increase in the crystallite size. The crystallite sizes were comparable to each other after heat treatment at 1100° C and 4.0 GPa when the specimen contained boron from 0.5 to 2.5 wt%. The lattice constant (c_0) and crystallite size (L_c) of boron-dispersed carbon containing 2.5 wt% boron were 677.0 pm and 30 nm, respectively, after heat treatment at 1200° C and 4.0 GPa.

1. Introduction

Metal-dispersed carbon of controlled morphology can be synthesized in high carbon yields by pressure pyrolysis of organometallic polymers [1–9]. Hirano *et al.* [2, 3] synthesized iron-dispersed carbons by pressure carbonization of divinylbenzene copolymerized with vinylferrocene giving a fine dispersion of iron particles in the resultant carbon matrix. Ferromagnetic particles, such as cobalt, nickel, iron–cobalt and magnetite, can also be dispersed in a carbon matrix by the pressure pyrolysis of organometallic polymers [4–6, 9].

The properties of metal-dispersed carbon reflect the nature of the carbon–carbon and carbon–metal bonds of the initial organometallic polymers. Three-dimensional cross-linkages of the carbon–carbon bond in a polymer matrix and thermally stable metal–carbon bonds of organometallic compounds prevent the initial aggregation of metal particles during pyrolysis [4, 7]. The morphology of matrix carbon can be controlled by selection of the pyrolysis conditions, such as temperature and pressure [3, 5, 9].

The present paper concerns the synthesis of boron-dispersed carbon by pressure pyrolysis of organoborane copolymers. The effect of boron in the carbon matrix on the graphitization of carbon was also investigated. Amorphous boron was successfully dispersed in a carbon matrix by the pressure pyrolysis of organoborane copolymers at below 650° C.

2. Experimental procedures

2.1. Starting materials

Tris-allylborane ($(CH_2{=}CHCH_2)_3B$; b.p. 55–70° C at 20 mm Hg) was prepared according to Mikhailov and Tutorskaya [10]. Commercially available divinylbenzene (a mixture of 55% *m*- and *p*-divinylbenzene and 45% ethylbenzene) and styrene were used for the preparation of the starting organic copolymers.

2.2. Synthesis of boron-dispersed carbon

All pressure work at 100 and 125 MPa was carried out with a hydrothermal apparatus of the cold-seal type. Tris-allylborane (AB) was dissolved in divinylbenzene (DVB) or styrene (St) under nitrogen, and the solution was sealed in a thin-walled gold capsule of 3.0 or 5.0 mm diameter and 50 mm length.

Various solutions of DVB or St containing AB were polymerized at 300° C and 100 MPa for 2 h and then pyrolysed at temperatures up to 700° C and 125 MPa. The heating rate was 10° C min^{-1} at a constant pressure of 125 MPa. The pressure was kept isobaric by releasing water 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 each experimental run.

2.3. Heat treatment at 4.0 GPa

As-prepared boron-dispersed carbon was heat-treated at temperatures from 1000° to 1200° C under 4.0 GPa with a girdle-type high pressure apparatus. The arrangement of the high pressure cell is shown in Fig. 1. The sample was heated by alternating electric current passed through the glassy carbon heater under pressure. The pressure was calibrated at room temperature by the phase transition of bismuth (2.55 GPa), thallium (3.67) and barium (5.5). The temperature was

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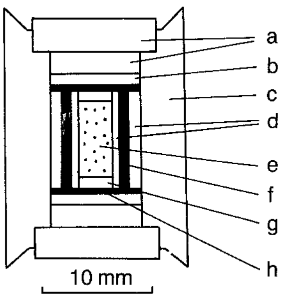

Figure 1 Sample arrangement of pressure apparatus. (a) WC disc; (b) SKH-9 disc; (c) pyrophyllite holder; (d) fired pyrophyllite sleeve; (e) sample; (f) GC heater; (g) fired pyrophyllite chip; (h) graphite plate.

determined on the basis of the relation of the melting points of silver, gold and nickel at 4.0 GPa to the applied electric power. The lattice constant c_{0002} and crystallite size L_{c002} of the specimen were determined from its (0 0 2) X-ray diffraction with highly pure silicon as the internal standard. The observed line profiles were corrected for absorption, Lorenz polarization and atomic scattering factor [11].

2.4. Characterization of products

Boron dispersed carbons were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) using wavelength dispersion. Infrared (IR) spectra of polymers, including the organoborane compound, were measured using both KBr discs and the liquid film method.

3. Results and discussion

3.1. Synthesis of boron-dispersed carbon

3.1.1. IR spectroscopy

Tris-allylborane (AB) consists of carbon, boron and hydrogen, and has three double bonds for copolymerization with divinylbenzene (DVB) or styrene (St).

Copolymerization of DVB with 21.0 mol % AB was investigated using IR spectroscopy. The absorption band at 1635 cm^{-1} ascribed to C=C bond of the allyl group decreased in intensity as the polymerization temperature increased from 200° to 280° C, and finally disappeared at 300° C and 100 MPa for 2 h. This result indicates the formation of a copolymer between AB and DVB at 300° C.

3.1.2. X-ray diffraction studies

A mixture of DVB–80.6 mol % AB was polymerized at 300° C and 100 MPa and then carbonized at 550° C and 125 MPa. The XRD profile of the product shown in Fig. 2a had a broad diffraction centred at $2\theta = 25.5°$ (Cu*K*α).

After heat treatment at 300° C for 2 h under air, the XRD profile of the specimen was composed of two sharp reflections at $2\theta = 27.9°$ and 14.7° superimposed on the broad diffraction at $2\theta = 25.5°$ (Fig. 2b). The first of these are attributed to boric acid, the second corresponds to turbostratic carbon. Boron dispersed in the carbon matrix is amorphous, and is highly susceptible to oxidation yielding boric acid.

3.1.3. Analysis with EPMA

Figs 3a and b show a secondary image of boron-dispersed carbon formed from DVB–80.6 mol % AB at 550° C and 125 MPa, and its B*K*α X-ray image, respectively. The intensity of B*K*α image was six times higher than that of the background. The uniform distribution of dots indicates the uniform dispersion of boron in the carbon matrix, although it could not be detected by the XRD analysis as shown in Fig. 2a.

3.2. Morphology of boron-dispersed carbon

Spherulitic carbon as shown in Fig. 4a was synthesized by pyrolysis of polystyrene itself at 550° C and 125 MPa for 3 h. On the other hand, boron-dispersed carbon synthesized under the same conditions had the morphology of coalescing polyhedra as shown in Figs 4b to d. The grain size of carbon decreased from 2.0 μm (Fig. 4b) to 0.2 μm (Fig. 4d), as the boron concentration in the parent organoborane copolymer increased from 1.3 to 5.7 wt %.

Fig. 5 summarizes the morphology of carbon formed from AB–St at temperatures from 550° to 700° C under 125 MPa. The morphology tended to change from spherulites to coalescing polyhedra via coalescing spherulites as the concentration of boron increased. The morphology of carbon is dependent upon liquid–liquid microphase separation of oligomers formed by decomposition of polymers during pyrolysis [12]. Polystyrene itself was pyrolysed under the same conditions to give carbon spherulites, which were formed via the homogeneous liquid–liquid microphase separation. The presence of boron evidently

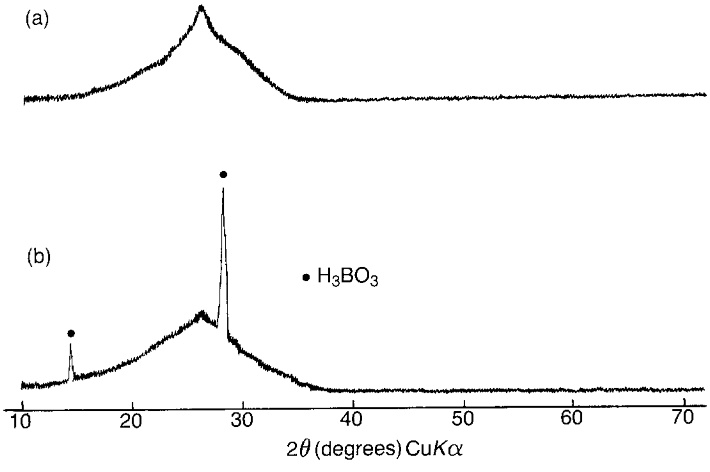

Figure 2 X-ray diffraction profile of carbons synthesized by pyrolysis of DVB–80.6 mol % AB at 550° C and 125 MPa. (a) As-prepared carbon. (b) After heat treatment of (a) at 300° C for 2 h in air.

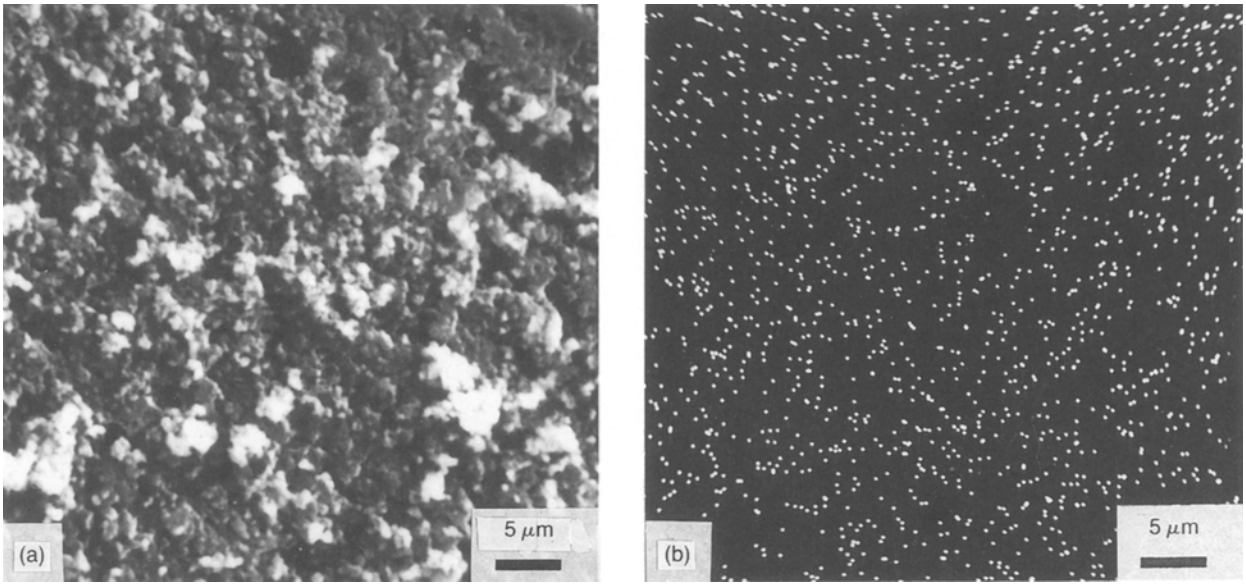

Figure 3 Secondary image (a), and B*K*α image (b) of boron-dispersed carbon formed from DVB–80.6 mol % AB at 550° C and 125 MPa.

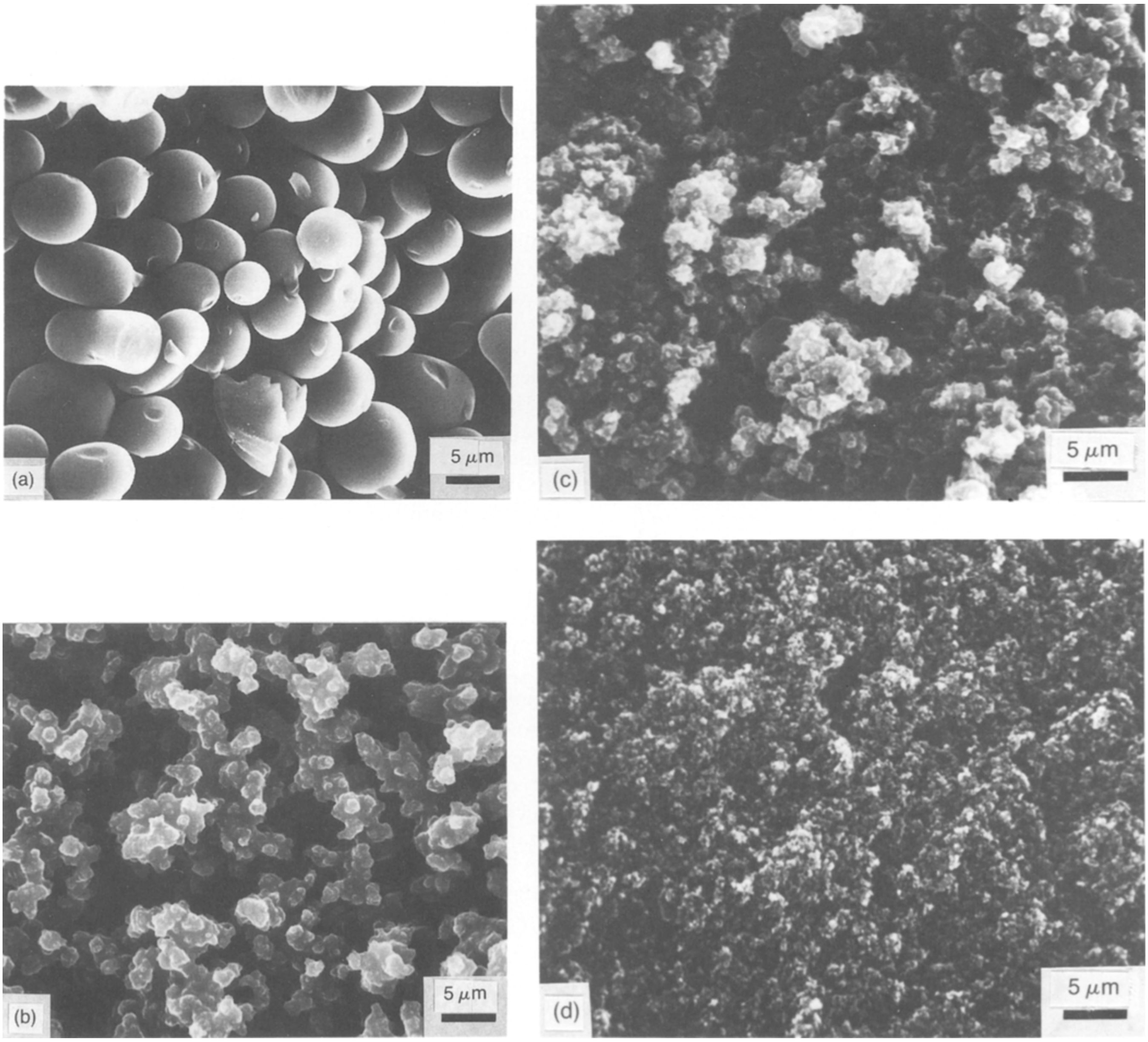

Figure 4 Morphologies of carbons containing various amounts of boron synthesized from St–AB copolymer by pyrolysis at 550° C and 125 MPa. (a) St polymer itself; (b) 1.3 wt % boron; (c) 3.8 wt % boron; (d) 5.7 wt % boron.

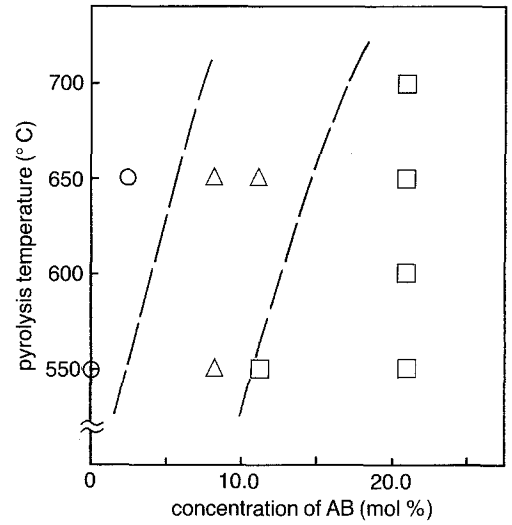

Figure 5 Morphologies of carbons formed from St–AB copolymer containing various concentrations of boron at temperatures from 550° to 700° C and 125 MPa. (○) spherulites (△) coalescing spherulites (□) coalescing polyhedra.

influenced the microphase liquid–liquid separation to induce heterogeneous phase separation, which led to the formation of coalescing polyhedra with irregular edges.

3.3. High pressure treatment of boron-dispersed carbon

As-prepared boron-dispersed carbons synthesized from St–AB copolymer at 550° C and 125 MPa were heat-treated at between 1000° and 1200° C and 4.0 GPa for 20 min. The lattice constant (c_0) and the crystallite size (L_c) of the specimen containing 2.5 wt % of boron are correlated to the heat treatment temperature (HTT) in Fig. 6. The c_{0002} decreased with increasing HTT, and reached a value of 677.0 pm at 1200° C. The crystallite size increased rapidly at between 1100° and 1200° C.

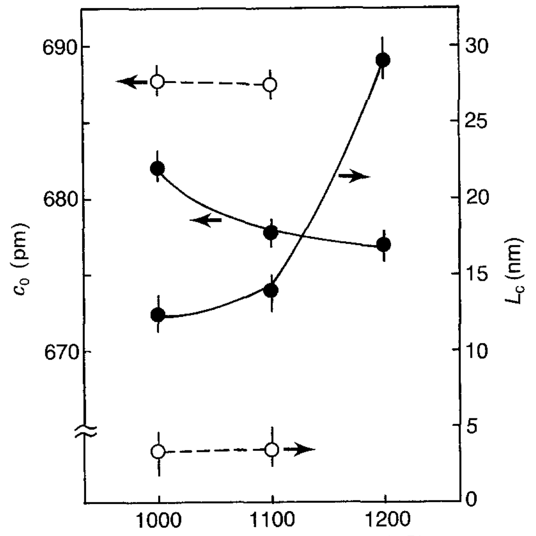

Figure 6 Lattice constant (c_0) and crystallite size (L_c) of boron-dispersed carbon including 2.5 wt % boron and boron-free carbon after heat treatment at various temperatures under 4.0 GPa. (●) boron-dispersed carbon, (○) boron-free carbon.

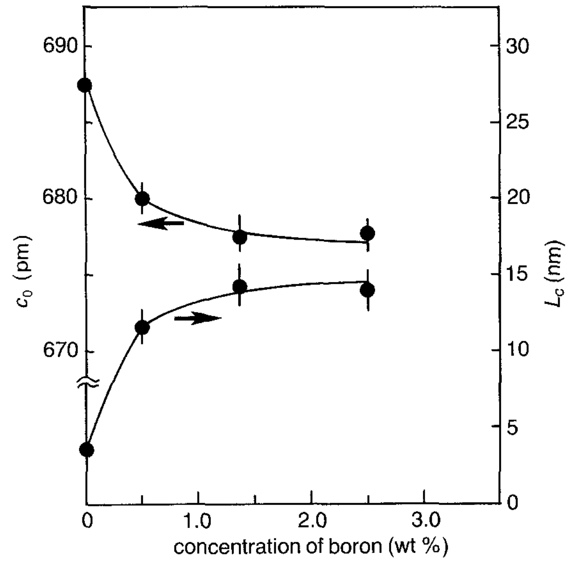

Figure 7 Variation of lattice constant (c_0 and crystallite size (L_c) of boron-dispersed carbon as a function of concentration of boron after heat treatment at 1100° C and 4.0 GPa.

The as-prepared carbon formed from styrene itself at 550° C and 125 MPa was heat-treated at 1000° and 1100° C under 4.0 GPa. Changes of c_0 and L_c with temperature are also shown (as dashed lines) in Fig. 6. After heat treatment at 4.0 GPa the specimen had a larger c_0 and a smaller L_c than those of boron-dispersed carbon.

The XRD profiles of the specimen after heat treatment at 1200° C and 4.0 GPa for 20 min comprised the (0 0 2) reflection as well as two weak broad diffractions centred at $2\theta = 43.0°$ and $54.0°$. The former broad diffraction is attributed to the 1 0 band, and the latter the (0 0 4) reflection of graphite. No other phases, such as boron carbide, were detected by XRD analysis when 2.5 wt % boron was used.

The values of c_0 and L_c of the specimen heat-treated at 1100° C and 4.0 GPa as a function of the concentration of boron are shown in Fig. 7. The c_0 of the heat-treated boron-dispersed carbon including 0.5 wt % boron was smaller than that of boron-free carbon. The c_0 decreased slightly with increasing boron content from 0.5 to 2.5 wt %. The L_c of boron-dispersed carbon ranged from 10 to 15 nm.

Boron is known to enhance catalytic graphitization [13–16]. Lowell [17] found that the solubility of boron in carbon reached a maximum value of 2.35 at % at 2350° C and atmospheric pressure. Even after heat treatment at 4.0 GPa, the specimen had almost no three-dimensional regularity of crystal lattice. Also, the minimum value of c_0 obtained was 677.0 pm, which was larger than the lowest value of 669.8 pm reported by Lowell [17]. However, the results in Figs 6 and 7 reveal clearly that boron particles dispersed in a carbon matrix accelerated the graphitization at 4.0 GPa.

4. Conclusions

Boron-dispersed carbon was successfully synthesized by pressure pyrolysis of organoborane copolymer. The results are summarized as follows:

(1) Amorphous boron uniformly dispersed in a

carbon matrix underwent oxidation easily to yield boric acid at 300° C in air.

(2) The grain size of carbon was dependent upon the concentration of boron, which affected the liquid–liquid microphase separation during pyrolysis to yield polyhedral carbons.

(3) Boron dispersed in a carbon matrix promoted the graphitization of as-prepared carbon at 4.0 GPa.

Pressure pyrolysis of organoborane copolymer was found to be one of the most effective methods for the uniform dispersion of boron in a carbon matrix at low temperatures.

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