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# Carbonization and graphitization of meso-carbon microbeads prepared by the emulsion method

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Meso-carbon microbeads (MCB) prepared from coal-tar and fluid catalytic cracking (FCC)-decant oil pitches by an emulsion method were carbonized and graphitized. When using the thermosetting process as a pretreatment, the weight gain of MCB by oxidation was approximately 5 wt %, and Fourier transform-infrared measurement showed that the oxidation occurred mainly at aliphatic components in MCB. In the course of carbonization, a heat treatment at 700 °C eliminated the C–H groups and the oxygen-containing functional groups, which had remained partly at 500 °C. MCB were fairly graphitizable, considering the high values of $L_{c(002)}$ obtained from X-ray diffraction measurement. The surface of MCB, which had been originally smooth, became slightly irregular during carbonization, and deformation in the shape of MCB was observed after the graphitization process. These are due to the anisotropic growth and shrinkage of the mesophase structure.

## 1. Introduction

Carbonaceous or carbon materials are noteworthy among the various organic materials, because of their excellent physicochemical properties such as chemical stability, thermostability, electroconductivity, mechanical strength, activation and lubrication possibilities [1]. Meso-carbon microbeads (MCB) are one of the carbonaceous materials named by Honda and co-workers [2, 3]. The origin of MCB is the carbonaceous mesophase spherules appearing in the early stage of the liquid carbonization process of pitch [4, 5]. Honda *et al.* separated these spherules from the pitch matrix by solvent fractionation, and evaluated their use in elucidation of liquid carbonization phenomena and in research of possible fields of utilization [6–13].

In many carbon materials, MCB with a spherical shape and lamellar structure which consists of oriented aromatic polycondensed hydrocarbon molecules, are expected to show specific adsorption, possibly on intercalation and the morphological advantage of their spherical shape, in addition to the above described characters. However, the quality of MCB prepared by a conventional method (separation from heat-treated pitch) has room for improvement, because of the wide distribution of particle size, condensation of free carbon particles (metaphase) on the surface of spherules, and low yield. Modifications of the preparation of MCB have been attempted by some workers, to obtain spherules of better quality [14–16].

We have reported a new preparation method for MCB using the fusible bulk-mesophase pitch. In this method, termed the "emulsion method", the fused pitch particles are spheroidized in a heat-stable liquid medium which has a lower solubility for pitch. Using this emulsion method, MCB with a narrow size distribution, a satisfactory spherical shape, and smooth surface have become available in higher yields [17, 18]. Thus, it is expected that MCB will have a good potential for various applied purposes [19, 20]. It is very important that examination and discussion of changes in the chemical properties with heat treatment are made in order to evaluate our MCB as a carbonaceous material.

In the present study, MCB prepared by the emulsion method were thermoset (oxidation) as a pretreatment, and heat treated at temperatures between 500 and 2800 °C. The carbonized and graphitized MCB were studied using various analytical methods.

## 2. Experimental procedure

### 2.1. Materials

The three kinds of MCB were prepared from bulk-mesophase pitches (coal-tar pitch, fluid catalytic cracking (FCC)-decant oil pitch and naphtha-tar pitch based) of which the mesophase contents observed by polarized light microscopy were 100%. These bulk-mesophase pitches were treated in a thermostable

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silicone oil at prescribed temperatures and treatments times. After heat treatment, MCB were separated from the silicone oil by centrifugation and were rinsed in benzene or acetone. Details of the procedure have been described elsewhere [17]. The MCB prepared from coal-tar pitch-based bulk-mesophase pitch (C-pitch) at 340 °C for 5 min are called C-MCB, those from FCC-decant oil pitch-based bulk-mesophase pitch (F-pitch) at 350 °C for 10 min are F-MCB, and those from naphtha-tar pitch based bulk-mesophase pitch (N-pitch) at 330 °C for 10 min are N-MCB. In present study, C-MCB and F-MCB are mainly evaluated throughout the heat treatment. N-MCB, which exhibits an optically isotropic texture [18], were used in graphitization for comparison of graphitizability. The elemental analysis of as-prepared MCB is shown in Table I.

### 2.2. Heat treatment

Thermosetting of MCB was carried out in an electric furnace in dry air at a heating rate of 2 °C min$^{-1}$ with a residence time of 30 min at 300 °C. Carbonization (500 and 1000 °C) of MCB was done in a nitrogen atmosphere at a rate of 5 °C min$^{-1}$ for 30 min and graphitization (1500, 2000, 2500 and 2800 °C) was done in an argon atmosphere.

### 2.3. Elemental analysis

The elemental analysis (C, H, N) of MCB (2 mg) was carried out with a Carlo Erba, model 1106, using antipyrine as a standard compound. The sulphur content was determined using the combustion tube method with 150 mg MCB.

### 2.4. X-ray diffraction

The X-ray diffraction (XRD) pattern was measured using Cu$K_\alpha$ radiation. Silicone powder was used as an internal standard, and diffraction angles for MCB were corrected from that of silicone. The crystallite thickness ($L_{c(0\,0\,2)}$) and interplanar spacing ($d_{(0\,0\,2)}$) were estimated according to the standardized method prescribed by 117 Committee of Japan Society for the Promotion of Science [21].

### 2.5. Spectroscopic analysis

Solid state $^{13}$C-NMR measurements of MCB (as-prepared, thermoset and 500 °C) were made using a Bruker AC-200 superconducting spectrometer operating at 50.3 MHz for carbon with combined high-power decoupling and CP/MAS techniques. The NMR signals were accumulated 1024 times at 3250 Hz sample spinning speed. The chemical shifts were referenced to tetramethylsilane (TMS).

TABLE I Elemental analysis (wt %) of MCB (as-prepared and heat-treated)

| | C | H | N | O | S | H/C |
|---|---|---|---|---|---|---|
| C-MCB | 93.59 | 3.79 | 1.63 | 0.85 | 0.14 | 0.486 |
| C-MCB-500 | 92.30 | 2.99 | 1.74 | 2.75 | 0.22 | 0.389 |
| F-MCB | 95.56 | 4.01 | 0.04 | 0.31 | 0.08 | 0.504 |
| F-MCB-500 | 93.86 | 3.40 | 0 | 2.57 | 0.17 | 0.435 |
| N-MCB | 94.71 | 4.97 | 0 | 0.27 | 0.06 | 0.630 |
| N-MCB-500 | 92.46 | 3.33 | 0.13 | 4.01 | 0.07 | 0.432 |

The Raman spectra were induced using 19 433.5 cm$^{-1}$ of an argon-ion laser line. To resolve the Raman-scattered light from the Rayleigh scattering, a double monochromator (Spex 1403) was used. The spectra of heat-treated MCB (1000, 1500, 2500 and 2800 °C) were obtained using a sample powder pellet in the range of Raman shift 1200–1800 cm$^{-1}$ and an integrated time of 6 or 8 s.

The infrared spectra of MCB (as-prepared, thermoset, 500 and 700 °C) were obtained in the wavenumber range 400–4000 cm$^{-1}$ using a diffuse reflectance method with a Biorad Digirab FTS-60 Fourier transform infrared (FTIR) spectrometer.

## 3. Results and discussion

MCB prepared by the emulsion method require a thermosetting process prior to heat treatment, because they are properly fusible. The thermosetting process, which is a very important step in producing pitch-based carbon fibres, is usually performed as an air oxidation at temperatures between 250 and 350 °C. Thermal stabilization is mainly achieved by polymerization with cross-linking of oxygen [22, 23]. MCB were thermoset at 300 °C for 30 min in dry air in an electric furnace. The average weight gains of C-MCB and F-MCB during the thermosetting process were 4.5 and 5.3 wt %, respectively. When the weight gain was less than 2 wt %, the thermosetting was insufficient to prevent MCB from fusing. After thermosetting, the quinoline-insoluble fractions of MCB increased from 20 wt % to more than 90 wt %. This indicates that the average molecular weight of MCB increased due to cross-linking of oxygen. In addition, there were no changes in surface and shape images of MCB during the oxidation process.

Fig. 1 shows scanning electron micrographs of carbonized (1000 °C) and graphitized (2800 °C) MCB. C-MCB was slightly distorted, and F-MCB exhibited some roughness of surface at a heat-treatment temperature (HTT) of 1000 °C. Moreover, a heat treatment of 2800 °C produced C-MCB and F-MCB with a warped shape. The polycondensed aromatic rings grow towards the layer directions (*a*- and *b*-axis), and the spacing of the perpendicular direction (*c*-axis) shrinks on the heat treatment. Thus, the shape of MCB is deformed due to the anisotropic growth and shrinkage of the mesophase structure, as shown in Fig. 2. MCB prepared by the emulsion method do not have a definite orientation of mesophase as in conventional MCB, therefore, the cracks which appear along a layer direction on conventional MCB are rarely observed [24]. On the other hand, a shape of N-MCB hardly changed during carbonization and graphitization because of its optically isotropic texture. (It is doubtful whether N-MCB have essentially isotropic molecular orientation, because N-MCB can adsorb large

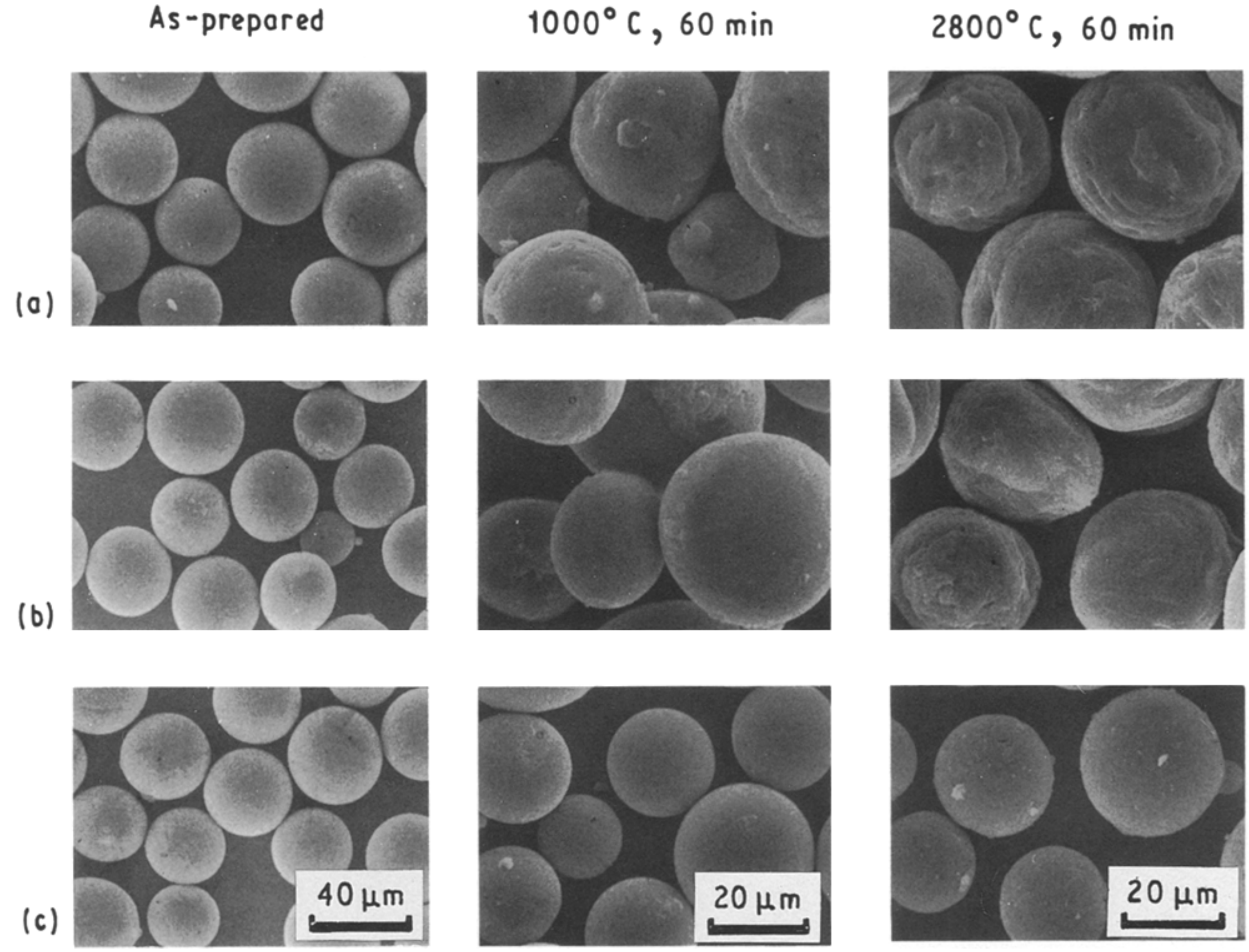

*Figure 1* Scanning electron micrographs of as-prepared, carbonized and graphitized MCB prepared by emulsion method. (a) C-MCB, (b) F-MCB and (c) N-MCB.

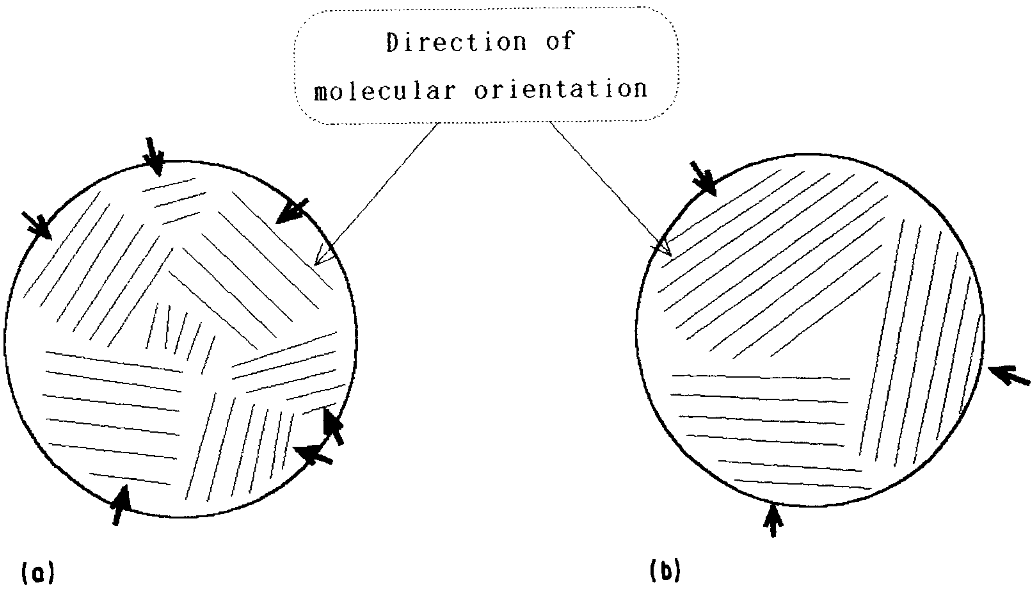

*Figure 2* Schematic concept of the internal structure of (a) C-MCB and (b) F-MCB, and their shrinkage direction during heat treatment.

amounts of iodine from aqueous or *n*-hexane solution, as can C-MCB and F-MCB. The apparent specific surface area estimated from the BET plot is approximately 500 $m^2 g^{-1}$. This value is much larger than the calculated geometrical surface area (approximately 0.2 $m^2 g^{-1}$) of N-MCB. Thus, iodine molecules undoubtedly permeate the internal structure of N-MCB; however, this permeation is a specific phenomenon of anisotropic carbon. Hence, the optical isotropy under polarized light and the essentially isotropic molecular directions are not always equal. Possibly, N-MCB appear to have a considerably disordered molecular orientation and broadened interplanar spacing.)

Fig. 3 shows FTIR spectra of MCB (as-prepared, thermoset, 500 and 700 °C). The spectrum of as-prepared MCB gives aliphatic C–H bands at 1380, 1450, 2860, 2920 and 2960 $cm^{-1}$, aromatic C–H bands at 760, 820, 870 and 3050 $cm^{-1}$ [25, 26]. Table II shows the relative absorbance ratio of the aromatic C–H band at 3050 $cm^{-1}$ to the aliphatic C–H band at 2920 $cm^{-1}$ ($K_{H-ar}/K_{H-al}$) of MCB. The spectrum of thermoset MCB at 300 °C for 30 min exhibits new strong peaks at 1200–1300 and 1700 $cm^{-1}$. The former absorption bands are ascribed to C–O stretching and O–H bending, the latter to C–O stretching, both indicating the formation of oxygen-containing functional groups on the MCB by oxidation. The spectrum also shows a reduction in the intensity of the C–H bands, which are prominent in aliphatic bands. Consequently, the ratios of $K_{H-ar}/K_{H-al}$ increase for both MCB, as shown in Table II. This result suggests that oxidation occurs notably in the aliphatic components, such as alkyl substituents, methylene, and alicyclic. In fact, F-MCB, being originally rich in aliphatic components compared with C-MCB, have a larger weight gain on thermosetting than C-MCB, as mentioned above. Thus, F-MCB appear to have a higher reactivity on oxidation than C-MCB.

The peaks due to oxygen-containing functional groups introduced by the thermosetting become smaller after a treatment at 500 °C for 30 min in a nitrogen atmosphere, e.g. the decrease of the two peaks at 1260 and 1700 $cm^{-1}$ is pronounced. However, on the whole, many functional groups appear to remain on the MCB. It was estimated by titration in aqueous solution, that C-MCB and F-MCB heat treated at 500 °C have 0.1 and 0.5 meq $g^{-1}$ acidic functional groups (carboxyl, phenolic hydroxyl, etc.). This is in agreement with the results of elemental analysis shown in Table I. On the other hand, the aliphatic C–H bands further diminish and the aromatic C–H bands enlarge on the spectra. These changes may be attributed to an elimination of low molecules and the proceeding aromatization. MCB heat treated at 700 °C for 30 min rarely give a definite structure on the spectra. Accordingly, at this temperature, the carbonization would proceed substantially, causing the disappearance of infrared-active atomic groups. Thus,

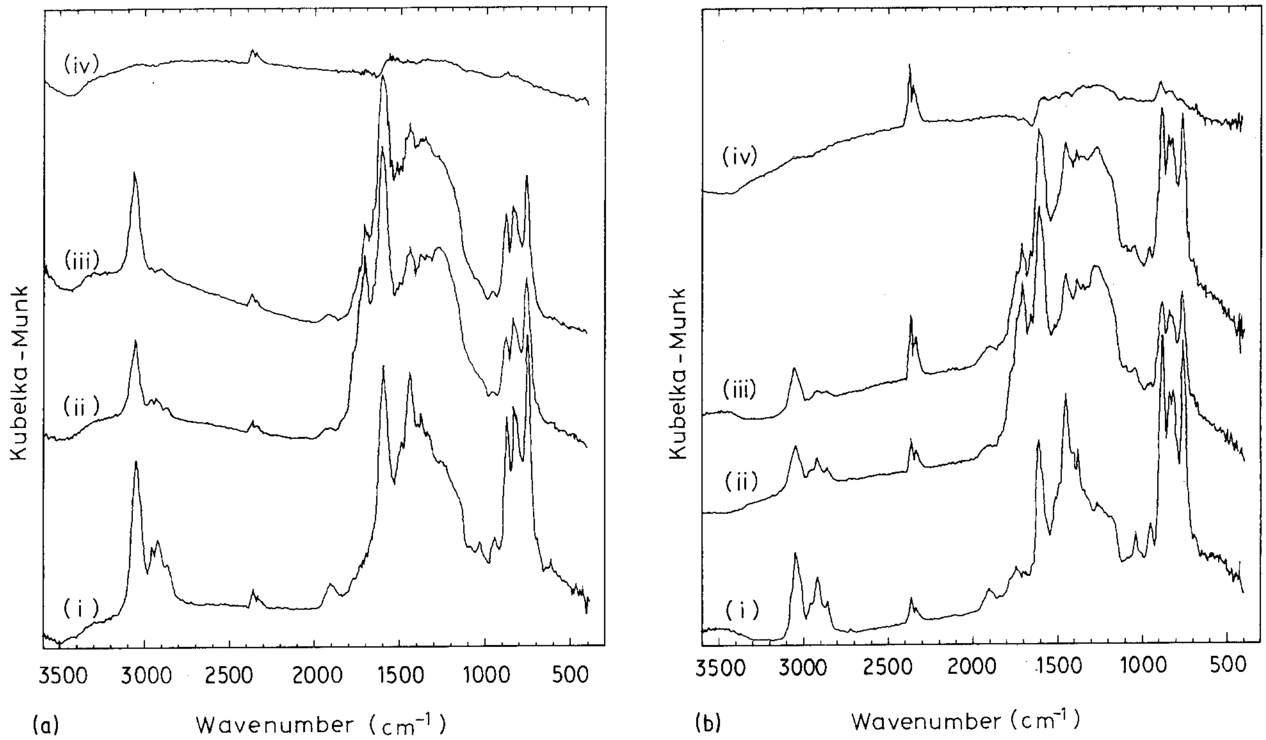

*Figure 3* FTIR spectra of (a) C-MCB and (b) F-MCB obtained by the diffuse reflectance method. (i) As-prepared, (ii) thermoset, (iii) 500 °C, and (iv) 700 °C.

TABLE II The relative absorbance ratios of the aromatic C–H band at 3030 $cm^{-1}$ and the aliphatic C–H band at 2920 $cm^{-1}$ observed by the FTIR diffuse reflectance method, and the aromatic carbon fraction, $f_a$, observed by the $^{13}$C-NMR CP/MAS method

| | FTIR spectra ($K_{H-ar}/K_{H-al}$ = 3030 $cm^{-1}$/2920 $cm^{-1}$) | | | $^{13}$C-NMR spectra ($f_a = C_{ar}/[C_{al} + C_{ar}]$) | | |
|---|---|---|---|---|---|---|
| | As-prep. | Thermoset (300 °C) | Heat-treated (500 °C) | As-prep. | Thermoset (300 °C) | Heat-treated (500 °C) |
| C-MCB | 2.18 | 4.00 | – | 0.958 | 0.964 | 0.979 |
| F-MCB | 1.47 | 1.63 | 4.20 | 0.946 | 0.958 | 0.987 |

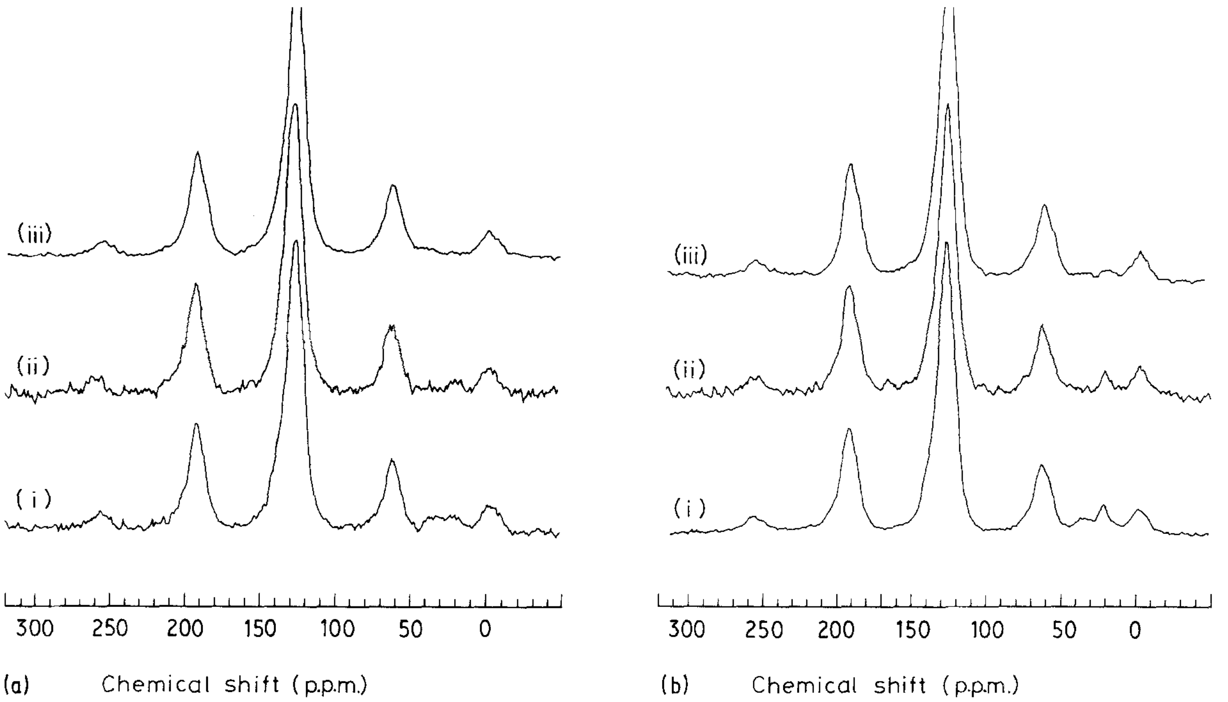

*Figure 4* $^{13}$C-NMR spectra of (a) C-MCB and (b) F-MCB observed by high-power decoupling and CP/MAS methods at 3250 Hz sample spinning speed. (i) As prepared, (ii) thermoset, and (iii) 500 °C.

at temperatures between 500 and 700 °C, MCB change in chemical composition and surface properties, and finally exhibit properties of a carbon compound.

Fig. 4 shows the $^{13}$C-NMR spectra of MCB (as-prepared, thermoset and 500 °C). The strong bands at 127 p.p.m. are assigned to aromatic carbons, and the peaks at 0, 60, 190 and 260 p.p.m. are spinning side bands. In addition, the peaks assigned to the aliphatic carbons were observed between 10 and 40 p.p.m. in the spectra of as-prepared MCB [27, 28]. After thermosetting, the peak at 35 p.p.m., due to α carbons bonded to aromatic rings, was reduced, while a new peak due to carbons in carboxyl groups appeared at 165 p.p.m. Because the intensity of the new peak in F-MCB is larger than in C-MCB, the degree of oxidation would be higher in F-MCB. This corresponds to the results from the elemental analysis and FTIR measurement. The carbons in methyl groups seem to be stable against oxidation, because their peak at 20 p.p.m. shows no decrease. Moreover, aliphatic bands almost disappeared after further heat treatment at 500 °C for 30 min. Table II shows the aromatic carbon fractions ($f_a$) estimated as the ratio of the areas of the peaks due to aromatic carbons to those of the whole peaks. On as-prepared MCB, $f_a$ of C-MCB is larger than that of F-MCB. $f_a$ increases as the heat treatment proceeds, resulting in 0.979 on C-MCB, 0.987 on F-MCB at 500 °C.

X-ray diffraction was performed in order to estimate the graphitizability of MCB (1000–3000 °C). Fig. 5 shows the changes in the values of interplanar spacing, $d_{(0\,0\,2)}$ and crystallite thickness, $L_{c(0\,0\,2)}$ with HTT. For reference, the changes in those values of the conventional MCB (Type M) are also shown in Fig. 5. For C-MCB and F-MCB, $d_{(0\,0\,2)}$ similarly decreased with an increase in HTT, reaching 0.3361 nm for C-MCB and 0.3368 nm for F-MCB at 2500 °C, and remaining approximately constant up to 3000 °C. $L_{c(0\,0\,2)}$ of C-MCB and F-MCB also changed in the same way below 2500 °C, markedly increasing above 1500 °C, at which carbonization would be complete. At 3000 °C, they were 77.8 nm and >100 nm for C-MCB and F-MCB, respectively. On the other hand,

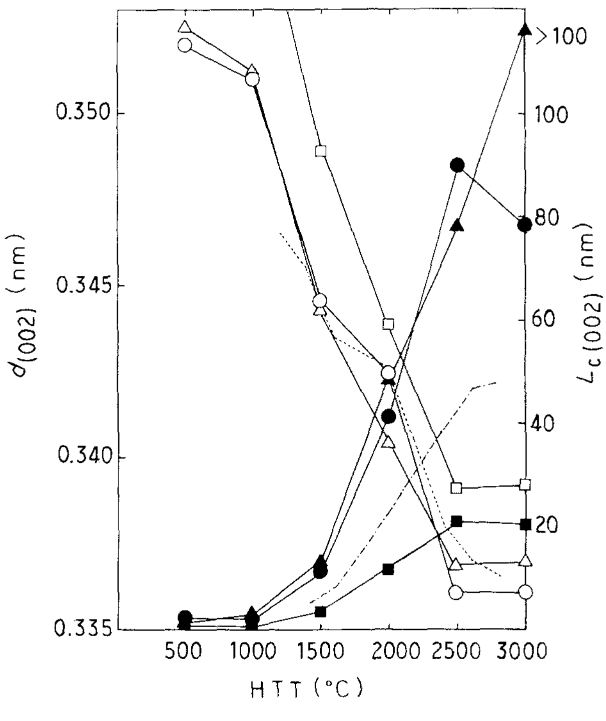

*Figure 5* Changes in XRD parameters (○, △, □) $d_{(0\,0\,2)}$ and (●, ▲, ■) $L_{c(0\,0\,2)}$ of heat-treated MCB as a function of HTT. (○, ●) C-MCB, (△, ▲) F-MCB, (□, ■) N-MCB. ○, △, □ (——) $d_{(0\,0\,2)}$ Type-M beads, (—.—) $L_{c(0\,0\,2)}$ Type-M beads.

$d_{(0\,0\,2)}$ of N-MCB decreased with increasing HTT; however, it remained larger than those of C-MCB and F-MCB at every HTT, resulting in 0.3392 at 3000 °C. In addition, the increase in $L_{c(0\,0\,2)}$ was much smaller, the value being only 26.3 nm at 3000 °C. As a result, both C-MCB and F-MCB seem to be fairly graphitizable, in contrast with N-MCB. These differences, as described above, can be attributed to the original texture of MCB. Observation with a reflected polarized microscope indicates that both C-MCB and F-MCB consist of domains with the accumulations of regularly oriented molecules, while the molecules seem to be poorly oriented in N-MCB. It appears that the differences in unit size of the optical anisotropic texture between C-MCB and F-MCB, discussed in a recent paper [18], do not affect the XRD parameters.

The Raman spectra were also measured to evaluate structural changes in MCB with HTT. Most carbonaceous materials exhibit two Raman bands at 1580 and 1360 cm$^{-1}$. The 1580 cm$^{-1}$ band is attributed to an originally Raman-active vibration of the hexagonal ring in graphite ($E_{2g}$ mode) with crystal symmetry, and the 1360 cm$^{-1}$ band is due to a vibrational mode arising from the distorted hexagonal lattice near the crystal boundary, lacking in transitional symmetry. Accordingly, compared with 1580 cm$^{-1}$, the 1360 cm$^{-1}$ band is greatly affected by changes in the amount of structure affected in the graphite crystal by the HTT [29, 30]. Fig. 6 shows the changes in half-band widths of 1360 and 1580 cm$^{-1}$, and relative intensity ratio ($R$) of these two bands. The structural defect in the graphite-like crystal certainly decreased; however, over 2000 °C, it decreased very slightly, i.e. the modification of structural defects in both MCB ceased at 2000 °C, and residual defects cannot be excluded even at 2800 °C. The $R$-value of C-MCB is larger than that of F-MCB at lower temperatures. Until carbonization ceases, C-MCB appear to hold relatively larger imperfections in the graphite-like layer planes than F-MCB. In the temperature range above 2000 °C, they showed no distinct differences in $R$-values.

For comparison of the graphitizability, the XRD parameters of MCB and other carbonaceous materials (mainly particle shape) heat treated at 2800 or 3000 °C are summarized in Table III [31–35]. The $d_{(0\,0\,2)}$ values of C-MCB and F-MCB are equal or smaller compared with conventional MCB, and are smaller than those of other carbon materials. Furthermore, C-MCB and F-MCB have larger values of $L_{c(0\,0\,2)}$ than the other materials. In addition, the apparent crystallite diameter, $L_a$ [36, 37], is found from calculation of the $R$-value to be approximately 100 nm. Namely, C-MCB and F-MCB have excellent graphitizability as spherical carbon materials. On the other hand, the X-ray parameters of N-MCB are the same as those of thermal black.

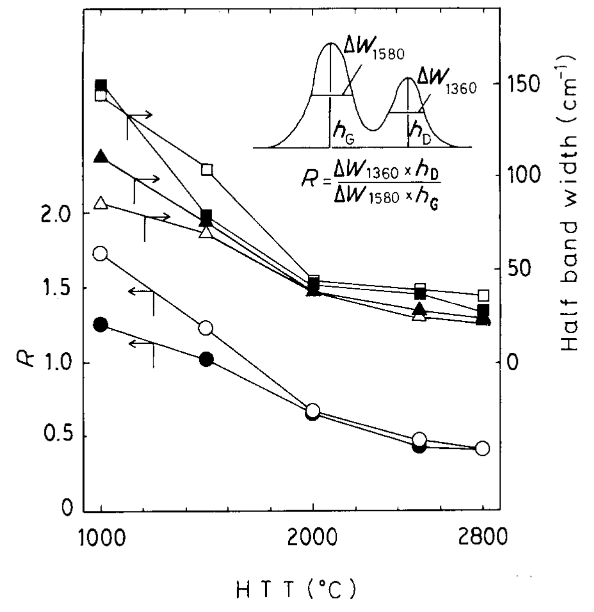

*Figure 6* Changes in $R$-value (intensity ratio) and half band width of the laser Raman bands of heat-treated MCB as a function of HTT (°C): (○, ●) $R$-value, (□, ■) $\Delta W_{1360}$, (△, ▲) $\Delta W_{1580}$. (○, □, △) C-MCB, (●, ■, ▲) F-MCB.

TABLE III X-ray diffraction parameters of MCB and various carbon materials

| | HTT (°C) | $d_{(0\,0\,2)}$ (nm) | $L_{c(0\,0\,2)}$ (nm) |
|---|---|---|---|
| C-MCB | 3000 | 0.3361 | 78 |
| F-MCB | 3000 | 0.3368 | > 100 |
| N-MCB | 3000 | 0.3392 | 20 |
| Type-M MCB [31] | 2800 | 0.3369 | 48 |
| Type-P MCB [31] | 2800 | 0.3370 | 45 |
| Carbon sphere [32] | 3000 | 0.3382 | 26 |
| Gilsonite coke [33] | 3000 | 0.3376 | 37 |
| Thermal black [34] | 3000 | 0.3395 | 30 |
| Pitch based carbon fibre [35] | 3000 | 0.3378 | 18 |
| Graphite | – | 0.3354 | > 100 |

## 4. Conclusion

The changes in chemical properties of MCB during thermosetting, carbonization and graphitization have been observed by various analytical methods. In the thermosetting process, the aliphatic carbons are mainly attacked by oxygen, and the weight gain of MCB is approximately 5 wt %. The C–H groups and the oxygen-containing functional groups partly remain after heat treatment at 500 °C; however, they were completely eliminated at 700 °C. Heat treatment at 1000 °C causes a slight irregularity on the surface of MCB. The results of XRD measurements indicate that both C-MCB and F-MCB have high graphitizability, which is ascribed to their original texture consisting of accumulations of regularly oriented molecules. The growth of graphite crystal observed above 1500 °C seems to be notable towards the perpendicular direction ($c$-axis) of the graphite layers, and results in the deformation in shape of MCB at 2800 °C.

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