CHARACTERIZATION OF ULTRAFINE PITCH PARTICLES PREPARED BY ANTI-SOLVENT METHOD

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Introduction

Ultrafine particle is one of recent topics in the materials field because it shows different properties from the bulk phase. A simple preparation method of ultra-fine pitch particles (UFP) having less than 40nm of diameter was developed. UFP were prepared from solvent-soluble coal-tar pitch by an anti-solvent method. The difference in solubility of pitch into two organic liquids permits us to produce very small size particles. When using the coal-tar pitch, a combination of quinoline and acetone as a good and poor solvent was favorable for getting satisfactory small and finely dispersed particles. The obtained UFP are considered as an unique carbon material and expected to be versatile. In present study, the characterization mainly focused on graphitizability and surface properties of UFP is presented.

Experimental

Pitch used was specially synthesized from coal-tar pitch for spinning high performance pitch based carbon fiber. This pitch shows 300°C of softening point (Mettler) and contains no quinoline insolubles, 31.5wt% of pyridine insolubles and 92.5wt% of xylene insolubles. Moreover, acetone solubles were pre-removed by a refluxing at its boiling temperature. The anti-solvent method is summarized in Fig.1. Arbitrary weight of pitch was completely dissolved in 100cm^3 of quinoline at 80° C. Then, prepared pitch/quinoline solution was gradually introduced into 1dm^3 of acetone with stirring. Promptly, pitch being unable to dissolve appeared in acetone as solid particle dispersoid, thus, the suspension comprising pitch/quinoline/acetone was available. Solid/liquid separation was carried out by the addition of distilled water into the suspension. The water acts as a flocculant. And the flocculated pitch particles were easily separated by filtration using sintered glass filter. To prevent the UFP from melting, they were heat-treated at in air. The thermoset (oxidized) UFP were used for the further heat treatment up to 3,000°C.

Results and Discussion

Figure 2 shows TEM and FE-SEM micrographs of typical UFP which appeared from 20g/dm^3 of pitch/quinoline solution. Though they are irregular in shape, their particle size are less than 40nm and particle size distribution is fairly narrow. The specific surface area of UFP by BET method using N_2 was obtained in the range of 50-200m^2/g depending on the preparation conditions (concentration of pitch solution, supplying rate into poor solvent etc.). After the optimization of these conditions, UFP having about 20nm of diameter could be obtained.

Preliminary experiments revealed the oxidation at 350°C for 60min was optimum for thermosetting. The thermoset UFP were no longer plastic and maintained their original shape up to 3,000°C (Fig.3). Changes in XRD parameters of UFP during carbonization and graphitization are shown in Fig.4. The d-spacing of UFP is wider and the Lc(002) is smaller than those of original pitch particles (pulverized between 45-53μm and thermoset under same condition mentioned above). The XRD parameters are comparable to those of a carbon black (20nm; Mitsubishi #2300). This low graphitizability of UFP would be ascribable to the disordered assembly of pitch molecules in the preparation process. Namely, when UFP appeared in poor solvent, pitch molecules randomly aggregated in a moment. And this assembly was fixed by the thermosetting; it was no room for changing the basic structure of UFP even at the temperatures above 2,000°C.

Figure 5 presents adsorption isotherm of nitrogen onto UFP at 77K. The shape of isotherm is Type IV classified by IUPAC. The hysteresis on the desorption branch can be attributable to the presence of mesopores. Besides, the peak of pore size distribution was around 10nm of radius from the estimation by Dollimore-Heal method using adsorption branch of the isotherm (Fig.6). The size of mesopores corresponds to the inter-particle space between primary UFP particles.

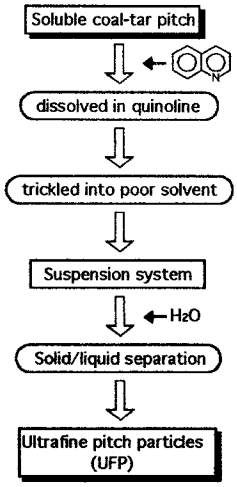

Figure 1. Procedure for preparing ultrafine pitch particles

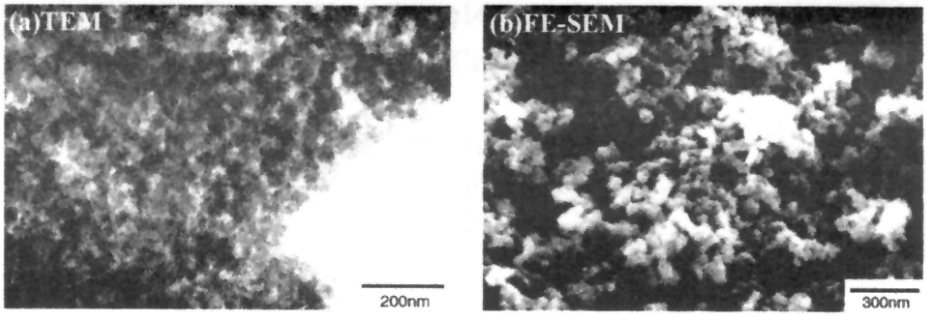

Figure 2. Electron micrographs of UFP prepared from 20g/dm^3 of pitch/quinoline solution by anti-solvent method.

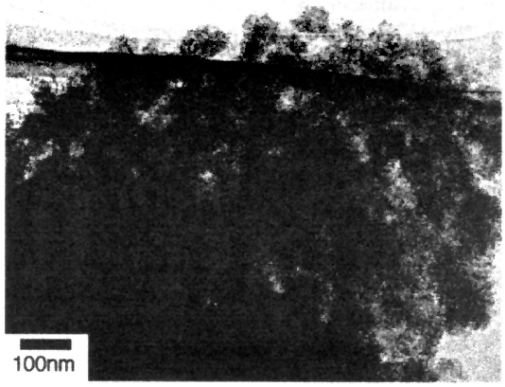

Figure 3. Transmission electron micrograph of UFP heat-treated at 3,000°C in Ar after thermo-setting at 350°C for 60min in air.

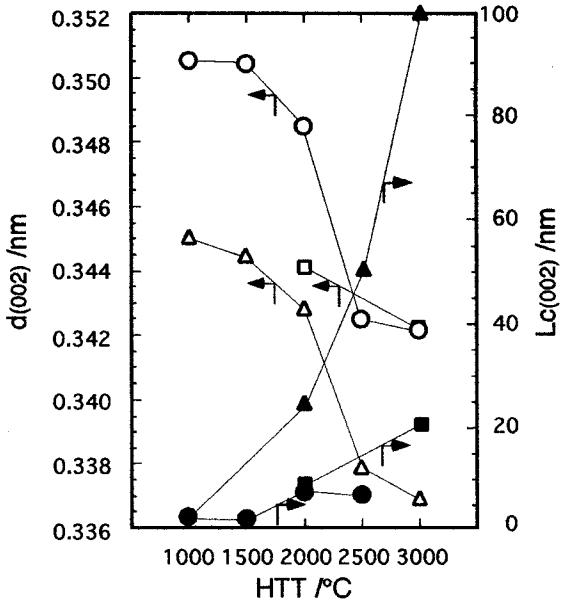

Figure 4. Changes in XRD parameters of UFP as a function of heat treatment temperature. ○●:UFP, △▲:pitch particle(45-53μm), □■ :carbon black(20nm), open:d(002), closed:Lc(002)

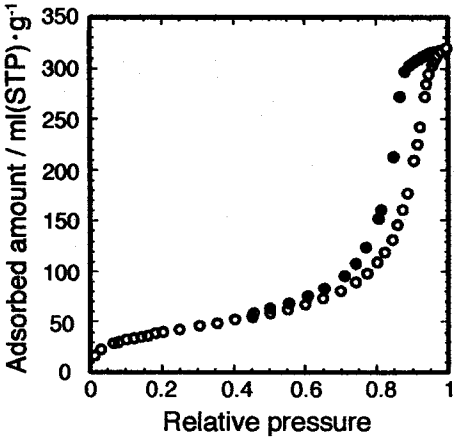

Figure 5. Adsorption isotherm of nitrogen on UFP at 77K.

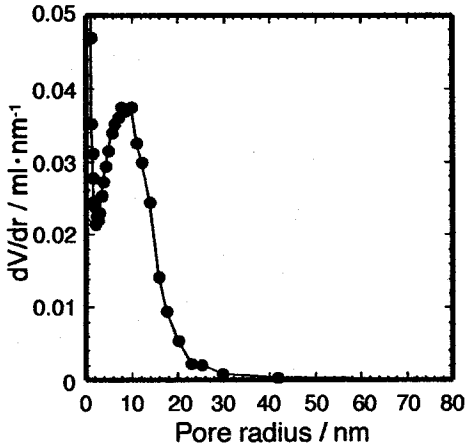

Figure 6. Pore size distribution (Dollimore-Heal method) of UFP calculated from adsorption branch of the isotherm.