Hydrothermal Processing of Carbon Nanotubes from Dense Fluids: Growth Mechanism

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We report in this communication the growth mechanism of multiwall carbon nanotubes during hydrothermal treatment of carbon soot at 800°C and 100 MPa. High-resolution electron microscopy (HRTEM) study reveals the formation of multiwall carbon nanotubes made of a hollow core enclosed in well-ordered concentric graphitic layers after hydrothermal treatment.

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1. Introduction

Iijima first prepared crystalline carbon nanotubes by using a graphite arc-discharge method, at temperatures exceeding 2000°C.¹⁾ Carbon nanotubes prepared by this method are of good quality, but the yield is low and the production cost high. Twenty years earlier, Baird obtained tubular nanofilaments of poorer quality by pyrolysis of hydrocarbons.²⁾ The synthesis mechanism of tubular carbon filaments by pyrolysis of hydrocarbons was proposed by Tibbet in 1984, and is now generally known as the vapor-liquid-solid (VLS) process.³⁾ Refinements of the earlier works using a VLS synthesis mechanism to synthesize carbon nanotubes at temperatures below 1200°C, based in the pyrolysis of hydrocarbons carried out in the presence of metal transition nanoparticles, are usually known as 'catalytic' methods for obtaining carbon nanotubes. The yield of nanotubes using catalytic methods is higher than using the arc-discharge method. Unfortunately, the nanotubes synthesized by 'catalytic' methods are of lower quality than those obtained by the arc-discharge process and usually covered with thick amounts of amorphous carbon.⁴⁻⁶⁾ The amorphous part is difficult to separate and remove from the hollow nanotubes. Besides, the complexity involved in methods using gaseous and toxic hydrocarbons is high, so an alternative and easy way should be employed for the synthesis of carbon nanotubes. A promising novel technique is hydrothermal processing of carbon.⁷⁾ The oxidative effect of hot water on amorphous carbon is currently used for purification of carbon nanotubes by hydrothermal treatment (immersion in water at moderate and high temperatures and pressures.^{8,9)} However, little is known about the possibilities of hydrothermal method for the synthesis of nano-structured carbons. Only recently, new carbon structures obtained in pure supercritical water—nanocells,¹⁰⁾ nanotubes^{11,12)} and graphite polyhedral crystals¹³⁾—have been reported by Yoshimura's group. The aim of the present communication is to present the growth mechanism during hydrothermal synthesis of multiwall carbon nanotubes by using water and amorphous carbon, without the addition of metal catalyst.

2. Experimental

Hydrothermal experiments were carried out using conventional Tuttle-type autoclaves made of stellite superalloy. Initial samples of amorphous carbon soot were placed into golden capsules of 3 mm in diameter and 5 cm in length, which were subsequently filled with double distilled water (≈ 0.3 g). The capsules were then sealed, to prevent any contamination from the autoclave, placed into the autoclave and treated at a temperature of 800°C and pressure of 100 MPa for 48 hours. Electron microscopy studies were carried out using a H9000NAR, Hitachi TEM at an operating voltage of 300 kV. Samples were prepared by adding methanol and dispersing the suspension in an ultrasonic bath. After ultrasonication, a drop was placed on a microgrid and dried in air before observation.

3. Results

The initial samples consists mainly of amorphous carbon, with clusters of graphitic structures of low crystallinity embedded in the amorphous matrix. This structure is typical of carbon soot deposits. Electron microscopy observations after hydrothermal treatment of the samples, at 800°C and 100 MPa pressure, revealed aggregates of needle-like or polygonal nanoparticles. Figure 1 shows a typical aggregate in the treated sample. An internal channel can be noticed inside the needle-like particles, indicating they are carbon nanotubes. Carbon nanotubes observed in the treated sample have diameters in the range of tens and length in the range of hundreds of nanometers. Observed individually, they reveal an internal hollow cores with diameters from 2 to 8 nm. Figure 2 is a HRTEM micrograph showing in more detail the section of a hydrothermal nanotube. The quality of the walls, showed by their the lattice fringe image, can be observed. The interlayer spacing in the carbon nanotube multiwall, ~ 0.34 nm, corresponds to the 002 interplanar distance of graphitic carbon.

Fig. 1 Electron micrographs showing an aggregate of carbon multiwall nanotubes after hydrothermal treatment.

Fig. 2 HRTEM micrograph of a nanotube showing the lattice fringe image of the wall.

4. Discussion

Our interpretation of the results is that hot water at high pressure may dissolve carbon in the form of carbon oxides, hydrocarbon radicals and carbon clusters. The movement of the fluid (*e.g.* by convection) also causes the dispersion of carbon clusters and facilitates the collisions and interactions of small clusters. Many authors have observed reactivity between water and carbon in supercritical conditions, and it is well known that dissolution of amorphous carbon can take place in pure water, without the need of any catalyst.^{7,8)} Ordered graphitic structures are more stable in supercritical fluid than disordered carbon. Thus, they can not only survive the treatment in supercritical water, but also act as seeds for growth of bigger clusters under conditions of dynamic equilibrium with the supercritical fluid, that results in the survival of only the most stable carbon structures. The reduced surface energy of closed graphitic multiwall tubes provides the added stability to grant the survival and subsequent growth of multiwall nanotubes; at the expense of the dissolution of

amorphous carbon. The dissolution of carbon in supercritical fluids plays a similar role that the dissolution of carbon inside metal particles used in other methods. The absence of any metal trace in EDS, XRD and TEM evidence support to a noncatalytic growth by addition of carbon hexagons, mechanism that is also supported by a relatively high quality of the walls formed, demonstrated by their Raman spectra, described elsewhere.¹⁰⁾

The formation of carbon nanotubes by dissolution-precipitation of amorphous carbon in hot hydrothermal fluids has similarities with high-temperature non-catalytic synthesis, as well as with VLS catalytic synthesis. Vacuum or inert atmospheres used in VLS-based growth act as dispersing media that prevent the carbon ions and radicals from reacting before they can reach the metal carbides. Therefore, the mechanism of hydrothermal growth by carbon cluster reaction can be easily understood if we consider that supercritical water plays the role of solvent, instead of high temperature plasma or liquid metal carbides in other synthesis methods. The enhanced surface diffusion in the aqueous fluid promotes the growth of well-ordered multiwall tubes at lower temperatures than in non-catalytic growth from gas-like conditions. However, the growth of hydrothermal nanotubes takes longer times than in non-catalytic synthesis at very high temperatures.

Synthesis from liquid phase allows the continuous dissolution-precipitation of undesirable amorphous carbon and the formation of crystalline multiwalls. The main reason is the reactivity of the aqueous hydrothermal fluid, compared to synthesis in gas-like conditions; the high reactivity enhances the kinetics of the crystalline multiwall formation. The reaction conditions in hydrothermal systems can be maintained stable as long as wished; which is of great importance, because the formation of nanotubes is a slow process, and it opens the possibility of a continuous flow system for hydrothermal synthesis. We believe these are the principal merits of the new method.

5. Conclusions

We have shown here that amorphous carbon transform into graphitic multiwall nanotubes as a result of hydrothermal treatment at 800°C and 100 MPa, under supercritical conditions. Formation of multiwall nanotubes with ordered graphitic walls has been observed in the C–H–O system in absence of catalyst at a relatively low temperature.

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