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SPECIAL TOPICS

Growth mechanism of iron-filled carbon nanotubes

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Iron-filled nanotubes were synthesized in a carbon arc in the presence of He and $\text{Fe}(\text{CO})_5$ gases. The consumption of the $\text{Fe}(\text{CO})_5$ inside the arc chamber was controlled by the pressure of the pentacarbonyliron $\text{Fe}(\text{CO})_5$ gas. Different shapes and filling extents of nanotubes were found depending on the pentacarbonyliron concentration supplied. Based on high-resolution transmission electron microscope images, we propose a growth model of iron-filled carbon nanotubes. The growth proceeds through the deposition and surface diffusion of carbon on the liquidlike metal. The hollow tubes probably grow spontaneously. © 1996 American Institute of Physics. [S0021-8979(96)06111-4]

Interest in graphitic tubules¹ has been stimulated greatly by the recent discovery of metal-filled nanotubes²⁻⁵ due to their potential unique properties and applications.

The growth mechanism of the encapsulated fibers is an interesting problem. Many explanations have been proposed based on a particle at the tip of the tubule. The growth is generally considered to be driven by the active catalytic graphitization of the carbon in the vapor phase by metal species.^{2,6} Growth models for catalytic chemical vapor deposition (CCVD) graphite fibers suggest that growth proceeds through the dissolution and diffusion of carbon around a seed catalyst particle until the particle becomes chemically poisoned or completely covered by a carbon deposit.^{7,8} However, no model can successfully explain all the results which have been obtained up to now. In this paper, we present a new result on iron-filled graphitic tubules using electric arc discharge which indicates a new growth mechanism.

We used pure graphite rods as the anode and cathode for the electric arc discharge. The discharge chamber was filled with He gas and pentacarbonyliron $\text{Fe}(\text{CO})_5$ gas which can be decomposed to Fe at high temperatures. The He pressure inside the chamber was 50 mbar, and the $\text{Fe}(\text{CO})_5$ pressure was varied from about 50 to about 200 mbar for different runs in order to vary the extent of Fe filling in the tubules. The voltage and current used for the discharge were 20 V and 100 A, respectively. The detailed setup will be described elsewhere.⁹ The soot formed during the discharge was dispersed in alcohol and then mounted on Cu grids with no substrate for transmission electron microscope (TEM) observation. Samples collected from the soot adhered on hard material with cylindrical shape formed between the two elec-

trodes were examined with both JEOL 2010F and JEM-3010 for high-resolution imaging and microdiffraction, respectively. In the soot collected from the chamber walls we found fullerene and carbon nanoparticles encapsulating iron metal or iron carbide.⁹

Three runs were performed with different concentrations of iron, controlled by the pressure of $\text{Fe}(\text{CO})_5$ which depended on the temperature of the reservoir of liquid $\text{Fe}(\text{CO})_5$. The actual concentrations of iron determined by chemical analysis of the soot that was deposited on the wall were 1.8, 4.6 and 12 wt % for these three runs. We found that the kind of product depends on the iron concentration. For the soot with iron concentration of 1.8 wt %, we mainly observed iron nanoparticles encapsulated by graphite. For the soot with high iron concentration of 12 wt %, we observed a large number of graphite tubules, some of which were filled with iron as shown in Fig. 1. A smaller number of iron-filled tubules were observed for the soot with 4.6 wt% iron. The diameter of those fibers range between 20 and 65 nm, and their lengths extend to 2.5 μm .

The fibers obtained in the present work resemble those grown by manganese-catalyzed carbon electric arc discharge,² but the interesting finding here is that many tubules were filled with iron for most of their lengths with a core diameter up to 50 nm. The shape of the fibers contrasts with the straight and perfect alignment of multilayers for the entire lengths of the hollow tubules. In some cases, the filling occurs only at a few positions in a long tubule as marked by arrows in Fig. 2.

Figures 3(a)–3(e) show, at high resolution, the inclusions trapped inside the hollows. The fiber shapes vary con-

FIG. 1. A low-magnification image of an iron-encapsulated carbon tubule with the inside filled for most of its length.

siderably. However, the graphite (002) planes that make up the walls always have the same spacing of 0.34 nm, equal to the value for bulk graphite. When we compare the observed fiber shapes with the straight lines that are generally observed for fibers without inclusions, we can come to the conclusion that the inclusion has a decisive influence on the shape. A typical sample is shown in Fig. 3a, in which the graphite multilayers grew and curved along the inclusion up to its end, and then grew straight. At position A in this figure, a gap between the carbon layer and the inclusion is observed which was probably caused by the shrinking of inclusion upon transformation from liquidlike to solid phase after cooling. Some high-resolution images of the filling material inside tubules show that the inclusion is a single crystallite (Fig. 3b), and in some cases it is a polycrystallite as indicated by an arrow in Fig. 3c. The lattice structure and composition of the inclusions determined by microdiffraction and EDX (energy-dispersive x-ray) analysis with a nanometer beam are those of iron carbide. One of the high-resolution TEM images and its corresponding diffraction pattern are shown in Fig. 4 together with the pattern of gold (standard). Based on the values of spacings, it is difficult to identify a definite iron carbide phase; however, in some cases it is possible that the inclusions are either FeC or Fe₃C. For the run with iron concentration of 7.14 wt %, however, the cementite Fe₃C in the soot was clearly observed by Mössbauer spectroscopy.⁹

FIG. 2. A low-magnification image of a twisted iron-encapsulated carbon tubule with the inside filled by iron at a few positions indicated by arrows.

FIG. 3. High-resolution images of graphitic nanotubes filled with iron carbide. Part of the filament is shown in each of the sections a–e. (a) The shape of graphite layers is determined by the inclusion. A gap between the carbon layers and the inclusion is indicated by arrow A. (b) Dislocations exist in the single-crystal inclusion, and in the graphite layers as well, as indicated by arrows. (c) An inclusion with polycrystalline structure. (d) The graphite layers grew straight after iron supply ceased. (e) A sudden increase and subsequent stoppage of the iron flux; the iron carbide overflowed the (vertical) carbon layers (position A).

The carbide Fe₃C was also observed in other studies either in electric arc discharge or in CCVD.^{4,6} Therefore, we assume that some tubules are filled with cementite as inclusions.

Although sometimes the inclusion shows a good single-crystalline structure, some dislocations still exist inside. In Fig. 3b we can clearly see a dislocation in a crystallite, and in graphite layers as well (marked by arrows). This means that during encapsulation there exists a quite high stress, probably caused by rapid cooling.

Based on the material which almost completely fills the tubule and its shape, we can propose a new growth model. At

FIG. 4. One of the high-resolution TEM images and corresponding diffraction pattern.

the beginning iron atoms formed by decomposition of $\text{Fe}(\text{CO})_5$ are deposited on the wall of the hard material with a diameter of 1.5 cm, which is formed by electric arc discharge between two electrodes, and then condense as a small particle in a liquidlike form. Subsequently, carbon atoms are deposited on the surface of the particle and diffuse all over it down to its edge contacting the wall of the hard material which acts as a substrate. The first carbon layer is then produced. New iron and carbon atoms continue to accumulate on the particle and its edge. The particle grows and the carbon layers develop by lateral growth along the external surface of the particle. As is well known, the melting temperature of graphite is much higher than that of iron, so upon deposition of carbon atoms on the surface of the particle, solid graphite layers are formed through diffusion, but the iron particle remains liquidlike until further cooling occurs. Therefore, the shape of the tubule changes with time depending on the condensation rate of the iron and carbon atoms on this inclusion and more specifically on the ratio of the iron and carbon fluxes. Normally, the iron and carbon supply cannot be kept constant during electric arc discharge for many obvious reasons. The temperature at each point also fluctuates. It is therefore quite understandable that we found a

variety of fiber shapes. When the iron supply ceases, there is a slow, direct growth of empty tubules. This growth does not depend very much on the carbon flux, so long as straight nanotubes are observed. The shapes of extended growth of the fibers in Figs. 3a, d support this mechanism. Further evidence is shown in Fig. 3e, which presents a part of a tubule having a mushroom shape. In it, an inclusion is crystallized with good lattice planes. It is encapsulated by two stacks of graphite layers, on the cap and along the tubule. It seems that an interesting phenomenon took place at position A in Fig. 3e. The graphite layers protruded to produce extended growth in the crystallized metal, and it appears that carbon atoms diffused into the inclusion. This image, however, can be explained by overflow of the liquidlike iron over the tubule due to the condensation of iron being much faster than carbon layer growth at this moment. New layers which are discontinuous with the layers described above are considered to have grown via surface diffusion. The shape of a new layer resembles a cap, probably due to the breaking off of iron supply after a superfluous layer. It is worth noting that the cementite crystal we found is formed only when cooling occurs.

In conclusion, growth proceeds through the deposition and surface diffusion of carbon on the liquidlike metal, and the iron probably does not play an important catalytic role during formation of iron-filled tubules. The hollow tubules probably grow spontaneously.¹⁰

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