CARBON FIBERS AND CARBON NANOTUBES

by Morinobu Endo and M. S. Dresselhaus

Shinshu University, Nagano, Japan

Massachusetts Institute of Technology, Cambridge, MA 02139

INTRODUCTION

Carbon fibers have been studied scientifically since the late 1950s and fabricated industrially since 1963. They are now becoming a technologically and commercially important material in the aerospace, construction and sporting goods industries, and carbon fibers are now becoming technologically significant even for applications in the electronics industry. The world carbon fiber market now has grown to about 12,000 tons/year of product, after 40 years of development.

'Carbon fibers' are defined as a one-dimensional filamentary form of carbon with an aspect ratio (length/diameter) of greater than 100. The earliest documented carbon fibers are the bamboo-char filaments made by Thomas Edison for use in the first incandescent light bulb in 1880. With time, carbon fibers were replaced by the more robust tungsten filaments in light bulb applications, and consequently, over time, carbon fibers disappeared from industrial view. But in the late 1950s, carbon fibers once again became commercially important because of the aggressive demand of aerospace technology for lightweight and strong composite materials, in which carbon fibers were used as a reinforcement agent with plastics, metals, ceramics and bulk carbons. The specific strength (strength/weight) and modulus (stiffness/weight) of carbon fiber-reinforced plastics show the highest value

1

for all engineering materials, due to the high performance of the carbon fiber constituent. More recently, carbon fibers have even been applied in the construction industry and in civil engineering applications using carbon fiber reinforced cement composites.

Since the necessary temperature and pressure to prepare a carbon fiber from the liquid phase is at the triple point ($T_t = 3900\,\mathrm{K}$, $p_t = 100\,\mathrm{bar}$), it would be very difficult to prepare carbon fibers from the melt under industrial processing conditions. Carbon fibers are therefore prepared from organic precursors. This preparation is generally done in three steps, including stabilization of an organic fiber (at $\sim$300°C) to form the precursor, carbonization of the precursor fiber (at $\sim$1100°C), and subsequent graphitization (above 2500°C). In a narrow sense, fibers undergoing only the first two steps of development are commonly called "carbon fibers", while fibers undergoing all three processing steps are called "graphite fibers". Carbon fibers are generally used for their high strength, while graphite fibers are used for their high modulus.

Graphite Whisker
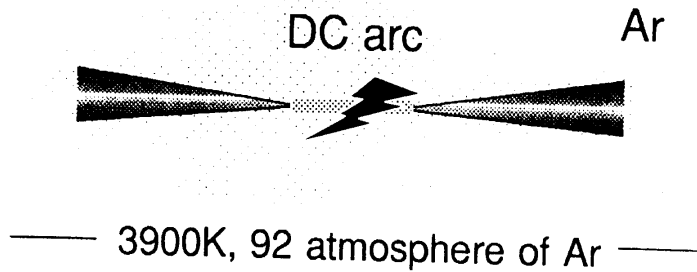
DC arc   Ar
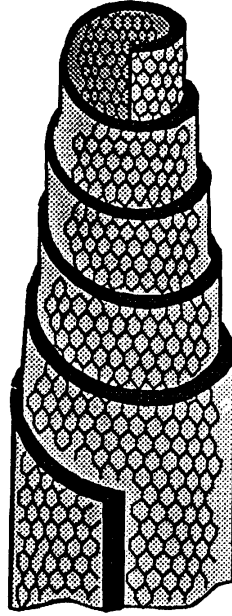
—— 3900K, 92 atmosphere of Ar ——

FIG. 1. Model for graphite whiskers grown by the DC arc-discharge of graphite electrodes (reported by Roger Bacon, 1960). The whiskers were reported to have the scroll structure of rolled up graphite sheets and to have very high mechanical strength and modulus along the fiber axis, similar to the ideal values of a graphene sheet.

Historically, Roger Bacon's graphite whiskers (see Fig. 1) had demonstrated the highest mechanical properties of a carbon fiber (with regard to both strength and modulus),

comparable to the ideal value for a graphite hexagonal network. These whiskers had for many years served as the performance target for carbon fiber technology, even though these whiskers have never been fabricated on a large scale production basis.

Much has happened in carbon fiber science and technology since the pioneering work by Thomas Edison on carbon filaments more that a century ago. Right now the field is very exciting as a new area is just emerging with the entry of a new family of nanostructured carbon nanotubes. Interestingly, one of the proposed applications of carbon nanotubes is to illumination through electron field emission, and these new devices may soon replace the incandescent light for certain applications. In this new area, multiwall carbon nanotubes and nanofibers would form the basis for future applications and would bridge the gap between conventional vapor grown carbon fibers and single wall carbon nanotube science through the anastomosis of the classical science of vapor grown carbon fibers with the quantum effects which characterize carbon nanotubes.

SYNTHESIS AND PROPERTIES

Micrographs along with appropriate structural models are shown in Fig. 2 for the three typical types of carbon fibers, namely PAN (polyacrylonitrile)-based fibers, mesophase pitch-based fibers, and vapor grown carbon fibers. The PAN-based fibers consist of small carbon structural units preferentially aligned with the carbon hexagonal segments parallel to the fiber axis, and the intertwined morphology is responsible for the high mechanical strength of PAN-based fibers. The mesophase pitch-based fibers consist of well aligned graphitic layers nearly parallel to the fiber axis, and this high degree of crystallinity is responsible for their high modulus or stiffness. Finally, the vapor grown fibers consist of coaxial cylindrical graphene sheets and are closely related to multiwall carbon nanotubes. These three different structures give rise to different physical properties, though each type of fiber features carbon hexagonal networks, which have the

4

strongest covalent bonds in nature. These strong interatomic bonds lie in sheets essentially parallel to the fiber axis, and are responsible for the high mechanical performance of carbon fibers.

Referring to Fig. 3 we see that PAN-based fibers have high strength and mesophase pitch fibers have high modulus, while vapor grown carbon fibers provide mainly high modulus materials. Also shown in Fig. 3(a) are isotropic pitch-based (general purpose grade) fibers, showing much lower modulus and strength, but widely used in composites because of their low cost, and good chemical stability.
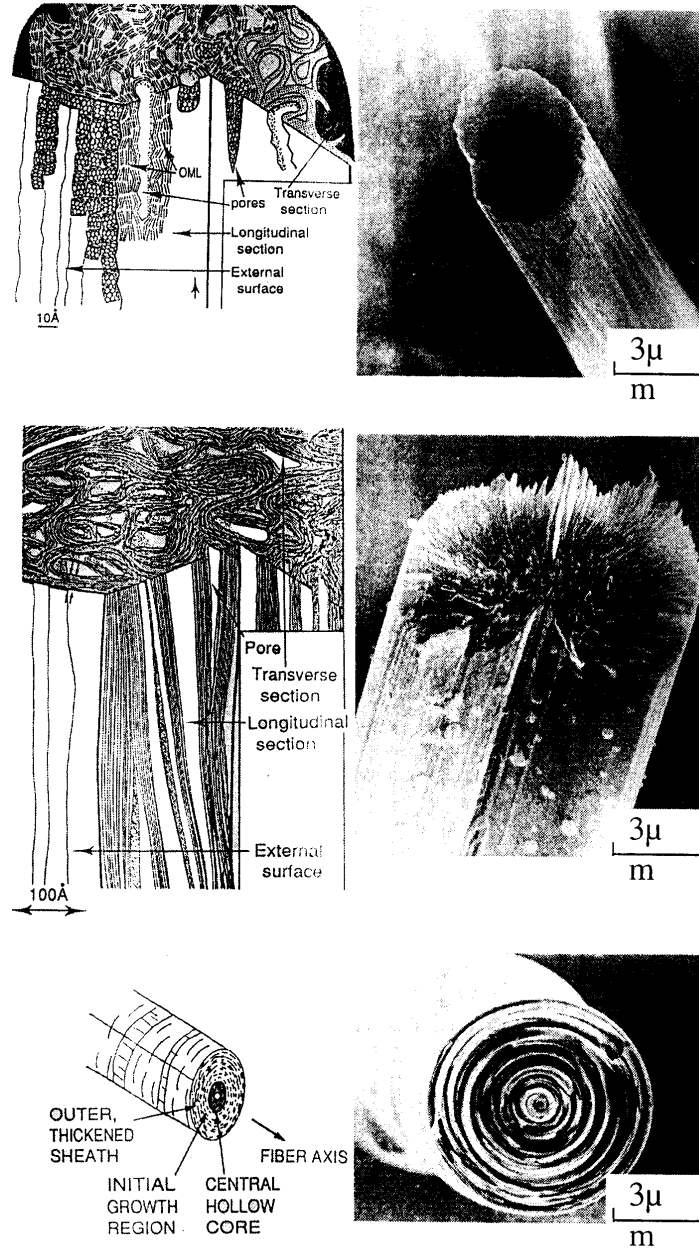
FIG. 2. Structural model and SEM micrographs of typical types of carbon fibers: (a) PAN-based high strength fibers, (b) PAN-based high modulus fibers, and (c) vapor grown carbon fibers.
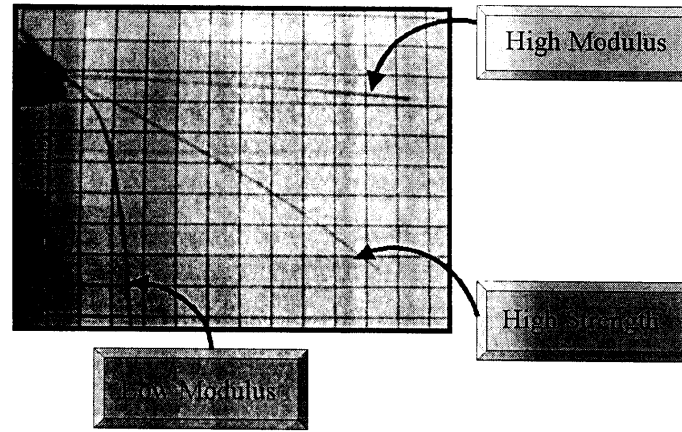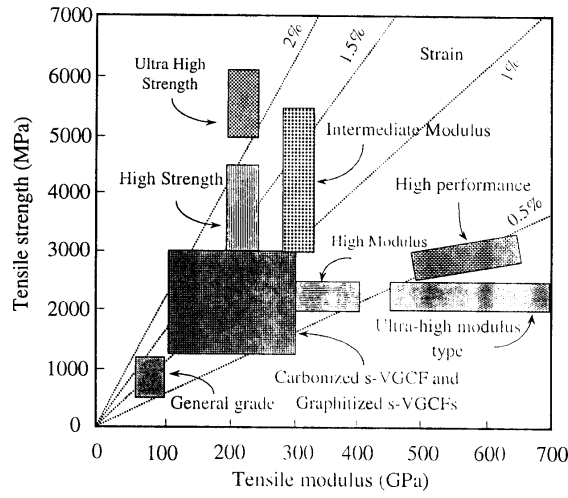
FIG. 3. (a) The mechanical properties of various kinds of carbon and graphite fibers. (b) provides a direct indication of the differences between the mechanical properties of carbon fibers, from low modulus - high strength to high modulus -low strength fibers from the lower right to the upper left of the photograph where a test yarn containing ∼500 fibers was kept in a horizontal position. These fibers are often combined with other materials in order to get suitable mechanical properties when used in various kinds of composite materials.

At the present time, PAN-based carbon fibers account for approximately 95% of the worldwide carbon fiber market. The major commercial applications areas for all types of carbon fibers are in composites with plastics, metals, carbon and cement, where as a

filler, the carbon fibers additionally serve to increase the mechanical strength and modulus of the matrix materials. These composites are used for their mechanical properties, in aircraft, space technology, sporting goods, building construction, and recently in motor vehicles to reduce the weight and thus increase the gas mileage, and sometimes also for their electrical and thermal properties, which also basically originate from the strong C–C covalent bond of the hexagonal carbon networks.
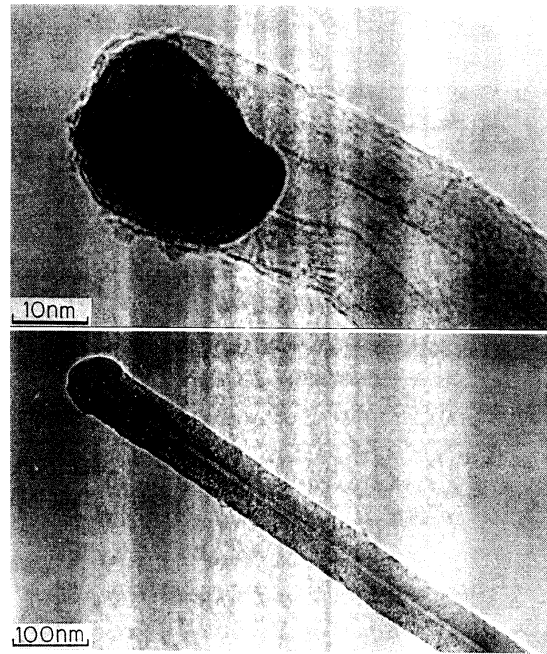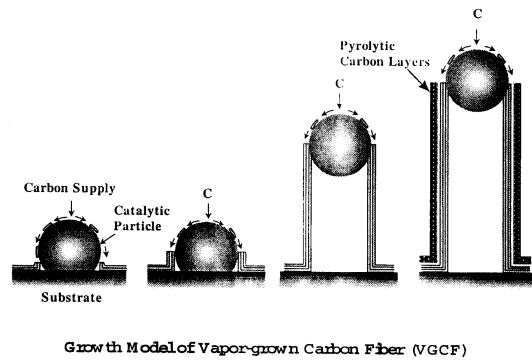
FIG. 4. (a) Growth mechanism of VGCFs using ultra-fine catalytic particles of metal. (b) Very early stage of fiber growth in which the catalytic particle is still active for promoting elongation growth. The primary fiber thus formed acts as a core for vapor grown fibers. (c) The fiber after the thickening growth has occurred by chemical vapor deposition of carbon layers on the thin primary fiber core. The encapsulated catalytic particle can be seen at the tip of the hollow core. (d) Vapor grown carbon fibers with diameters around 10 μm grown on a cylindrical ceramic substrate by seeding with catalytic particles and (e) vapor grown carbon fibers grown from a conventional carbon fiber as an application of seeding to form so-called "fox tail" fibers.

Vapor grown carbon fibers are synthesized by a somewhat different preparation process than for PAN-based fibers and mesophase pitch based-fibers insofar as vapor grown fibers are not prepared from a fibrous precursor, but rather are prepared directly from a hydrocarbon gas such as benzene or methane, using a catalytic growth process outlined in Fig. 4(a). Ultra-fine iron particles of diameter $< 10\,$nm are dispersed on a ceramic substrate, and a hydrocarbon gas diluted with hydrogen is introduced at temperatures of about 1100°C. Hydrocarbon decomposition (also called aromatic condensation) takes place on the catalytic particle, leading to continuous carbon uptake by the catalytic particle and continuous output by the particle of well-organized tubular filaments of the carbon honeycomb lattice, as shown in Fig. 4(b). The rapid growth rate of several tens of μm/min, which is 10^6 times faster than for the growth of common metal whiskers, allows the production of commercially useful quantities of vapor grown carbon fibers. Evidence in support of this growth model is the presence of catalytic particles in the resulting thin vapor grown carbon fibers shown in Fig. 4(c). The primary fiber is first formed by the catalytic process (with a diameter of several nanometers), and the fiber is then thickened by a successive CVD (chemical vapor deposition) process that deposits carbon layers on the primary core fiber, as shown in Fig. 4(c), where a long continuous central hollow core with about 5 nm diameter can be clearly seen. Figures 4(d) and (e) demonstrate fibers with diameters around $10\,\mu$m grown on a cylindrical ceramic substrate and the VGCFs grown from a conventional carbon fiber as an application of seeding to form so called "fox tail" fibers, respectively. By controlling the thickening process, the fiber diameter can be varied from several nm (approaching the range of carbon nanotubes) to about ten microns (the most common range of commercial carbon fibers).
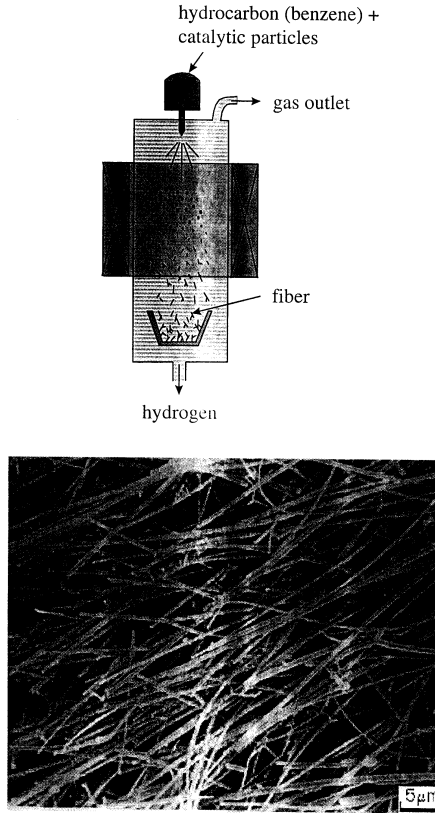
FIG. 5. (a) The fiber formation system used for the floating catalyst growth method in which ultra-fine metal catalyst particles, such as iron, are introduced with a mixture of hydrogen gas and a hydrocarbon feed stock, such as benzene and methane, to the vertical hot zone. The fibers grow while the catalytic particles are floating in the growth region of the reactor. (b) The vapor grown carbon fibers (VGCFs) obtained under controlled growth conditions of the flowing catalyst method. The growth conditions are selected to produce very pure fibers. These fibers are commercially available and have been used commonly as an important additive to the anode material of Li ion batteries.

Such a high elongation growth rate of the primary fiber provides the possibility of employing a three-dimensional growth process without any solid substrate [shown in Fig. 5(a)], whereby the nanometer-sized catalytic particles can float (or be suspended) for a long enough time in the heated zone of a reaction chamber to produce the growth of thin (100 nm homogeneous diameter) vapor grown carbon fibers, with lengths of several

11

hundred microns. The resulting vapor grown carbon fiber sample in Fig. 5(b) shows clean, straight fibers, which implies that the individual fibers experience uniform reaction conditions as they pass through the growth region in the reactor. By proper choice of growth conditions, large quantities of high purity vapor grown carbon fibers are obtained. Furthermore, the fiber diameter can be varied through control of the residence time of the fiber in the reaction zone and of the pressure of the hydrocarbon feed stock. This basic process could be promising for the large scale production of carbon nanotubes (a new member of the carbon fiber family) by modifying the present catalytic growth process.

In Fig. 6(a) we see the broken edge of a vapor grown carbon fiber. At the center of the annular ring structure, we can clearly observe a protruding carbon nanotube (with diameter of $\sim 5\,\mathrm{nm}$), which serves as the central core of the resultant thicker carbon fiber. This structural feature, which is common to vapor grown carbon fibers, also implies a discontinuity in the microstructure between the core and the thickened periphery of the carbon fiber, consisting of chemically vapor-deposited (CVD) carbons, as discussed further below. Such a discontinuity in structure can be retained even after heat treatment at temperatures as high as 3000°C, which is sufficient to yield a fully developed graphite structure in the peripheral region of a vapor grown carbon fiber, which assumes a polygonal shape, as shown in Fig. 6(b). Figure 7(a) shows the early stage of fiber growth of a thin fiber corresponding to a single wall carbon nanotube which has both an exposed region and a region partially coated with pyrolytically deposited carbon. Also seen in this photograph is a vapor grown fiber which has already undergone substantial thickening to reach a diameter of about 30 nm and a hollow core of 6 nm. Sometimes we can see an isolated carbon nanotube without a pyrolytic carbon coat in an early stage of growth, such as the fiber in Fig. 7(b), which was heat treated to 2800°C in argon. This type of nanotube can be produced through the same process as VGCFs by carefully controlling the vapor pressure of the hydrocarbon. It is not yet known whether or not a catalytic

particle is needed for the growth of such a nanotube, since catalytic particles have not yet been observed anywhere on the nanotube for the as-grown state.
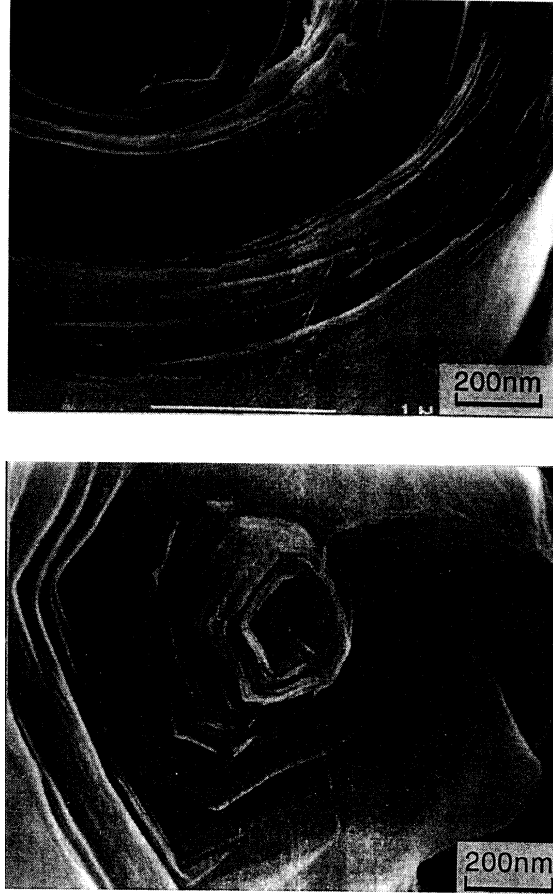

FIG. 6. (a) Carbon nanotube exposed on the breakage edge of a vapor grown carbon fiber as grown (a) and heat-treated at 3000°C (b). The sample is fractured by pulverization, and the core diameter is ~50 Å. (b) These photos suggest a structural discontinuity between the nanotube core of the fiber and the CVD deposited carbon layers. The photos show the strong mechanical properties of the nanotube core which maintain its form after breakage of the periphery.
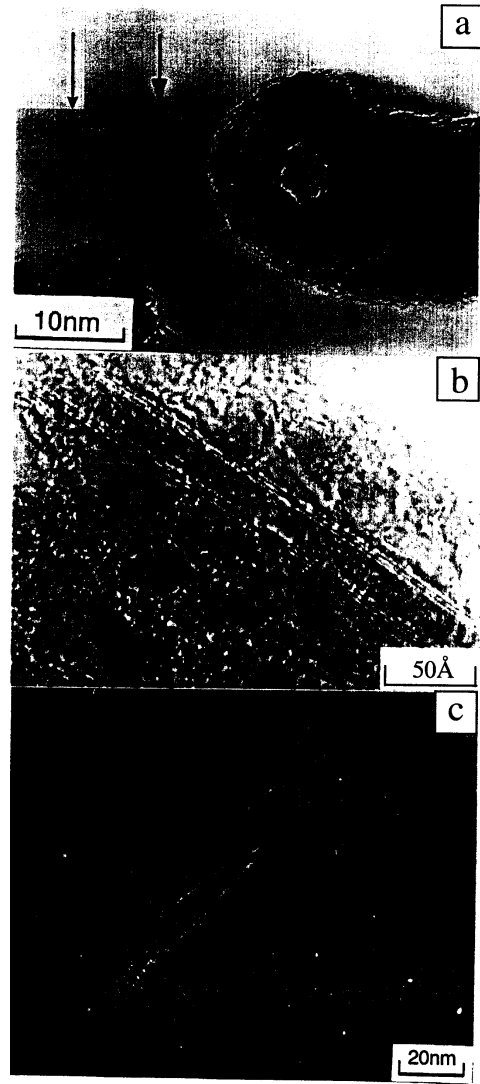
FIG. 7. (a) Co-existence of a VGCF and a single wall carbon nanotube (with a diameter about 20 nm) obtained by the pyrolysis of benzene. The partial deposition of a carbon layer on the carbon nanotube during the thickening process is seen. (b) Carbon nanotube (obtained by benzene decomposition) and subsequently heat treated at 2800°C, yielding the same structure as nanotubes prepared by the arc method. (c) A carbon nanotube heat-treated at 2800°C, showing its ability to sustain twisting and bending motion without breaking, which is very different from the properties of conventional carbon fibers.

The remarkable mechanical properties of carbon nanotubes are seen in Fig. 7(c) which shows that nanotubes do not break when twisted or bent, which is very different from the

brittle and fragile characteristics usually associated with common carbon fibers. The high strength and flexible characteristics of individual carbon nanotubes is demonstrated also in Fig. 7, in which a nanotube can be seen to follow the rough nanoscale edges. Thus when the diameter of the VGCF decreases and reaches the nanometer range, the central core region contributes in a major way to the fiber's physical properties. Therefore very thin VGCFs are expected to have properties which differ from VGCFs with diiameters in the micrometer range, on one hand, and from carbon nanotubes wiith nanometer diameters, on the other hand. For this reason, we denote VGCFs with diameters in the range 10 to 100 nm by the term 'nanofibers'. In the nanofiber range, the central core contributes importantly to the structural, electrical, and mechanical properties of these nanofibers.
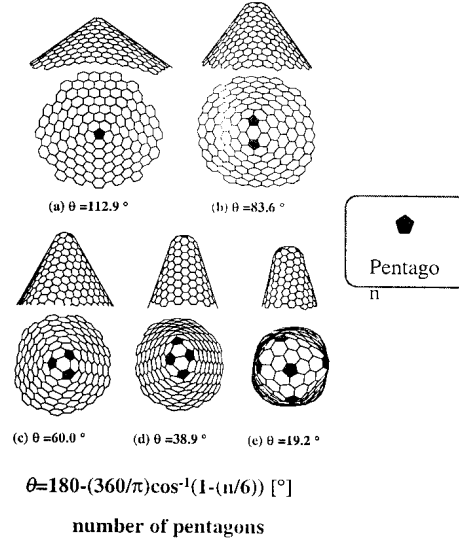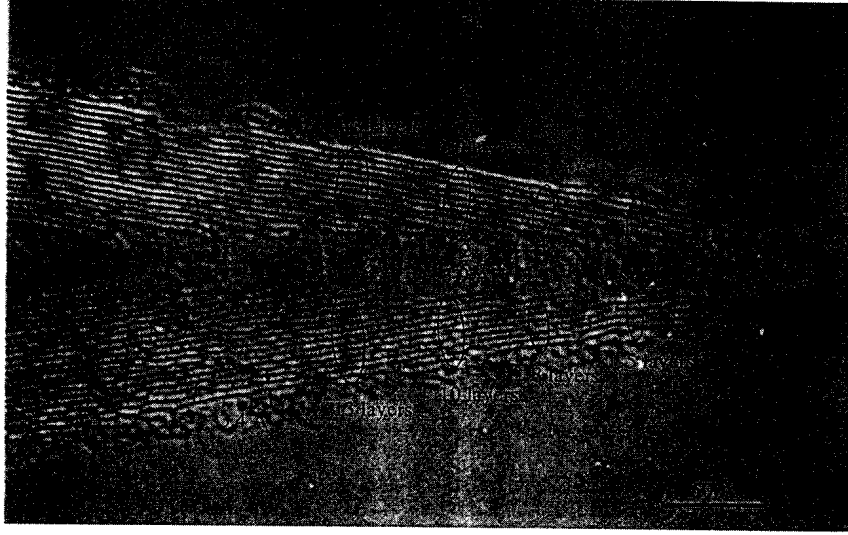
(a) θ =112.9°   (b) θ =83.6°

Pentagon

(c) θ =60.0°   (d) θ =38.9°   (e) θ =19.2°

$$\theta=180-(360/\pi)\cos^{-1}(1-(n/6))\ [°]$$

number of pentagons

FIG. 8. Tip of the VGCF nanotube making an angle of $\sim 20°$ (a), and possible cone struc-
tures for the nanotube tip showing (b) pentagons in a hexagonal carbon network.

Now we discuss how the pyrolytic carbon nanotubes grow. Figure 8 shows a typical tip
of a multiwall carbon nanotube which is heat treated at $2800°C$ to stabilize the structure
of the as-grown tube; this temperature is almost the same as that used in the production
of so-called arc-grown carbon nanotubes. Typically, the tip shows a hemispherical cap
on a hollow-core, which shows a symmetrical structure with respect to the tube axis,
and a tip angle of $\sim 20°$. This tip angle corresponds closely to a hemispherical cap with

5 pentagons in the hexagonal tip network. No catalytic particle is observed in the tips of such as-grown tubes, which suggests that the growth mechanism might be associated with the active pentagon sites, located within the growing tip of the tube. By adding C_2 carbon species to the active tip site, a nanotube with helicity can be grown continuously.
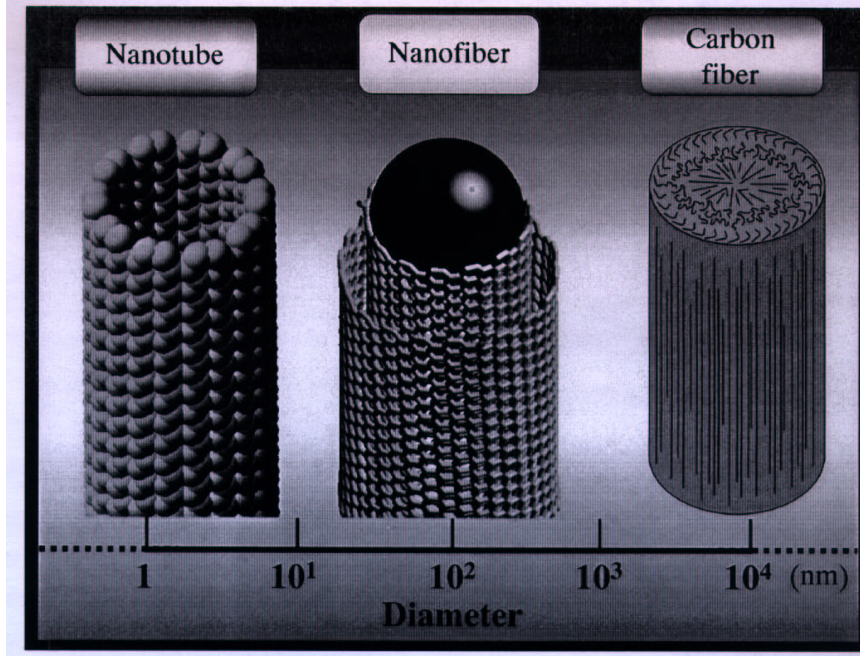

FIG. 9. Comparison of the size of the diameters of various types of fibrous carbons from the nanotube to the nanofiber to a conventional carbon fiber.

The wide range (factor of 10^4) of diameters in fibrous carbons from $10\,\mu$m to $1\,$nm expands the materials potential for both new science and practical applications. The classical bulk properties of graphite dominate the properties of large diameter fibers ($>$ $1000\,$nm), while the carbon nanotubes (diameter $< 10\,$nm) are dominanted by quantum phenomena. Figure 9 shows a comparison of the diameter sizes of various types of fibrous carbons mentioned above. The diameters can be varied from $\sim 1\,$nm for carbon nanotubes to $\sim 10^4\,$nm for carbon fibers, and vapor grown carbon fibers are located somewhere between these limits, With thick fibers showing bulk properties, and also quantum effects in fibers of very small diameter. Especially in the intermediate range ($\sim 10^2\,$nm) are the

17

carbon nanofibers, which exhibit remarkable properties between those characteristic of the bulk and yet close to the quantum limit. These carbon nanofibers, in particular, also have significant potential for the next generation of carbon fiber applications, along with carbon nanotubes. The carbon nanofibers could only be produced by methods similar to those used for VGCFs, based on a floating catalytic method. The field of fibrous carbons thus covers a wide range from conventional carbon fibers to carbon nanotubes via vapor grown carbon fibers. The related science as well as technology between these categories of fibers will develop largely through mutual synergy across these types of fibrous carbons. As a material for the next century, carbon fiibers are thus expected to be important not only for composite materials but also as a functional material in areas such as eneergy storage and electronics.

SUGGESTED READING

- M. S. Dresselhaus, G. Dresselhaus, K. Sugihara, I. L. Spain, and H. A. Goldberg, *Graphite Fibers and Filaments* (Springer-Verlag, Berlin, 1988), Vol. 5 of *Springer Series in Materials Science.*

- R. Bacon, Appl. Phys. Lett. **31**, 283 (1960).

- S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Casswell, and H. Dai, Science **283**, 512–514 (1999).

- M. Endo, R. Saito, M. S. Dresselhaus, and G. Dresselhaus. In *Carbon Nanotubes: Preparation and Properties*, edited by T. Ebbesen, pages 35–110, CRC Press, Inc., Boca Raton, Florida, USA, 1997. Chapter II.

- J.-C. Charlier, Science Spectra page 64 (1999). issue 17.

- M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, New York, NY, 1996).