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TEM observation of carbon tubes produced by a continuous process

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Historically, the growth of tubular carbon fibers involves a time-intensive batch process. Recent advance has lead to continuous growth of carbon tubes which exhibit several unique characteristics. In this study, we have investigated the microstructure of carbon tubes produced by a continuous process. It was observed that carbon tubes can be produced by continuous process with microstructure similar or superior to that produced using laboratory scale techniques. The result also encourages the improvement of carbon nano tube (CNT) production due to the similarities between micro-sized carbon tubes and CNT. © *1999 Kluwer Academic Publishers*

1. Introduction

Carbon tubes is produced through the pyrolysis of hydrocarbon gases in the presence of a transition metal catalyst. Historically, the metal catalyst was supported on a substrate, which was then placed at room temperature in a reactor for subsequent fiber growth at higher temperatures [1]. This method involves a time-intensive batch process. Therefore, the duty cycle of the equipment is low, resulting in low production rates and high costs. The floating catalyst method was developed in order to reduce the time and, therefore, the cost of carbon fiber production. This method eliminates the need for supporting the catalyst and for cooling the furnace prior to removing the fibers and their supports. Instead of supporting the catalyst on a substrate within the furnace, the catalyst is injected into the flowing gas, where it nucleates and grows carbon tubes [2]. Recent advance in the floating catalyst method has further lead to continuous growth of such tubular carbon [3, 4]. Carbon tubes thus produced exhibit unique X-ray diffraction patterns of sp^2 and sp^3 bonding, [5] and various surface states and chemistry [6]. In this study, we have further investigated the microstructure of carbon tubes produced by this continuous process.

2. Experimental

The reactor used for continuous growth of carbon tubes consisted of a horizontal tube with a length and an inner diameter of 244.0 and 13.5 cm, respectively. The feedstock for fiber growth was a mixture of 73.1% methane, 10.0% ammonia, and 16.9% hydrogen sulfide, by volume. Hydrogen sulfide was used as a source for sulfur since the nucleation rate can be markedly enhanced by addition of quantity of sulfur, which forms an iron sulfide eutectic, and enables liquid phase diffusion of carbon through the catalyst [7]. The catalyst use was iron pentacarbonyl which was injected into the reactor with the gas mixture. Carbon tubes were then grown continuously at a temperature of approximately 1100 °C in the reactor and harvested by pneumatic transport every 2 min. It is noted that the pneumatic action allows the tubes to be quenched from the reaction condition to room temperature. Carbon tubes were then analyzed using by transmission electron microscopy (TEM).

3. Results and discussion

The general appearance of the carbon tubes is shown in Fig. 1. The tubes are curved and entangled. This, coupled with the fact that both ends of a fiber are rarely seen in most of the TEM observations, suggests that the tube length is much greater than 50 μm. These tubes exhibit a range of inner and outer diameters. Some of the tubes have a section of a bamboo-like structure, as shown in Fig. 2. Fig. 2 also shows two catalyst particles

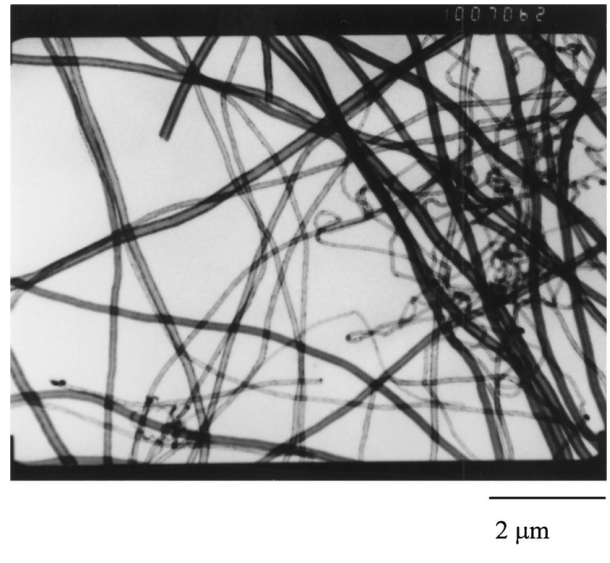

Figure 1 General appearance of VGCF.

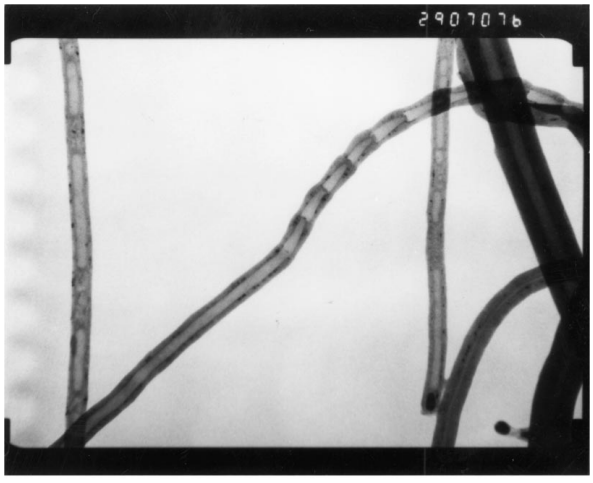

Figure 2 VGCF exhibiting a section of bamboo-like structure.

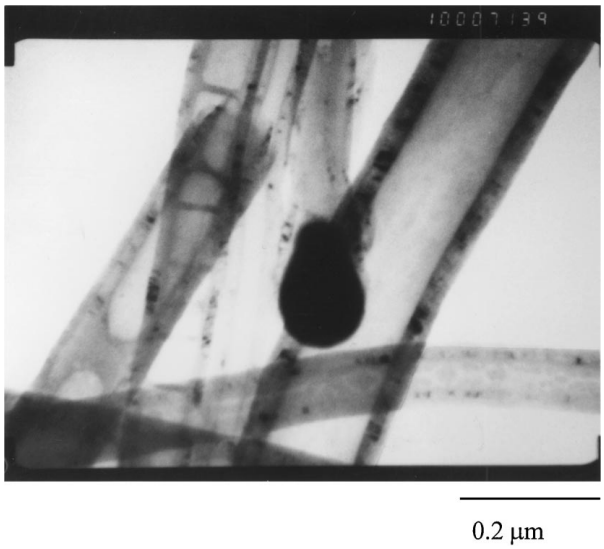

Figure 3 Micrograph showing a pear-like catalyst at one end of fiber.

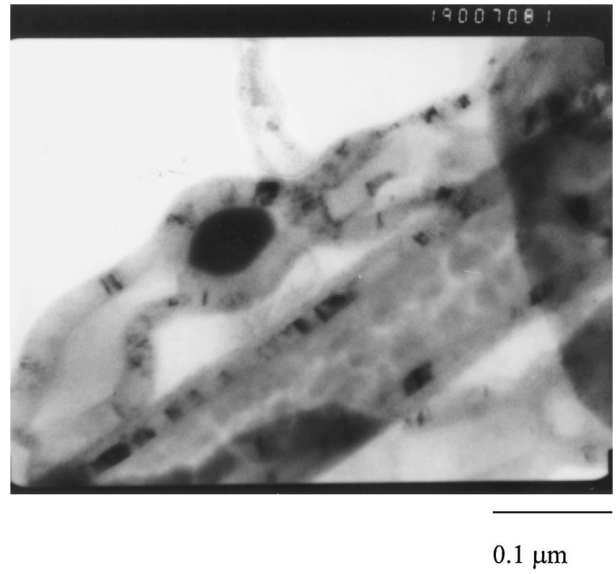

Figure 4 An oval shape catalyst embedded in a fiber.

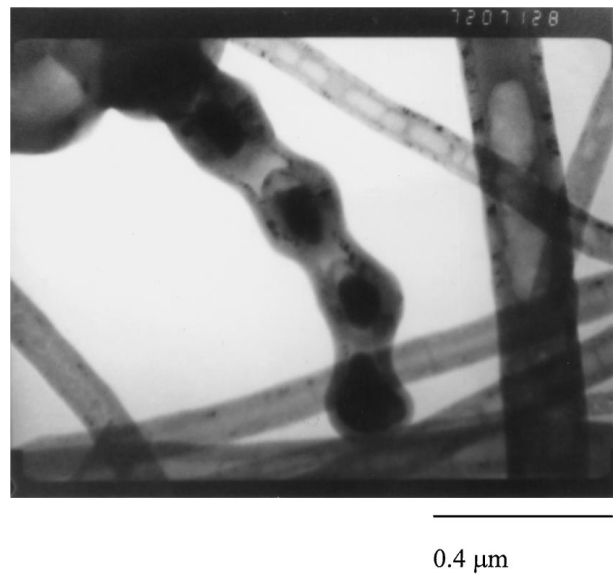

Figure 5 A VGCF having more than one catalyst particles.

at the ends of two different tubes (lower-right corner). The catalyst particles found at tube ends have either a pear-like shape or spherical shape (Fig. 3). However, when carefully observing at different orientations, we concluded that almost all the spherical catalysts seen were in fact the smaller curvature surface of a pear-like catalyst particle. It was further found that the larger curvature side of pear-like catalyst particle points toward to the direction of tube growth, as commonly observed for carbon tubes produced in a laboratory scale [8]. This experimental result can be explained mathematically using a two-dimensional model [9].

Metal catalysts were also found away from tube ends. These catalyst particles exhibit an oval-like shape. Fig. 4 shows such an example. In the growth of nano-sized carbon tubes, bi-directional growth of tubes was observed such that catalyst particles were embedded in the fibers at points away from tube ends [10]. However, the shape of these catalysts, unlike the present observation, is diamond-like. The growth of nano-sized carbon tubes often involved only the so-called first or lengthening stage of growth [11]. In the current study, following the lengthening stage during which the catalyst is believed to be in a diamond-like shape, the so-called second or fattening stage was allowed to occur. In this fattening stage, the catalyst has been perturbed and become inactive, and the reaction is purely chemical vapor deposition that thickens the tubes. During the fattening stage, surface tension would favor the change from diamond-like shape to oval-like shape. It is possible that compressive stress, developed as a result of carbon layer formation, could exceed the elastic limits of these catalyst particles. Therefore, faceted diamond-like catalyst particles catalyst particles were forced to become oval-like particles that have smooth sides touching the inner wall of the tubular carbon. Thermodynamic calculation supports the formation of hollow, cylindrical carbon tubes [12], which can make the catalyst particles tend to conform to the inner cylindrical wall of the tube. Occasionally, multiple catalyst particles were found in a single tube. It also is noted that the shapes of these catalyst particles are different, as seen in Fig. 5. It is unclear at present time that why there are more than one catalyst in a single tube. These catalyst particles

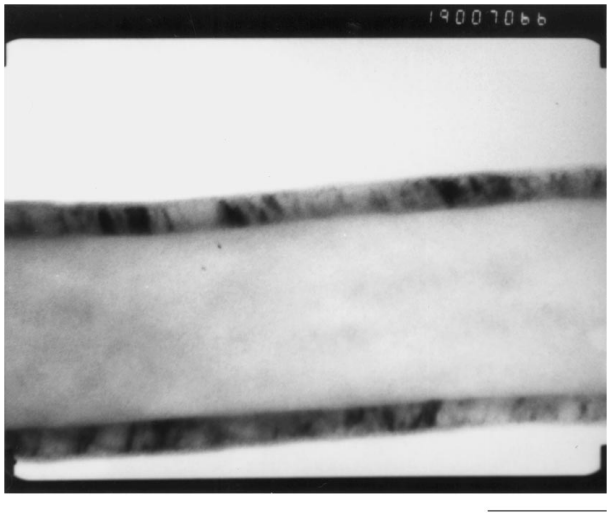

Figure 6 Bright field image of a tubular fiber.

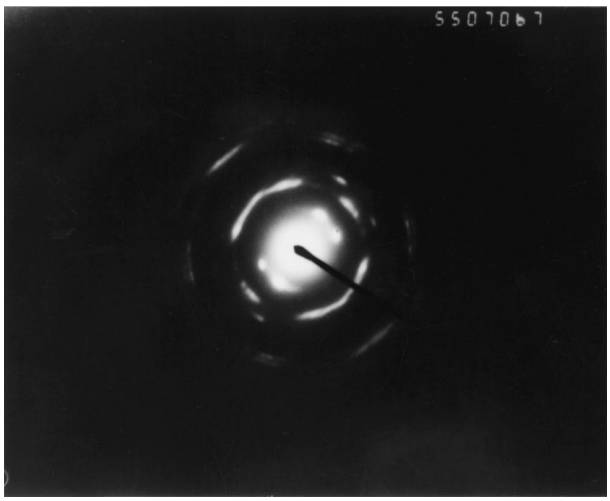

Figure 7 SAED pattern of the fiber shown in Fig. 6.

might originate from the separation of one catalyst due to the aforementioned compressive stress. Energy dispersive analysis of X-ray (EDAX) of all the catalyst particles indicated the presence of only iron. However, the presence of carbon or other light element cannot be ruled out, since the EDAX used for the analysis is not sensitive to low atomic member elements.

Shown in Fig. 6 is a bright field image of a tubular carbon having outer and inner diameters of 0.21 and 0.16 μm, respectively. The selected area electron diffraction (SAED) pattern shows diffraction spots consistent with [0 0 0 2] planes of carbon (Fig. 7). Discontinuity on the rings and the sharp spots indicate texture or preferred orientation of crystalline. Close examination of the dark field images reveals that the wall of the tubular carbon shown in Fig. 6 consists of a surface layer and an inner-layer exhibiting two different types of microstructure. This is shown in Fig. 8. It can be seen that the dark field image using one of the diffraction spot pairs lightens up both the upper and lower surface layers and only inner-layer of the upper side. The thin surface layer exhibits a micro-crystalline or disordered structure, and the inner layer have an ordered structure.

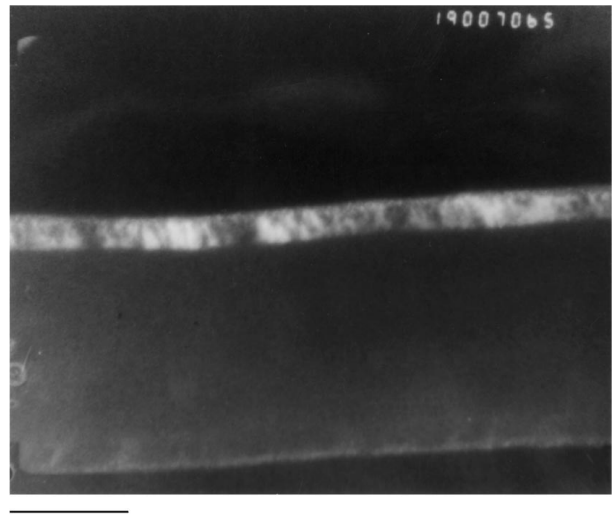

Figure 8 Dark field image of the fiber shown in Fig. 6.

The inner-layer structure is composed of crystals with [0 0 0 2] planes at an angle of about 20.3° from the fiber axial direction.

4. Conclusion

Research on tubular carbon fibers has been mostly limited to the availability of round quantity produced using laboratory scale techniques. Our recent and present studies have shown that carbon tubes can be produced by continuous process with microstructure similar or superior to that produced using laboratory scale techniques. The result also encourages the improvement of carbon nano tube (CNT) production due to the similarities between micro-sized carbon tubes and CNT.

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