TEM OBSERVATION OF VGCF PRODUCED BY A CONTINUOUS PROCESS

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Introduction

Vapor grown carbon fiber (VGCF) was produced continuously in a horizontal tube furnace using iron pentacarbonyl as the catalyst. The feedstock for fiber growth was a mixture of methane, ammonia, and hydrogen sulfide. Fibers thus produced were analyzed using a transmission electron microscope (TEM) for microstructural and crystallinity.

Experimental

The reactor used for continuous growth of VGCF consisted of a horizontal tube with a length and an inner diameter of 244.0 cm and 13.5 cm, respectively. The feedstock for fiber growth was a mixture of 89.9% methane, 9.9% ammonia, and 0.2% hydrogen sulfide, by volume. The catalyst used was iron pentacarbonyl which was injected into the reactor with the gas mixture. VGCF was then grown continuously at a minimum temperature of 1100 °C in the reactor and harvested by pneumatic transport every 2 minutes, approximately. Fibers were then analyzed using by transmission electron microscopy (TEM).

Results and Discussion

The general appearance of fiber is shown in Fig.1 (#61). The fibers are curved and entangled. This, coupled with the fact that both ends of a fiber are rarely seen, suggests that the fiber length is much greater than 50 μm. It appears that fibers exhibit a range of diameters. Closer examination also reveals the tubular nature of the fibers. However, fibers that exhibit a section of a bamboo-like structure are also seen, as shown in Fig. 2 (#76). Catalysts with two different shapes were observed. At higher magnifications, one is in a pear-like shape (Fig. 3A, #79) and the other appears to be a sphere (Fig. 3B, #160). However, when observing at different orientations, it was concluded that almost all the spherical catalysts were in fact in a pear-like shape. It was further found that the larger curvature side of a pear-like catalyst coincides with the direction of fiber growth, as commonly observed for VGCF produced in a laboratory scale [1] and explained mathematically using a two-dimensional model. [2]

Metal catalysts were, however, also found away from fiber ends. These catalyst particles exhibit an oval-like shape as shown in Fig. 4 (#81). In this case, a different growth mechanism, i.e. bi-directional growth of fiber, is believed to have occurred. [3] However, the shape of the catalyst, i.e., oval-like, in the present study is different from what has been observed, i.e., diamond-like, for nano-sized VGCF. The growth of nano-sized VGCF often involved only the so-called first or lengthening stage. [4] In the current study, following the lengthening stage where the catalyst is believed to be in a diamond-like shape, the second or fattening stage was allowed to occur. In this stage, the catalyst has been perturbed and become inactive, and the reaction is purely chemical vapor deposition that thickens the fiber. During the fattening stage, surface tension would favor the change from diamond-like shape to oval-like shape. Other factor making such a change is discussed later.

Occasionally, multiple metal catalysts with various shapes were seen in a single fiber, as shown in Fig. 5 (#128). It is highly unlikely that fibers grew from these catalysts, individually, and then merged to become one single fiber, although it has been observed in nano-sized VGCF. [5] It is unclear at present time why there is more than one catalyst particle in a single fiber. It also is noted that the shapes of these catalyst particles are different, as seen in Fig. 5. It is possible that compressive stress, developed as a result of carbon layer formation, could exceed the elastic limits of these catalyst particles. Therefore, the catalyst particles were forced to change shapes. Likewise, the compressive stress could also contribute to the formation of oval-like catalyst in Fig. 4.

As noted above, VGCF exhibit a tubular nature. The selected area electron diffraction (SAED) analysis shows that the tube wall consists of a thin surface layer consisting of randomly oriented microcrystalline, and a inner layer consisting of crystals with [0002] planes at an angle of about 20° from the fiber axial direction.

Conclusion

VGCF produced using a continuous process was examined by TEM. The fiber length was estimated to be greater than 50 μm while the diameter varied. It was also found that VGCF exhibited tubular nature. The tube wall consists of two different layers exhibiting different microstructure.

Acknowledgment

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References

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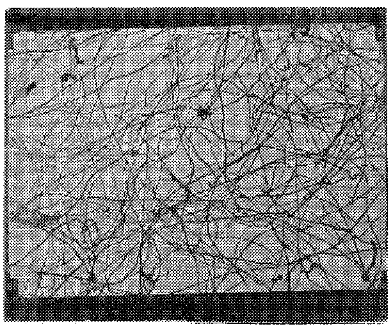

Fig. 1. General appearance of fiber.

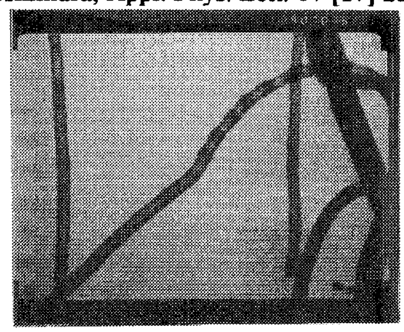

Fig. 2. Bamboo-like structure in VGCF.

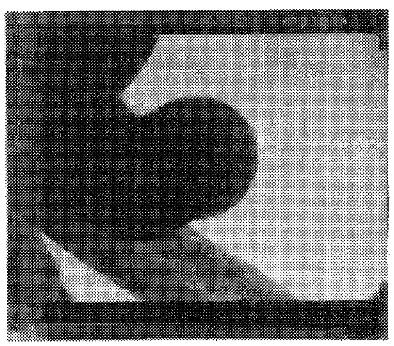

Fig. 3A. A pear-like catalyst

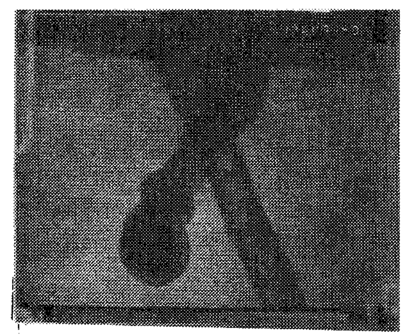

Fig. 3B. A spherical catalyst.

Fig. 4. An oval-like catalyst.

Fig. 5. Multiple metal catalysts with various shapes in VGCF.