Observation and Explanation of a Kind of New Large Vapor-Grown Carbon Fibers (VCGF)

Jian Dong, Wanci Shen, Feiyu Kang and Baofa Zhang
Department of Materials Science and Engineering, Tsinghua University
Beijing 100084, P.R.China

Introduction

Vapor-grown carbon fibers (VGCF) grow from the decomposition of hydrocarbons at high temperature. Generally, the carbon layers of these fibers are parallel to the axis of the fiber, and their cross sections are circles [1]. The growth of fibers with such structure must be related to catalysts except that of multiwalled nanotubes. when we densified some carbon-carbon structure by chemical vapor infiltration (CVI), one kind of CVD methods, one kind of large VGCF appeared, and it seems that they grow without catalysts. Now in this paper, the morphology, structure and growth mechanism are investigated.

Experimental

The VGCF were synthesized in the common CVD apparatus shown in Fig 1. CVD furnace is 0.8 m in diameter and 1.5m high, and it is heated by a high-frequency (450KHz) induction coil and deposition occurs at low pressure (2kPa). The temperature is about 900°C, and the gas is propylene and nitrogen (volume ratio; 1:1). The deposited VCGF are collected on the brim of the graphite cylinder close to the gas outlet. The depositing time is 150 hours. The carbon-carbon structure required to be densified is put inside the graphite cylinder.

Field emission scanning electron microscopy (FESEM) using JEOL-6301F. The elemental analysis is carried out by the EDS (ISIS Link 300) attached on the JSM6301F. Atomic emission spectroscopy (AES) was carried out by ICAP9000SP.

Results and discussion

After CVD process, the outskirt of graphite cylinder is coated with a thick layer of pyrolytic graphite. The layer (Fig. 2) can be easier stripped off the outskirt of cylinder. VGCF in large size are observed by naked eyes lie in the same direction, and they only appear in the brim close to the gas outlet, while nothing in the opposite brim. In addition, there is no fibers appearing on the carbon-carbon structure. It seems that they all grow toward the ground, which look like the stalactite in the cave. Diameter of VGCF ranges from several microns to 1mm, and the length is so long as to 50cm for some fibers.

A kind of quasi-VGCF are observed with which VGCF contact (Fig. 2). They are short, thick and rough, compared with the present VGCF.

Fig 3 shows the microscopic morphology of quasi-VGCF and VGCF, Fig. 3a shows that quasi-VGCF are composed of the same convex deposit as common CVD product, however, the convex deposit arranged in a certain direction. Although there are some convex deposit on the surface of VGCF, their surface is more smooth than quasi-VGCF (Fig. 3b). The fracture surface of the VGCF shows that the carbon layers are parallel to the axis of the fiber (Fig. 3c), which is similar with the structure of common VGCF with the aid of catalysts. Fig. 3d shows that small and straight fibers lie in any direction, which appears on the surface of outskirt, while the large VGCF grow toward the ground.

EDS and AES shows there is no other elements except carbon and little oxygen inside the deposit layers and fibers, which means that the growth of such fibers is not related to the catalysts. The growth mechanism of these fibers must be different from that of common ones.

As for the all kinds of synthesis method for VGCF, The decomposition of hydrocarbons serve as the approximately homogeneous source of atomic carbon. Accordingly, there is competition among the homogeneity of the free carbon source (which is responsible to form closed structure, such as convex pyrolytic graphite), the asymmetry of carbon bonds at the temperature of 1000°C and the asymmetry associated with the metal particles. In addition, The directed flux of carbon vapors is also an asymmetry source.

As shown in Fig. 1, the propylene gas flows from the end to the top, especially for the left part that is close to the gas outlet, the flowing rate is faster than the right part. Accordingly, the carbon flux also flows from the end to the top, thus, directed carbons leads to the growth of tube structure in the direction of the incoming flux. Therefore, when the catalysts are absent, the directed flux of carbon vapors determine the formation of the present VGCF.

Notice the condition of vapor layer close to the surface of the pyrolytic graphite is different from that of vapor in distant zone. Carbon particles arriving on the substrate are reflected from the surface. The reflected particles collide with the newly arrived ones and after several collisions the carbon particles distribution becomes homogeneous, thus, small fibers grow along with different orientation. When just formed tube grows to a certain length, it will be influenced by the directed carbon flux. The directed flux of carbon vapors become the most important asymmetry source, when axes of those tubes are parallel to the directed carbons, they can grow longer and thicker. If not parallel, they will curve to make themselves to have the same direction as the directed carbons, or stop growth.

The above experiment shows that a CVD process can synthesize long VGCF, if we change some parameters, the long tubes with diameter in nano-sized might be synthesized.

Reference

[1] M. Endo, R. Saito, M. S. Dresselhausa and G. Dresselhaus, in Carbon nanotubes preparations and properties, From carbon fibers to Nanotubes, Edited by T.W. Ebbesen, (CRC Press, New York,1997)

Acknowledge

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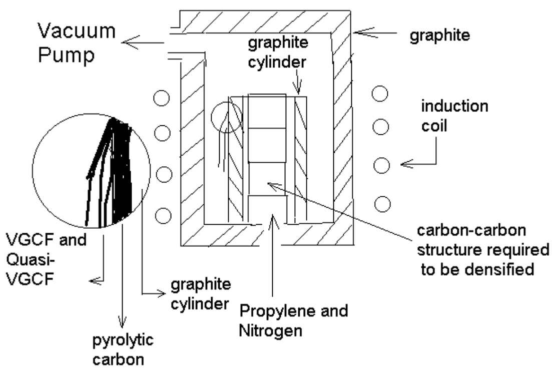
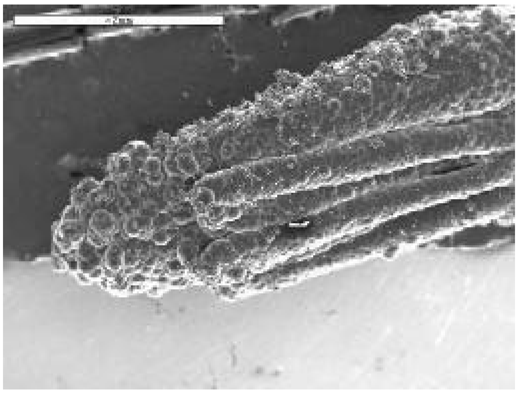
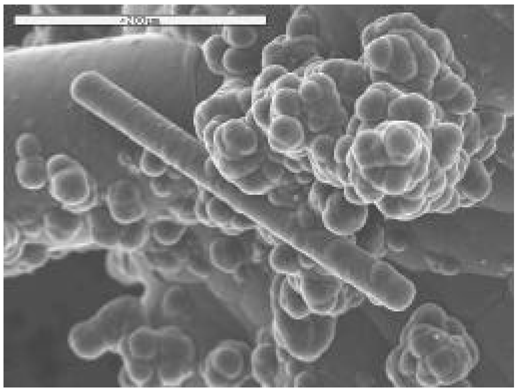


Fig. 1. the schematic diagram of CVD apparatus

Fig 2 macroscopic image of quasi-VGCF (shown by white arrow) and VGCF (shown by black arrow)



a



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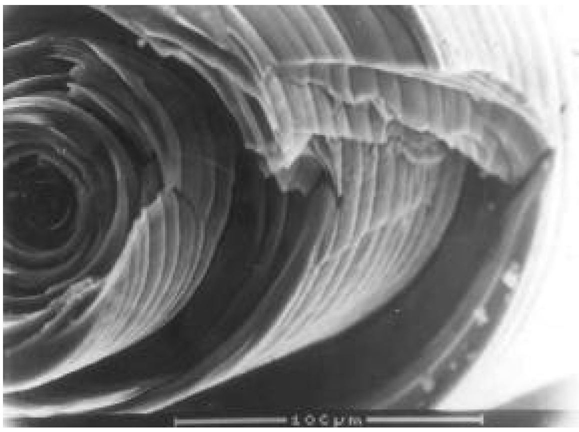

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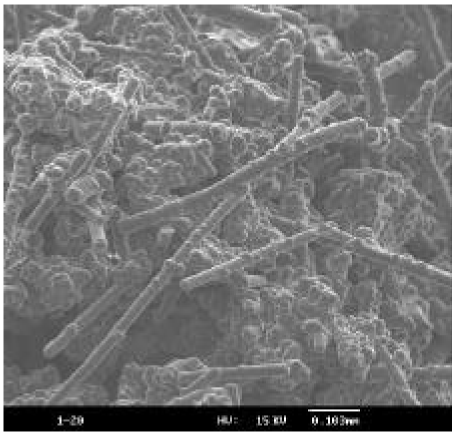

d

Fig 3 SEM images of quasi-VGCF and VGCF.a, quasi-VGCF. b, smooth VGCF with two apparent ends. c, fracture surface of VGCF.d, small VGCF and pyrolytic graphite particle.