# Vapor Grown Carbon Fibers Obtained by Fluid Ultra Fine Catalytic Particles

Morinobu ENDO, Masahiko SHIKATA and Tohru MOMOSE
Faculty of Engineering, Shinshu University,
Wakasato, Nagano, 380, Japan
and
Minoru SHIRAISHI
National Research Institute for Pollution and Resources,
Yatabe, Ibaraki, 305, Japan

## Introduction

Vapor-grown carbon fibers have been prepared by thermal decomposition of hydrocarbon such as benzene and methane at temperatures around 1100°C using the seeding method of catalytic particles. Ultra-fine particles of metals such as iron with diameter about 100Å, which are seeded on the surface of the ceramic substrate in advance, act as effective catalyst for primary formed thin carbon fibers(1). On these fibers, thickening process are taken place, and the carbon fibers with diameter about 10μm are obtained. The growth rate in length is as high as 1 to several tens of mm per minute. The thickening speed is generally about 0.1μm/min, which depends strongly on the temperature and partial pressure of hydrocarbon in the mixture with hydrogen. The formation of the present vapor-grown carbon fibers can be characterized by such high growth rates as can be compared with those of metal and non-metallic whiskers, which makes them to be formed by the fluid seeds of catalysis instead of fiber growth on the substrate.

In the present paper, the morphology and the structure of the vapor-grown carbon fibers from benzene decomposition by fluid catalytic seeds are shown, and the growth mechanism of the fibers is discussed. These fibers are very useful for composite applications and also for new fields as a functional carbon fiber.

## Results and discussions

As the fluid catalytic seeds, ferrocene is also used to form the floating iron particles, instead of the particles doped on the substrate surface(1).

Several methods have been possible to form the fibers by floating systems. Fig.1 is an example showing the sub-furnace system, in which the evaporated ferrocene forms the fluid iron particles. And high concentrated benzene-hydrogen mixture is simultaneously introduced into the reaction tube, kept about 1100°C with the ferrocene vapor. The other example is direct introduction of benzene-ferrocene solution into the reaction tube by infusion pump with constant rate. Then, the solution is evaporated immediately and carried to the hot zone of the reaction tube. The evaporation speed of ferrocene as well as the benzene partial pressure and the concentration of ferrocene in benzene solution have direct effect on the morphology of resultant carbon fibers. The temperatures for fiber growth is same as that of the seeding method(1).

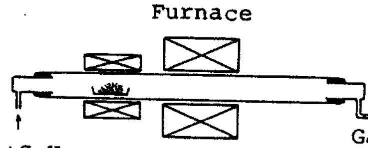


Fig.1 Fluid method for fiber growth using sub-furnace for ferrocene evaporation.

Fig.2 shows the resultant fibers which deposited like a sponge near the gas outlet of the reaction tube. The diameter of the sponge-like deposits are almost similar to the diameter of the reaction tube. By changing the conditions of pyrolysis, the needle-like fibers go out from the gas outlet, instead of the sponge-like deposits.

By X-ray diffraction of these deposits using Cu Kα radiation, it has been known that they have a turbostratic structure of carbon with interlayer spacing of 3.48 Å. This is almost similar to that of the carbon fibers obtained by doped seeds on the substrate surface.

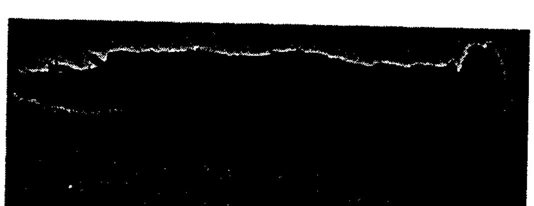

Fig.2 Sponge-like fiber deposit by fluid seeds.

Fig.3 shows the SEM pictures of the sponge-like deposits, which consist of the thin vermicular fibers. The diameter is possible to be changed from 0.1μm to 1μm in average, and the lengths are up to several cm. These small fibers are formed at central hot portion of the reaction tube, and then brought up to the other end of the tube by the gas flow. Different types of fiber morphology, for example like as columnar, have been obtained by changing the pyrolysis conditions.

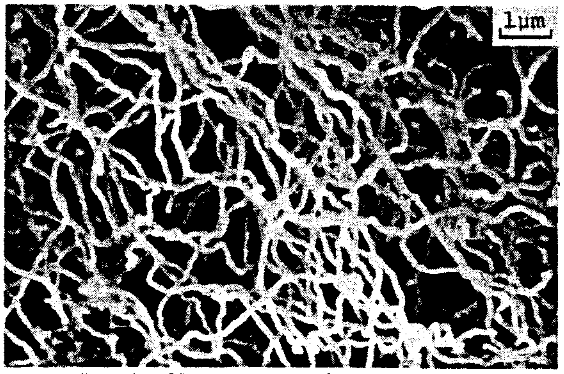


Fig.3 SEM picture of the fibers.

Fig.4 shows the transmission electron micrograph and the selected area electron diffraction pattern of the fibers. The preferred orientation of carbon layers along the fiber axis is clear, and which is exactly similar to that of the conventional vapor-grown carbon fibers. They have also the central hollow tube with almost similar diameter as the catalytic particles located at the tip of the tube. The small catalytic particles have a relatively constant diameter of 50 Å in each fiber. This indicates the homogeneous nucleation during the formation of metal particles in the process. The other end of the fibers exhibits the encapsulated hollow tube by pyrolytic carbon as shown the figure. The 002 dark-field image indicate some structural differences with increasing the diameter of the fiber. The bright domains corresponding to the turbostratic crystallites change with their diameters.

The proposed growth mechanism for the seeding method using substrate could be applied to the present fluid system.

## Conclusion

Vapor-grown carbon fibers are successfully prepared by using fluid catalytic seeds. The morphology of the fibers can be possible to control by growth conditions. These fibers offer promise for the utilization as various kinds of composites and as a host material for intercalation compounds of fibrous graphite.

## Reference


1)M.ENDO and K.KOMAKI; 16th Biennial Conference on Carbon, University of California, San Diego(1983)523.


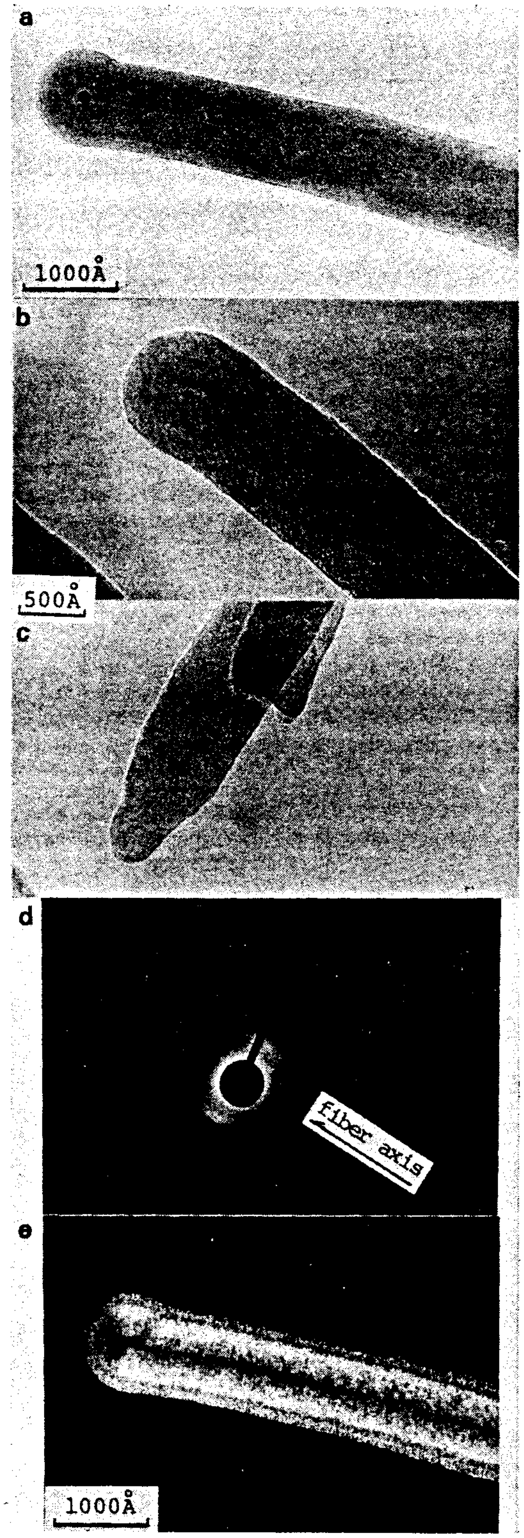


Fig.4 TEM observations on the fibers, (a)(b) tip of the fibers with catalytic particle, (c) root of the fibers with encapslated hollow tube, (d) selected-area electron diffraction pattern from the the fiber, (e) 002 dark field image.