Synthesis and Structural Analyses of Duplex Carbon Nanofibers

Atsushi Tanaka[1)], Seong-Ho Yoon[1)], Isao Mochida[1)], Jun-Hwa Chi[2)]

1) Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga Fukuoka 816-8580, Japan
2) KEPRI
Yusong-ku, Taejon, 305-380, Korea

ABSTRACT

Carbon nanofibers (CNFs) with a new structure were synthesized from CO/H_2 mixture over Fe-Mn alloy catalysts at a temperature range of 500 to 650^oC. High temperature over 600^oC provided a tubular structure, whereas CNFs synthesized at low temperatures of 500 ~ 560^oC were found to be formed by parallel bonding of two fibrils, which is called 'duplex carbon nanofiber'. The shape and size of inner space between two fibrils were also found to depend on synthesis temperatures. Structural model of duplex CNF was proposed on the basis of SEM and HR-TEM observation.

KEYWORDS : carbon nanofibers, carbon nanotubes, catalytically grown carbon; catalyst, chemical vapor deposition; texture

1. INTRODUCTION

Carbon nanofibers (CNFs) have been recognized as unique forms of carbon materials [1-4]. The diversity of CNFs can be classified as variable aligments of laminated c-plane layers along the fiber axis, which provided typically three types of CNFs such as platelet (alignment perpendicularly against the fiber axis), tubular (alignment parallel along the axis), and herringbone (alignment angled to the axis) CNF [4].

Recently, our group has developed to synthesize three types of CNFs using Fe alloy catalysts. Both Fe and Fe-Ni catalysts were first found to produce selectively tubular or platelet CNFs from CO and hydrogen mixtures when synthesis temperatures changed in the range of 500 ~ 670^oC [5]. Nickel was an effective secondary metal to decrease synthesis temperature of tubular formation as well as to

improve homogeneity of the product. Fe-Mn catalysts further decreased the synthesis temperature for tubular CNFs at such low temperatures under 600^{o}C [6].

In structural studies, platelet CNFs synthesized over Fe catalysts were found to show duplex structure which consist of two flat-ribbon-like fibrils. Such duplex structure was also found in CNFs synthesized over Fe-Mn catalysts at such low temperatures of 500~560^{o}C although hollow in the middle of a fiber was observed.

This work investigates such duplex structure in CNFs from CO/H_2 mixtures over Fe-Mn catalyst to propose a new structural model of CNFs.

2. EXPERIMENTAL

Non-supported Fe-Mn catalysts used in this study were prepared by the precipitation of the ferric and manganese carbonates from the ferric nitrate and manganese nitrate solution using ammonium bicarbonate as described in detail by Best and Russell [7].

A horizontal furnaces with temperature controller were used for the preparation of CNFs. Specially designed flow units allowed the introduction of reactant gas mixture (carbon monoxide / hydrogen / helium) to a quartz tube (45-mm ID and 50-cm long). The flow mass was accurately regulated by the mass flow controllers. Powdered Fe-Mn alloy catalyst was put on quartz boat and were placed at the center of the quartz tube in the reaction furnace. The reactant gas mixture of CO / H_2 (1:4 (v/v), total volume = 200 cm^3/min) was introduced into the reactor. After 1 h reaction, the product was cool down to room temperature.

3. RESULTS AND DISCUSSIONS

Figure 1 shows SEM image of platelet CNFs consisting of two flat-ribbon-like fibrils, which indicates the duplex structure.

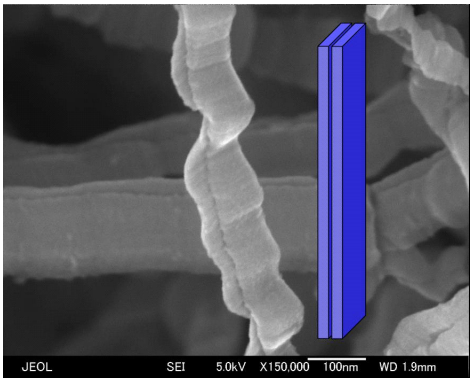

Fig.1. SEM image of duplex platelet CNFs.

Figure 2 shows TEM images of CNFs produced at (A) 630, (B) 560, (C) 540 and (D) 500^{o}C over Fe-Mn alloy. Tubular CNFs at 630^{o}C changed to CNFs without hollow at 560^{o}C. Hollow in the fiber recovered with temperature decrease to 530 and 500^{o}C, whereas the alignment of c-plane layers became uneven. CNFs at 500^{o}C showed a bamboo-like structure. These HR-TEM photographs appear to show typical structures of tubular and

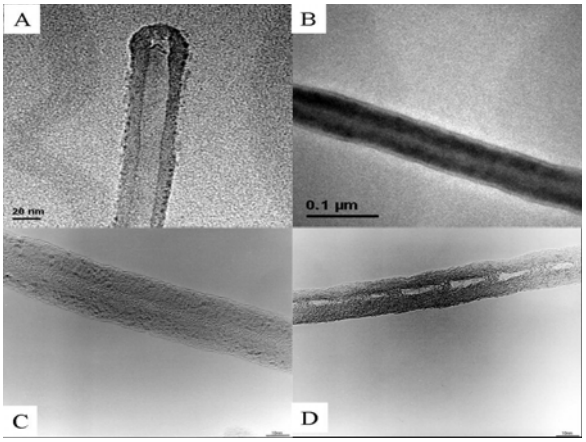

Fig.2. TEM images of CNFs produced at (A) 630, (B) 560, (C) 540 and (D) 500°C over Fe-Mn catalyst.

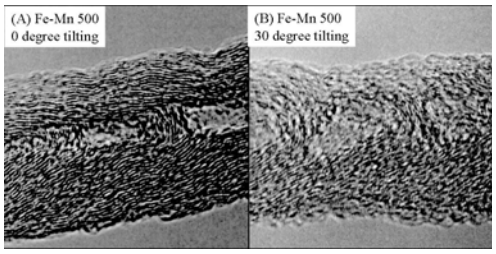

Fig.3. Titled HR-TEM images of CNFs synthesized at 500°C over Fe-Mn catalyst.

platelet. However, combination of tilted HR-TEM and SEM images suggests a new structure of CNF. In observations at the same point at various angles such as Figure 3, the hollow in the fibers seems not symmetric. SEM showed CNFs comprising two pieces of fibrils as shown in Figure 1.

Hence we suggested a new model of CNFs, so called 'duplex structure' as shown in Figures 4 and 5. the outer diameter increase and the inner diameter decrease by increase of reaction temperature. Figure 5 shows models of duplex fibril bridge structure of CNF produced at 500°C.

Although more examination on the linkage between two fibrils in a fiber is needed, the duplex structure is certainly observed. Duplex CNFs of this work are expected to show a novel surface function in various applications.

TEM is a very powerful tool for observation of nanostructure, but limitation from its 2-D images always needs careful consideration to establish 3-D structure.

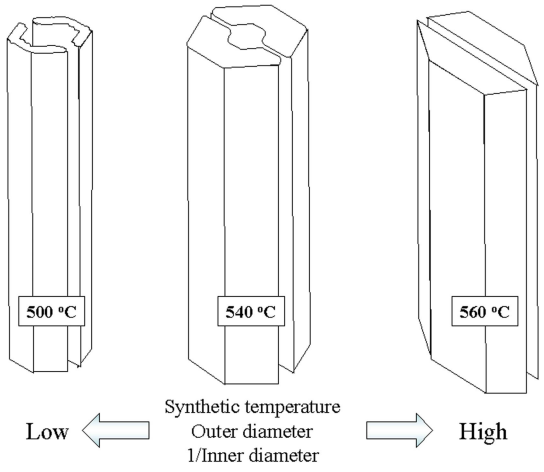

Fig. 4. Models of duplex CNFs.

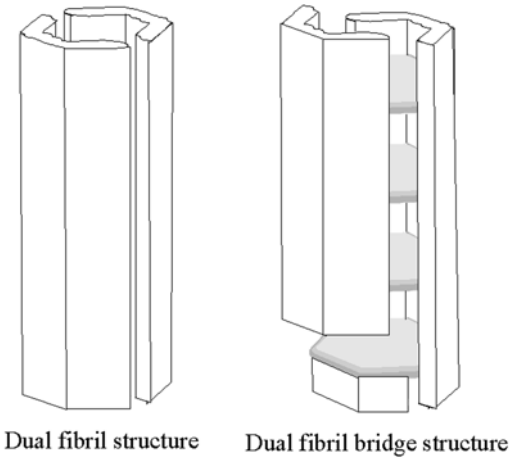

Fig. 5. Models of duplex fibril bridge structure of carbon nanofiber produced at 500 °C

ACKNOWLEDGEMENT

This work was carried out within the framework of the CREST program. The present authors acknowledge the financial support of Japan Science and Technology Corporation (JST).

REFERENCES

[1] Iijima, S. *Nature* **1991**, *354*, 56.
[2] Rodriguez, N. M. *J. Mater. Res.* **1993**, *8*, 3233.
[3] Dekker, C. *Phys. Today* **1999**, *May (5)*, 22.
[4] Rodriguez, N. M.; Chambers, A.; Baker, R.T.K. *Langmuir* **1995**, *11(10)*, 3862.
[5] A. Tanaka, S. H. Yoon, Y. Korai, I. Mochida, R.T.K. Baker, N.M. Rodriguez, *Carbon '02 on Carbon, Beijing* (2002) p35.
[6] A. Tanaka, S. H. Yoon, Y. Ota, Y. Korai and I. Mochida, *Carbon '02 on Carbon, Beijing* (2002) p207.
[7] R. J. Best, and W. W. Russell, *J. Amer. Soc.* **76** (1954) 838.