SYNTHESIS OF CARBON NANOTUBES AND NANOFIBERS BY CVD USING Co-Fe CATALYST

Guobin Zheng, Hideaki Sano, Yasuo Uchiyama
Department of Materials Science and Engineering, Faculty of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521 Japan
Corresponding author e-mail address: gbzheng@net.nagasaki-u.ac.jp

Introduction

Catalytic chemical vapor deposition (CCVD) has been established as a main method to synthesize carbon nanotubes in large-scale, which exhibit various structures [1]. It has been shown that the composition and structure of catalysts have a significant effect on the structure of carbon nanotubes [2]. In this report, carbon nanotubes were synthesized by CCVD method using cobalt-iron binary alloys as catalysts, and their structures were investigated using high-resolution transmission electron microscopy (HRTEM).

Experimental

Alumina plates as substrates were dip-coated with 0.1M nitrate aqueous solution with 5mass% polyvinyl alcohol (PVA). The atomic ratios of Co and Fe were 10:0, 8:2, 7:3, 5:5, 3:7, 2:8, and 0:10, respectively. The role of PVA is to form a uniform film and prevent the aggregation of the nitrates during drying. After dried at 80ºC for 2 hours, the coated alumina plates were set in a quartz reactor and the catalysts were decomposed and reduced in hydrogen. Subsequently, carbon nanotubes or nanofibers were synthesized at 600ºC, 700ºC and 800ºC for 30 min with the flow rates of H_2, C_2H_2 and N_2 being set to 150 ml/min, 30 ml/min and 100 ml/min respectively. The structures of the products were examined using HRTEM.

Results and Discussion

TEM observation shows that the products synthesized at 700ºC using pure Fe or Co as catalyst mainly consisted of nanofibers without inner hollow tube. The diameter of these nanofibers ranged from 50 to 140 nm. However, if the catalyst was composed of both Co and Fe, carbon nanotubes with inner hollow tube were obtained. Fig.1a shows the TEM micrographs of nanotubes synthesized by $Co_{0.7}Fe_{0.3}$ catalyst. The average outer diameter of carbon nanotubes was found to be 61 nm, and the average diameter of the inner hollow tubes was about 32 nm. Fig. 1b shows the HRTEM image of a nanotube with a diameter of about 40 nm. It can be seen that the 002 planes are stacked slantly at an angle of 13º to the nanotube axis, indicating that the nanotube is not a typical multi-walled nanotube, in which the graphenes are rolled to cylinder shape. The graphitization degree of the wall structure of the nanotube is rather good.

It was also found that carbon nanotubes could be obtained using $Co_{0.5}Fe_{0.5}$ and $Co_{0.8}Fe_{0.2}$ as catalyst. However, in the case of $Co_{0.3}Fe_{0.7}$, both carbon nanotubes and nanofibers were obtained. These results indicated the synergy effect of Co and Fe on the formation of carbon nanotubes.
At 600ºC, only carbon nanofibers were synthesized for Fe, Co or their binary alloys.

At 800ºC, the carbon yields of the products were much lower than those at 600ºC and 700ºC. HRTEM observation revealed that very short carbon nanotubes were obtained. It is probably because the fast carbonization of acetylene on the metal surface wrapped the catalyst particles with carbon and deactivated the catalysts.

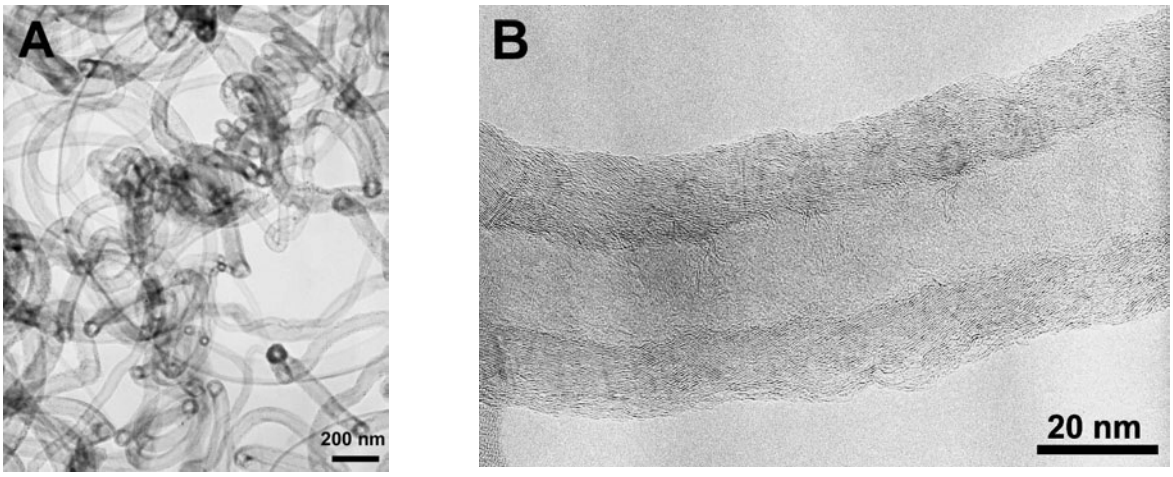

Fig. 1 Carbon nanotubes synthesized using $Co_{0.7}Fe_{0.3}$ as catalyst at 700ºC.

An improved dissolution-diffusion-precipitation model, based on the shape change of catalyst particles during the growth of carbon nanotubes or nanofibers, was proposed to explain the variety of carbon nanostructures formed in the CCVD system [3]. The catalyst particles are changed to conical shape because of the stress during the growth of nanotubes. Nanotubes are obtained from those catalyst particles changed to thin, long conical shape, and nanofibers are obtained from those difficult to change. The alloying of cobalt and iron make them easy to change shape, thus nanotubes are obtained. This improved model gives us some insight on how to control the structure of carbon nanotubes and the synthesis strategy of carbon nanotubes.

Conclusions

If pure cobalt was used as catalyst at 700ºC, the product was mainly composed of carbon nanofibers. With the increase of iron in Co-Fe catalyst, nanotubes were obtained. However, if iron is main component, carbon nanofibers were obtained. At 600ºC, nanofibers dominated in the product. At 800ºC, only a small amount of product was obtained.

References

[1] Terrones M, Science and technology of the 21th century: synthesis, properties, and applications of carbon nanotubes, Annu. Rev. Mater. Res. 2003; 33: 419-501.
[2] Willems I, Konya Z, Colomer JF, Tendeloo GV, Nataraju Ni, Fonseca A, et al., Control of the outer diameter of thin carbon nanotubes synthesized by catalytic decomposition of hydrocarbons, Chem Phys Lett, 2000; 317: 71-76.
[3] Zheng GB, Kouda K, Sano H, Uchiyama Y, et al., A model of the structure and growth of carbon nanofibers synthesized by the CVD method using nickel as a catalyst, Carbon, 2004; 42: 635-640.