Structure change of carbon nanotubes and nanofibers at high temperature

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Introduction

Carbon nanotubes and nanofibers synthesized by catalytic CVD method exhibit various structures, depending upon the synthesis conditions. They are expected to be applied in many areas, such as additives in plastics, electrode in lithium ion batteries and supercapacitors, and catalyst supporter, etc. It was reported that the structure change by heat-treatment was different from that of conventional carbon materials [1,2]. In this report, the change of microstructure of carbon nanotubes and nanofibers after high temperature heat treatment is investigated in a detail.

Experimental

The carbon nanotubes (CNT) were synthesized by CVD method at 700ºC using $Co_{0.7}Fe_{0.3}$ as catalyst and acetylene as carbon source, and the nanofibers (CNF) were synthesized at the same conditions using $Co_{0.7}Ni_{0.3}$ as catalyst. The as-synthesized carbon nanotubes and nanofibers with or without 1 at% boron addition were heat-treated at 2000ºC and 2500ºC for 1 hour in argon, respectively. The samples were designated as CNT2000, CNF2000, CNT2000-B, CNF2000-B, etc., respectively. Their structures were analyzed using x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM).

Results and Discussion

HRTEM observation shows that the structure of as-synthesized carbon nanotubes was stacked-cup type, with the graphenes stacking slantly to the tube axis. On the other hand, the as-synthesized carbon nanofibers showed less-order structure without an inner tube. Table 1 shows the d_{002} spacing and $L_{c(002)}$ values of carbon nanotubes and nanofibers measured according to the Japan Gakushin method. It is seen that the d_{002} spacing of carbon nanotubes were not decreased after heat-treated at 2000ºC and 2500ºC, even increased a little at 2000ºC, but the $L_{c(002)}$ increased apparently with heat-treatment temperature (HTT). It is also found that the boron addition had no significant effect on the d_{002} and $L_{c(002)}$. The tendency of CNF with

Table 1 The d_{002} spacing and $L_{c(002)}$ of carbon nanotubes and nanofibers.

Samples	d_{002} (nm)	$L_{c(002)}$ (nm)	Samples	d_{002} (nm)	$L_{c(002)}$ (nm)
CNT	0.3395	8.4	CNF	0.3386	8.5
CNT2000	0.3402	11.3	CNF2000	0.3393	12.3
CNT2000-B	0.3393	12.6	CNF2000-B	0.3390	13.7
CNT2500	0.3393	14.5	CNF2500	0.3388	14.0
CNT2500-B	0.3392	14.2	CNF2500-B	0.3387	15.0

HTT is similar to that of CNT from Table 1. These results indicate that heat-treatment increased the stacking order of graphenes, but showed no effect on d spacing, which generally decrease with HTT for graphitizable carbon such as cokes or pyrolytic carbon.

The carbon nanotubes and nanofibers were observed using HRTEM. Fig. 1 shows the HRTEM micrographs of carbon nanofiber and nanotube that were heat-treated at 2500ºC. It is seen that many loop structures were formed on surface of carbon nanofibers. The neighboring graphenes bonded each other to form loop structures with 1 to 4 layers of graphenes. In such loop structures, graphenes are subjected to stress because of graphene curvature, if not restricted by neighboring graphenes, the loops showed a large diameter. The formation of so many loop structures gave rise to stress in a tendency to enlarge the d spacing, and thus make them difficult to get small d spacing near to that of graphite although they become more orderly in a whole. In some thin nanofibers, the graphite structure was destroyed by such loop structures. For carbon nanotubes, there are also some loop structures formed on the surface, although they are not as many as carbon nanofibers. In the inner wall of the tube, some loop structures were observed, and graphenes also formed in the inner cross sections. In carbon nanotubes, the graphenes stacked in a smaller angle with the tube axis. Such structure also made them difficult to get small d spacing with heat-treatment.

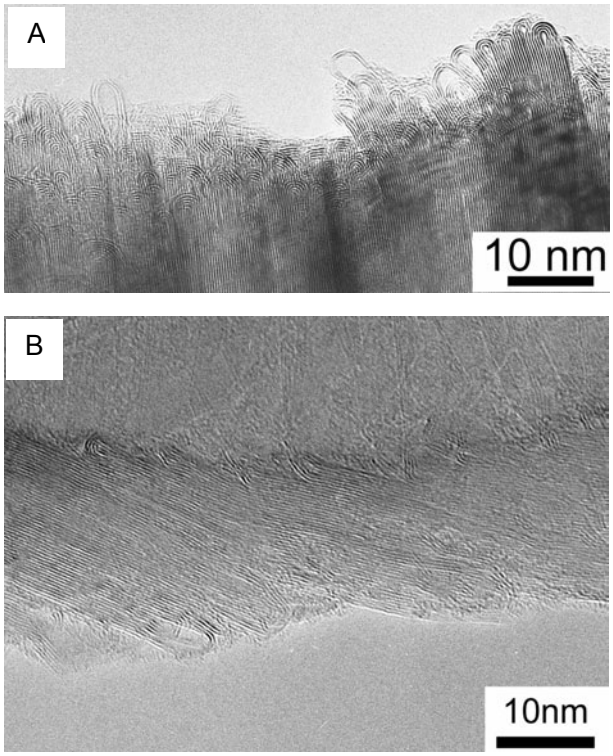

Fig. 1 HRTEM micrographs of carbon nanofiber (A) and nanotube (B) after heat-treatment at 2500ºC.

Conclusions

The structure change of carbon nanotubes and nanofibers after heat-treatment with or without boron addition was investigated. Although the $L_{c(002)}$ increased with heat-treatment temperature, the d spacing did not decrease, or even increased after heat-treatment with or without boron addition. HRTEM observations found that many loop structures were formed on the surface of carbon nanotubes and nanofibers. It is thought that the stress in such structures made the d spacing difficult to decrease.

Reference

[1] Zheng GB, Sano H, Uchiyama Y, New structure of carbon nanofibers after high-temperature heat-treatment, Carbon, 2003; 41:853-856.
[2] Endo M, Kim YA, Hayashi T, Yanagisawa T, et al., Microstructural changes induced in "stacked cup" carbon nanofibers by heat treatment, Carbon, 2003; 41: 1941-1947.