Structural Change of α-Carbon Nanotube Through Annealing

Hitoshi Nishino,* Ryouichi Nishida, Katsuhide Okimi, Yasunori Yokomichi, Takeo Matsui,† and Isao Mochida††
Material Business Promotion Department, Osaka Gas Co., Ltd., 6-19-9, Torishima, Konohana-ku, Osaka 554-0051
†Advanced Materials Research Laboratory, KRI, Inc., 134, Chudoji-Minamima-machi, Shimogyou-ku, Kyoto 600-8813
††Institute of Advanced Material Study, Kyushu University, 6-1, Kasugakoen, Kasuga-shi, Fukuoka 816-8580

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Amorphous carbon nanotube (α-CNT), which was prepared through the deposition onto ferrous fluoride whisker, was thermally annealed to observe the changes of carbon structure in its wall of the nanosized diameter. The totally amorphous carbon wall, although it was of a typical nongraphitizable carbon, changed its structure to graphitic one below 3073 K. Such a graphitization is against Franklin's rule, which is widely accepted in carbon science. The nanosized thickness and defects in the as-deposited amorphous carbon structure of α-CNT wall may force the rearrangement of nongraphitizable carbon configuration into aligned graphitic layers at 3073 K. The surface of α-CNT may suffer strong stress by the amorphous hexagon alignment in the nanothick cylindrical wall. Such stress can be relaxed by the denser stacking of graphene sheets.

Nanocarbons have attracted much attention because of their high potential in future technology, which must reflect their broad variation in their unique structure.[1–4] The structural variation may promise the broaden application. The present authors have reported a unique type of amorphous carbon nanotube,[1,5] which has amorphous carbon wall of several tens-nm thick, being prepared through the deposition onto ferrous fluoride whisker. It is important to observe the structural change of the nongraphitizable carbon in the wall of α-CNT when heated up to 3073 K, to confirm the stability of its unique structure and to broaden the variety of structure in nanocarbons.

α-CNT was prepared from a mixture of powdered poly(tetrafluoroethylene) (PTFE) and ferrous chloride in a carbon plate (27 and 3 g, respectively) by heating in a furnace under vacuum by a rotary pump after twice nitrogen replacement as reported in a previous paper[1] up to 1173 K. The diameter of the present α-CNT and its wall thickness distributed around 40–80 nm and 10–20 nm, respectively. A series of annealed CNTs were prepared by the same procedure under 100 KPa of argon with the annealing temperature programmed at 10 K/min of heating rate and 60 min of final holding time at 1473, 1773, 2073, 2473, and 3073 K, respectively. The black powder products, α-CNT (1173 K) and annealed CNTs (above 1473 K), formed in the carbon plate were collected after cooling.

Figure 1 shows the XRD profiles of α-CNT and the annealed CNTs mounted on Al holder (Rigaku RINT2400). No diffraction peak from the holder was confirmed in the range of $15^\circ < 2\theta < 30^\circ$. The peak of α-CNT around 20–30° attributed to (002) diffraction of hexagonal layers was gradually sharpened according to their annealed temperature. The interlayer spacing was calculated from the diffraction angle to be reduced from 0.42 to 0.34 nm.

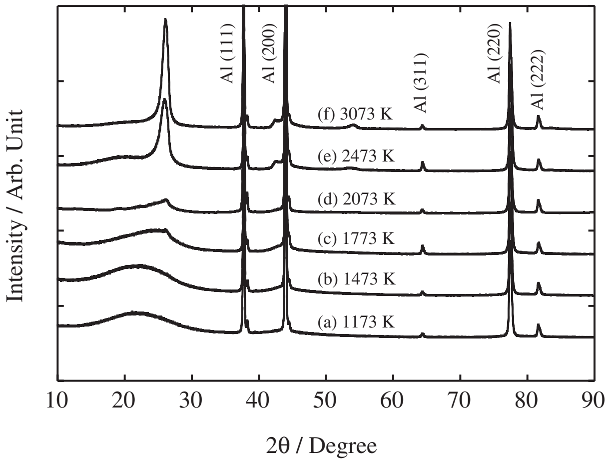

Figure 1. X-ray diffraction patterns of α-CNT (a) and the annealed CNTs (b–f) at 1473–3073 K.

α-CNTs were found to be annealed homogeneously at each temperature under TEM observation (Hitachi HF-2000 at 200 kV). The TEM images of typical CNTs were illustrated in Figure 2. The diameter of the annealed CNT and its wall thickness distributed around 40–80 nm and 10–20 nm, respectively. The right and left sides of the wall appeared not always symmetric in their thickness in a single α-CNT as shown in Figure 2a, where the totally amorphous alignment of small carbon clusters was definitely observed. A large magnification shown in the box of the photograph confirmed such an amorphous alignment. Marked graphitization took place stepwise according to the annealing temperatures in consistent with the XRD results. Small graphitic clusters became obvious at 1473 K. The graphitic clusters grew further at 1773 K, scattering still randomly in the wall (Figure 2c). The definite graphitic layers of around 2-nm thickness were observed along the inner surface of the annealed α-CNT at 2073 K as shown in Figure 2d. Major part of the wall become definitely graphitic in the annealed α-CNT at 2473 K as shown in Figure 2e, where several graphitic belts covered loosely the outer surface. The whole wall became highly graphitic at 3073 K. It must be noted that inner surface of the thick part in the wall carried graphitic belts with looped heads, which was reported in the platelet carbon nanofibers annealed above 2000 K.[6]

The structural change from nongraphitizable carbon to graphitic one in a series of annealed α-CNT at 1473–3073 K is not predicted from Franklin's rule.[7] Wang et al.[8] and Ci et al.[9] claimed the graphitization of an amorphous carbon nanotube. However, their walls appeared typical graphitizable carbon defined by Franklin. Several graphitization progresses under specific conditions have been reported, such as the heat treatment under high pressure and stress,[10] or catalytic graphitization.[11] However, the present structural change process under the usual annealing condition is unique. The thin wall and as-deposited

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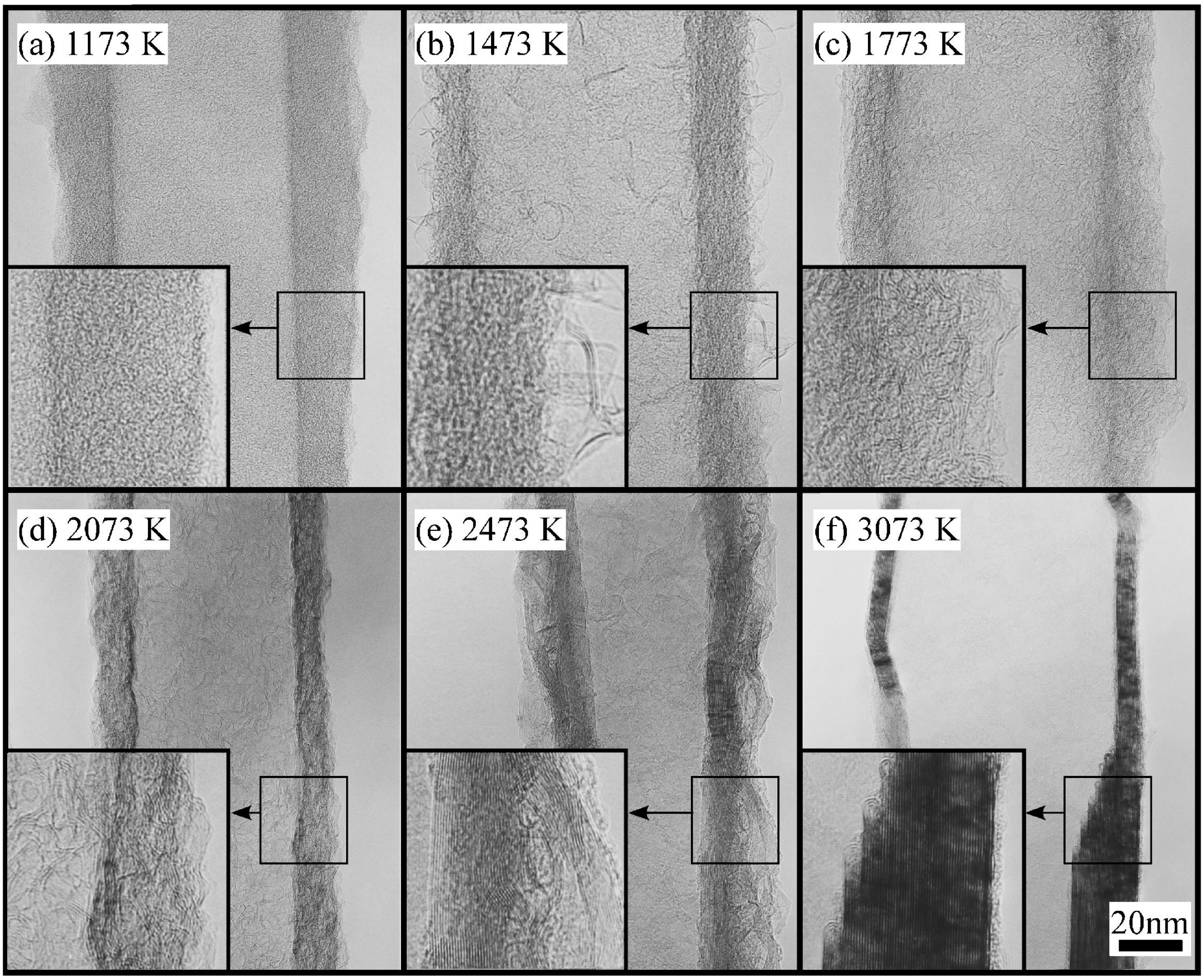

Figure 2. High resolution TEM images of α-CNT and the annealed product.

amorphous carbon structure of α-CNT may force the rearrangement of nongraphitizable carbon configuration into aligned graphitic layers at 3073 K. The surface of α-CNT may suffer stronger stress by the amorphous hexagon alignment in the nano-thick cylindrical wall. Such stress can be relaxed by the denser stacking of graphene sheets. The graphitization starts from the inner surface of the wall as shown in Figures 2d and 2e, where the larger stress is expected, because of the more amorphous natures of carbon deposited onto ferrous fluoride surface and its smaller diameter.

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