HIGHLY CRYSTALLINE MULTI-WALLED CARBON NANOTUBES USING THE TRANSIENT METAL AS GRAPHITIZATION ACCELERATOR

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Introduction

A catalytic thermal chemical vapor deposition (CVD) synthesis method has been considered as one of the promising techniques for larges-scale production of carbon nanotubes, especially when using a floating reactant technique. Among the various application fields of carbon nanotubes, the largest anticipated large-consumption of carbon nanotubes is as a filler for various high performance composite materials, when exploiting the excellent mechanical and electrical properties of carbon nanotubes. In this sense, the structural perfection with high crystallinity is a determining factor in order to get advanced composite materials (e.g., strength, toughness, conductivity). In this study, highly disordered carbon nanotubes around 20 nm obtained by the floating reactant method were mixed with the transient metal salt in solution, and the mixture was heat treated below 2000^{o}C in argon atmosphere. Then, we will describe the effect of transient metal as crystallization accelerators in terms of structural change of multi-wall carbon nanotubes as a function of heat treatment temperature.

Experimental

In the fabrication of carbon nanotubes, almost the same synthetic conditions were applied [1] except that in the vaporization of the benzene solution containing ferrocene before feeding the solution into the reactor, a smaller amount of ferrocene and a lower feeding rate is used.Thermal annealing of the nanotubes was performed at specific for 30 minutes using a graphite-resistance furnace, operating in a high-purity argon atmosphere. High-resolution transmission electron microscopy (HRTEM) (JEOL JEM 2010FEF, 200kV), X-ray diffractometry (Rigaku RINT 2100, CuK_{α} (λ=1.54056Å)), and Raman spectroscopy (Renishaw Raman Image Microscope System 1000 equipped with a CCD multi-channel detector) were used to investigate the structural changes of these carbon nanotubes by thermal annealing.

Result and discussion

The amount of metal impurities incorporated in nanotubes is critical factor when applying nanotubes as filler in composite. Therefore, there have been many studies on the removal of metal impurity. Among them, thermal treatment is very promising because this process induced the removal of metal particles completely around 2000^{o}C and also structural development of nanotubes. The thermal annealing (above 1800^{o}C) of carbon nanotubes is one of the most efficient methods for the removal of metallic particles in the tips or in the hollow core, and also for the structural development from disordered fringes to straight, crystalline layers. Their wall thickness is about 11 nm (ca. 33 graphene layers), and also the interlayer spacing is 0.34 nm. A cross-sectional HRTEM image reveals that the hollow core of the nanotube is not circular, but rather has some facets (pentagon-like), and also contains a crack-like void (denoted by the short arrow). These morphological phenomena resulting from annealing are attributed to large density changes, which result in the shrinkage of the outer and also the expansion of hollow diameter, and also crack-like voids developed along the tube axis. It is expected that this type of defects (voids along the tube axis) will develop with increasing heat treatment temperature, resulting in reduced mechanical strength (the appearance of "sword-in-sheath" failure mode). This structural transformation from a disordered carbon nanotube to a highly ordered multi-wall carbon nanotube, accompanied by the growth of crystallites, is a stepwise process; (1) straightening and rearrangement of distorted small graphene layers, (2) fusion between graphene layers, (3) growth to larger graphene layers along the tube axis and then removal of stacking faults between graphene layers within a confined space (hexagon-like cross sectional morphology).

References

[1] M. Endo, Y. A. Kim, Y. Fukai, T. Hayashi, M. Terrones, H. Terrones, and M. S. Dresselhaus, Appl. Phys. Lett. **79**, 1531 (2001).

Acknowledgements

This work was supported by the CLUSTER of Ministry of Education, Culture, Sports, Science and Technology.