Transactions of the Materials Research Society of Japan 28 [2] 441-443 (2003)

Synthesis of Carbon Nanotubes by Pulsed Wire Discharge

Ryouta Kobayashi, Hisayuki Suematsu, Tsuneo Suzuki, Weihua Jiang and Kiyoshi Yatsui
Extreme Energy-Density Research Institute, Nagaoka University of Technology
Nagaoka, Niigata 940-2188, Japan
Fax: +81-258-47-9890, E-mail: ryotak@etigo.nagaokaut.ac.jp

We have attempted to produce carbons nanotubes by pulsed wire discharge (PWD). Experimentally, one thousand carbon fibers with diameter of 7 μm were installed between electrodes in nitrogen gas of 2.67×10^4 Pa and were discharged by use of a 20 μF capacitor charged at 5 kV. Soot (carbon nanosized powders) was collected after the discharge and was observed by transmission electron microscopy. In the soot collected, we found carbon nanotubes of about 3 nm in inner diameter. From these results, we concluded that carbon nanotubes was successfully synthesized by PWD.
Key words: plasma, carbon, nanotubes, pulsed wire discharge

1. INTRODUCTION

Diamond, graphite and amorphous carbon are known as allotropes of carbon. Among the allotropes, carbon nano-tubes (CNT) [1] and fullerene [2] have interesting characters and have been candidates for various applications, i.e., electron emitters, chemical probes and hydrogen storages. Fullerene and CNT were collected in soot which was synthesized by arc discharge [3], laser vaporization [4], [5] and chemical vapor deposition [6] methods. Since the energy conversion efficiency of these methods are not high, other synthesis methods are required to be developed.

Pulsed wire discharge (PWD) has been successfully applied to the production of nanosized powders [7]~[11]. Using PWD, various powders of metals and compounds have been synthesized by discharging metal wires in various gases. In PWD, since the wires are evaporated by Joule heating, the wires must be conductive materials. Not only wires of metals but also carbon fibers were discharged by PWD to prepare soot, in which fullerene was found [12]. However, no efforts have been carried out to synthesize CNT by PWD. In the present work, the production of CNT have been attempted by using PWD.

2. EXPERIMENTAL

Figure 1 schematically shows the arrangement of the experimental apparatus. A wire made of 1000 carbon fibers with a diameter of 7 μm was located in a stainless steel chamber filled with N_2 gas. A simple circuit consisting of a capacitor, a gap switch and electrodes was connected to the wire. Pulsed current was driven through the wire. The current deposited the electric energy in the wire due to its finite resistance. The deposited energy melts, evaporates, and ionizes the carbon wire, producing high-density, high-temperature plasma that expands into N_2 gas. The plasma was rapidly cooled by the interaction with the gas, giving rise to high-temperature vapor of the wire material, which was condensed uniformly in the ambient gas. After the discharges, soot was collected through membrane filters. Experimental conditions are summarized in Table I.

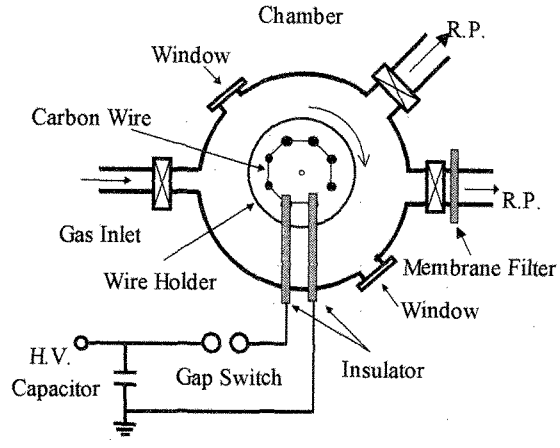

Fig. 1 Experimental setup.

Table I Experimental conditions.

Wire	TORAY 'TORAYCA' M40-1000-50A ϕ 7μm×1000 fibers 25mm
Capacitance	20μF
Charging voltage	5kV
Heat to be Evaporated	103 J
Stored Energy	250 J
Electrode	Copper, Stainless steel
Atmosphere gas	N_2
Ambient Pressure	2.67×10^4 Pa

The soot was characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray analysis (EDX).

Patterns of XRD were obtained using CuKα radiation. For HRTEM observations and EDX analyses, soot was dispersed in acetone and ground in an agate mortar. Small particles, which were suite for HRTEM observations and EDX analyses, were scooped on a carbon microgrid supported by a copper mesh. Then, the mesh was installed in a transmission electron microscope operated at an accelerating voltage of 200 kV.

3. RESULTS

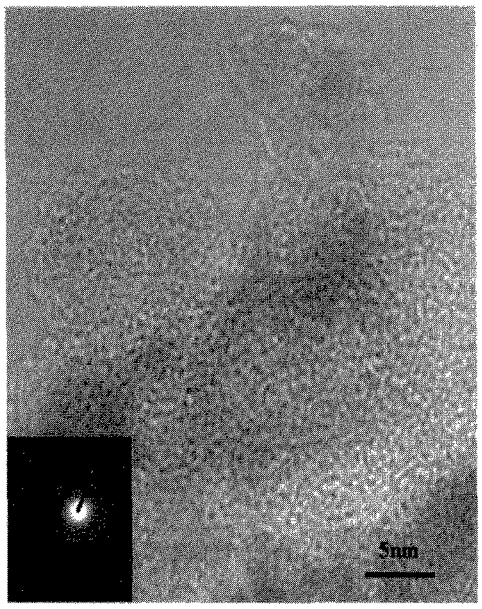

Fig. 2 HRTEM image and diffraction pattern of soot prepared byPWD using copper electrodes.

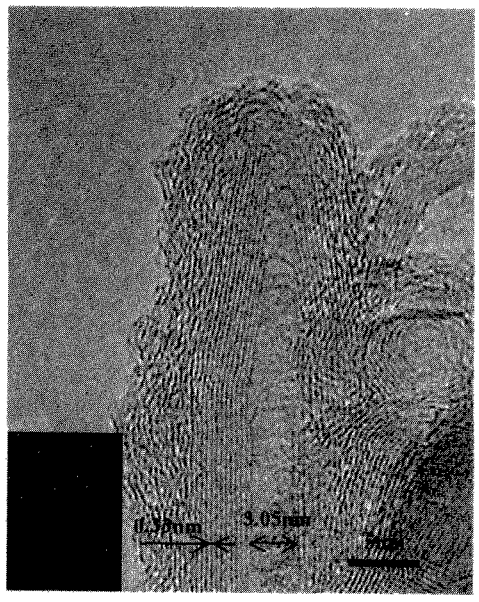

Fig. 3 HRTEM image and diffraction pattern of soot prepared byPWD using stainless steel electrodes.

Figure 2 shows a typical HRTEM image with the diffraction pattern of soot prepared by PWD using copper electrodes. In the grain, no lattice fringes are observed. Since only difuse rings are seen in the diffraction pattern, this grain is thought to be an amorphous phase. Thus, amorphous carbon particles were obtained by PWD using copper electrodes.

Figure 3 shows an HRTEM image of soot prepared by PWD using stainless steel electrodes. The lattice spacing interval is 0.33 nm, which is identical to the (002) inter planar spacing of graphite. In the upper part of Fig. 3, the lattice was sharply bent by 180°. Between the lattices, there are 3.05 nm of spacing. This is similar to typical HRTEM images of multiwalled carbon nanotubes (MWCNT). From Fig. 3, MWCNT were successfully synthesized by PWD using stainless steel electrodes.

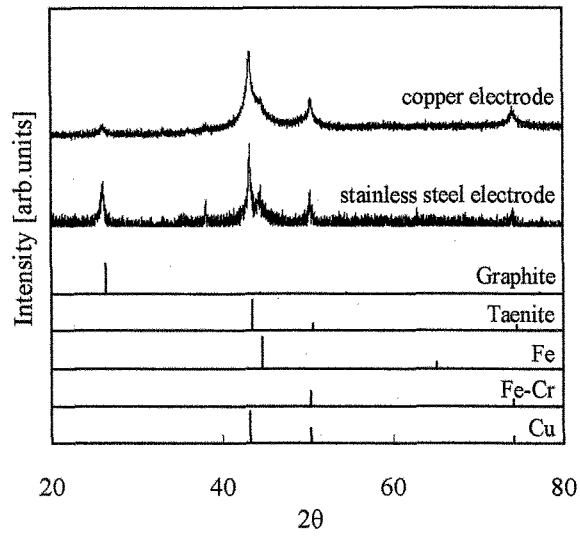

Fig. 4 XRD data of soot prepared by PWD.

The soot was analyzed by XRD and EDX to know the reason why MWCNT were synthesized only with stainless steel electrodes.

The XRD patterns of these two soot that were produced by PWD are shown in Figure 4. In the pattern for the soot prepared with copper electrodes, a peak at 26° corresponds to those for graphite. However, their intensity is very weak.

From this result and Fig. 2, most of carbon grains in the soot must not be crystalline. There are three other strong peaks at 43° , 50° and 74° , whose diffraction angles are not close to those for carbon. This result indicates that soot has been contaminated with foreign materials. In the XRD pattern for soot prepared with stainless steel electrodes, the graphite peak is also observed. Furthermore, the other peaks also exist in the pattern. The peaks of 43° , 50° and 74° is close to those for Fe, Fe-Cr, Taenite or Cu, which are constituent elements of the electrodes and the chamber. However, it is difficult to identify the phases because some of the peak positions are very close.

Thus, an EDX apparatus attached with the TEM was utilized for analysing composition in the soot. Spectrum of EDX for soot prepared with stainless steel electrodes are shown in Fig. 5. A peak for C is seen. Furthermore, peaks for O, Cr, Fe, Co, Ni, Cu and Zn are seen. Since the TEM sample was supported by a Cu mesh, the Cu peaks may come from the mesh. Other elements, except O, are constituent elements of the electrodes and the chamber. These transition metal nanosized particles may be oxidized in air. Thus, soot prepared with stainless steel electrodes must be contaminated with elements in the atmosphere, the electrodes and/or the chamber. Spectrum of EDX for soot prepared with copper electrodes are shown in Fig. 6. Small peaks of Al and Si, which may be contamination from the mortar. Other peaks are the same as those in Fig. 5. This result indicates that the soot has also been contaminated with the atmosphere, electrodes and/or chamber. These results are in agreement with those of XRD (Fig. 4). However, peak intensity for Fe was one eighth of that in Fig. 5.

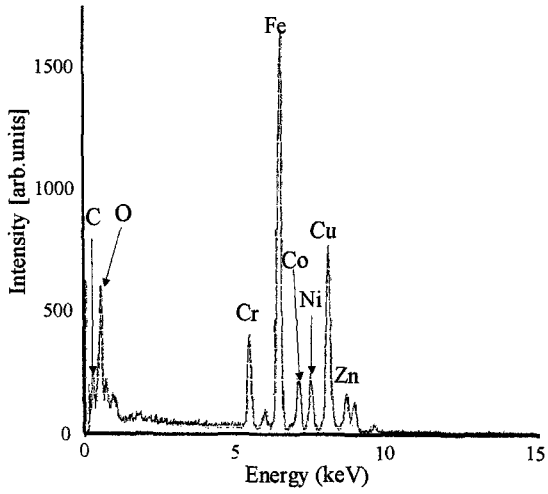

Fig. 5 EDX data of soot prepared by PWD and with the use of stainless steel electrodes.

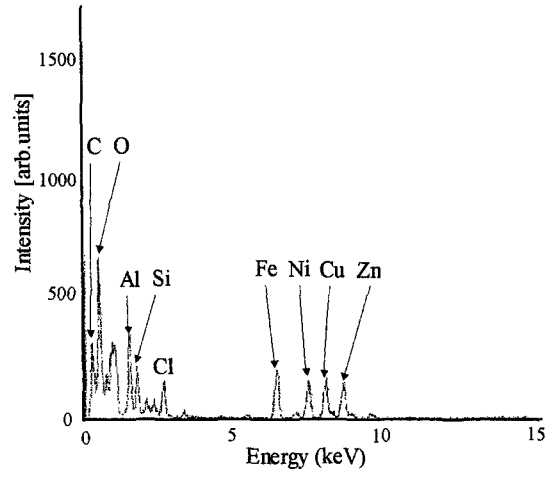

Fig. 6 EDX data of soot prepared by PWD and with the use of copper electrodes.

4. DISCUSSIONS

In the synthesis of the soot, copper or stainless steel electrodes were used. These electrodes were connected to the carbon wire that was evaporated because of Joule heating generated by the pulsed current. It is obvious that small amount of the electrodes has been melted or evaporated by the heat and contaminated in the soot. It is also possible that other part of the chamber has been melted or evaporated to be mixed with the soot.

From Figs. 5 and 6, peak intensity of Fe is higher in soot prepared with stainless steel electrodes than that prepared with copper electrodes. The MWCNT were only observed in the soot prepared with stainless steel electrodes (Figs. 2 and 3). These results may indicate that presence of Fe enhance to form MWCNT. In other synthesis methods to prepare MWCNT, it is known that transition metals such as Fe are good catalysts. Thus, it may be possible that Fe particles, which may be formed during the discharge of the carbon wire, acts as a catalyst to synthesize MWCNT.

5. CONCLUSIONS

From the HRTEM photographs of the soot, multiwalled carbon nanotubes (MWCNT) were successfully synthesized by pulsed wire discharge. The amount of MWCNT were enhanced by the presence of iron and nickel electrodes.

REFERENCES

[1] S. Iijima: *Nature* **354**, 56-58 (1991).
[2] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley: *Nature* **318**, 162-163 (1985).
[3] S. Iijima and T. Ichihashi: *Nature* **363**, 603-605 (1993).
[4] T. Guo, P. Nikolaev, A. Thess, D. T. Colbert and R. E. Smalley: *Chem. Phys. Lett.* **243**, 49-54 (1995).
[5] A. Thess, R. Lee, P. Nikolave, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fischer and R.E. Smalley: *Science* **273**, 483-487 (1996).
[6] H. Dai, A.G. Rinzler, P. Nikolaev, A. Thess, D.T. Colbert and R.E. Smalley: *Chem. Phys. Lett.* **260**, 471-475 (1996).
[7] W. Jiang and K. Yatsui, *IEEE Trans. Plasma Sci.* **26(5)**, 1498-1501 (1998).
[8] C. Sangurai, Y. Kinemuchi, T. Suzuki, W. Jiang and K. Yatsui, *Jpn. J. Appl. Phys.* **40(2B)**, 1070-1072 (2001).
[9] T. Suzuki, K. Keawchai, W. Jiang and K. Yatsui, *Jpn. J. Appl. Phys.* **40(2B)**, 1073-1075 (2001).
[10] Y. A.Kotov, E.I. Azarkevich, I. V. Beketov, T. M. Demina, A. M. Murzakaev and O. M. Samatov, *Key Engineering Materials* **132**, 173-176 (1997).
[11] M. Umakoshi, T. Yoshitomi and A. Kato, *Journal of Materials Science* **30**, 1240-1244 (1995).
[12] Submitted for publication to, *Jpn. J. Appl. Phys.* (2002).

(Received December 21, 2002; Accepted March 26, 2003)