*Transactions of the Materials Research Society of Japan* 29 [2] 501-504 (2004)

# Synthesis of Twisted Carbon Nanofiber by Catalytic CVD Method

Takashi Katsumata, Youhei Fujimura, Makoto Nagayama, Hiroshi Tabata,
Hirofumi Takikawa, Yoshihiko Hibi, Tateki Sakakibara, Shigeo Itoh*
Department of Electrical and Electronic Engineering, Toyohashi University of Technology,
Toyohashi, 441-8580 Japan, Fax: 81-0532-44-6727, e-mail: takikawa@eee.tut.ac.jp
* Product Development Center, Futaba Corporation, Japan

Helical carbon nanofibers (HCNF) were synthesized by the catalytic CVD method. The catalyst was a compound comprised of nickel (Ni) and copper (Cu), or their oxides, in the form of a multi-layer or mixture-layer film. They were prepared on a quartz substrate by physical vapor deposition (PVD) and sol-gel drop-coat methods. First, the dependence on source gas and dependence on presence/absence of a hot-filament assist were tested using Ni/Cu PVD film as a catalyst. The dilute gas used was helium (He). When acetylene ($C_2H_2$) gas was used, carbon nanocoils (CNCs) and carbon nanoropes (CNRs) were deposited without hot-filament assist and with assist, respectively. When ethylene ($C_2H_4$) gas was used with hot-filament assist, carbon nanotwists (CNTws) were deposited. Secondarily, the catalyst mixture of Ni oxide (NiO)/Cu oxide (CuO), prepared by the sol-gel drop-coat method, was tested for use with $C_2H_2$ gas. The influence of the mixing ratio of catalysts, process temperature, and the source/dilute gas ratio was examined. Optimum conditions for efficient HCNF synthesis were found to be as follows: NiO/CuO ratio, 2/8; process temperature, 500-600°C; $C_2H_2$/He flow rate ratio, 3/10 – 4/10. The obtained product in the latter experiment was mainly CNTw.
Keywords: helical carbon nanofiber, carbon nanotwist, catalytic CVD, Ni/Cu multi catalysts, optimization

## 1. INTRODUCTION

Since 1953, when carbon fiber with a helical structure was first reported [1,2], various types of chemical vapor deposition (CVD) methods have been developed, a variety of catalysts have been examined under various process conditions, and many carbon fiber growth models have been proposed. In 1990, Motojima *et al.* fabricated regular-coiled carbon fibers with high reproducibility [3]. They are referred to in review articles [4, 5]. Recently, helical, spiral, or twisted carbon fibers on an under-submicron scale, have been prepared by the CVD method with an ion (Fe) on indium-tin-oxide (ITO) film [6], and nickel (Ni) or zinc (Zn) on a copper (Cu) substrate [7-10]. Such helical carbon nanofibers (HCNFs) have field emission properties [9, 11], and are considered to be useful for various applications such as nano-springs, electric nano-inductors, electromagnetic shields, gas storage, fillers in polymers and various types of rubbers.

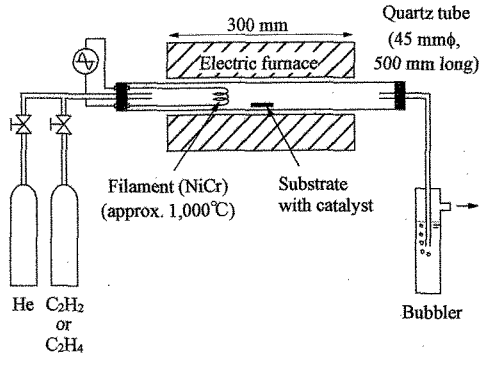



Fig. 1. Experimental setup of the catalytic CVD apparatus with hot-filament.

In the present paper, HCNFs were fabricated using a compound catalyst of nickel (Ni) and copper (Cu), or their oxides (NiO, CuO). First, various shapes of HCNFs were synthesized by a Ni/Cu multi-layer catalyst of thin solid film prepared by physical vapor deposition (PVD) using the vacuum arc plasma. Second, the influence of mixing ratios of catalysts, process temperatures, and the source/dilute gas ratio was examined using an NiO/CuO compound film prepared by the sol-gel drop-coat method.

## 2. EXPERIMENTAL DETAILS

Figure 1 shows the experimental setup of the catalytic CVD apparatus with a nickel-chromium alloy (NiCr) hot-filament. The electric furnace and the quartz tube process chamber were horizontally arranged. Source gases were acetylene ($C_2H_2$) and ethylene ($C_2H_4$). The dilute gas was helium (He). When the hot filament was turned on, the temperature was set at 1,000°C approximately 30 mm upstream from the substrate. The substrate was quartz measuring approximately 10×10 $mm^2$ and 1 mm in thickness. The experimental procedure was as follows. After the catalyst-coated substrate was placed at the center of the quartz tube, the temperature of the electric furnace was increased from room temperature to the set temperature during approximately 1 hour with He gas flow of 420 ml/min. Then the source gas was introduced for 10 or 20 min with/without the hot filament assist. After the deposition process, the furnace was cooled down to the room temperature over approximately 1 hour with He gas flow

of 420 ml/min.

Two methods were employed for preparing the catalyst-coated substrate. The first method was shielded cathodic arc deposition [12]. This method is a type of physical vapor deposition (PVD), in which the ions emitted from the cathode spot of vacuum arc discharge plasma are plated on the substrate. The deposition apparatus is depicted in Fig. 2. A cathodic arc was generated from the cathode and diffusively expanded to the chamber anode. To prevent macrodroplet particle adhesion, a shield plate was placed between the cathode and the substrate. Using this apparatus, a 100-nm Cu film was deposited on the substrate and then a 5-nm Ni film was prepared on it at a pressure of 3.0 Pa with 30-ml/min Ar flow.

The second method for preparing the catalyst-coated substrate was the sol-gel drop-coat method. Commercial sol-gel solutions for NiO and CuO coating, containing 3 wt% of Ni and Cu, were ultrasonically mixed. Then the

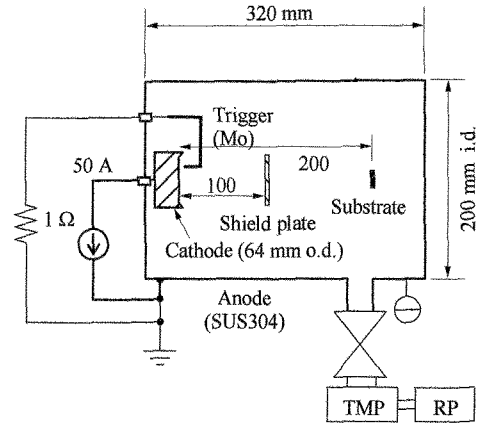
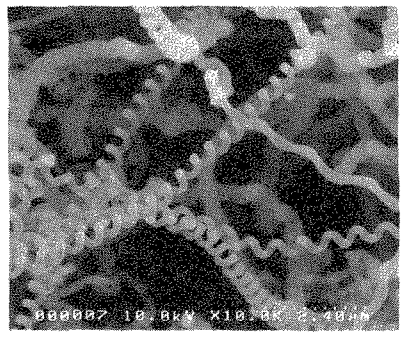
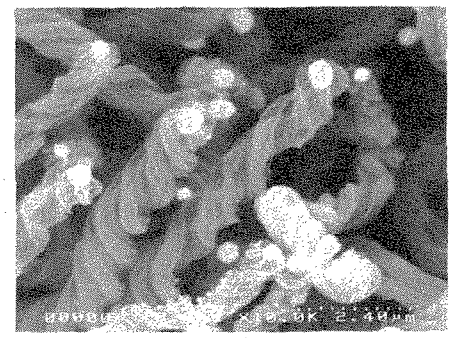


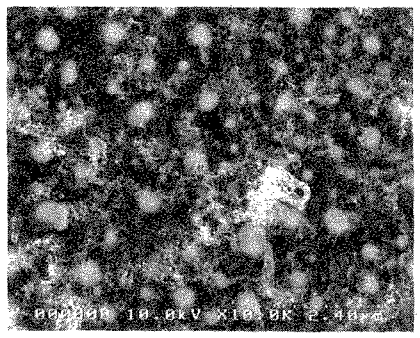

Fig. 2. Shielded cathodic arc deposition apparatus. TMP: turbo-molecular pump, RP: rotary pump.



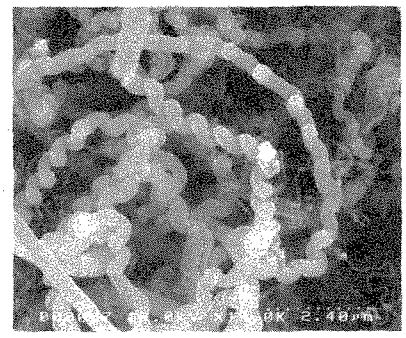
(a) $C_2H_2$ gas, without HF (carbon nanocoil, CNC)



(b) $C_2H_2$ gas, with HF (carbon nanorope, CNR)

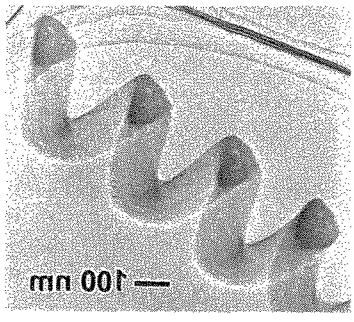


(c) $C_2H_4$ gas, without HF

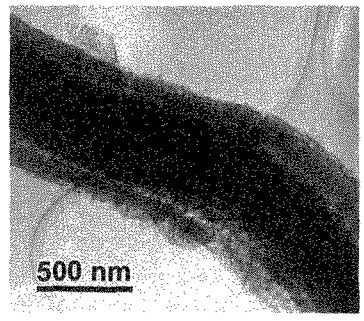


(d) $C_2H_4$ gas, with HF (carbon nanotwist, CNTw)

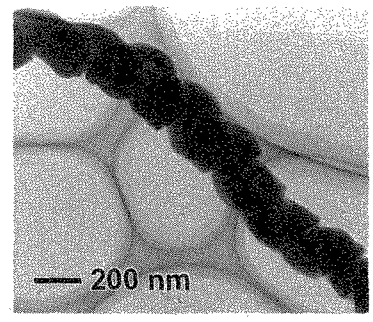
Fig. 3. FE-SEM micrographs of various helical carbon nanofibers (HCNFs) prepared with Ni/Cu multi-layer PVD-coated film catalyst. HF: hot-filament assist.




(a) Carbon nanocoil (CNC)




(b) carbon nanorope (CNR)




(c) Carbon nanotwist (CNTw)

Fig. 4. TEM micrographs of various HCNFs prepared with Ni/Cu multi-layer PVD-coated film catalyst.

mixed solution was dropped from a pipette on the substrate and dried at 200°C on a hot plate. This method was less complex than that of the PVD coating method.

The deposited carbon film was observed with a field emission type scanning electron microscope (FE-SEM; Hitachi, S-4500), a transmission electron microscope (TEM; JEOL, JEM-2010), and by energy dispersive X-ray (EDX; Phillips, DX-4) attached to SEM (JEOL, JSM-6300).

## 3. RESULT AND DISCUSSIONS

### 3.1 Ni/Cu multi-layer PVD-coated film catalyst

In this experiment, the flow rate of the source gas was 180 ml/min and the process time was 20 min. The FE-SEM and TEM micrographs of the deposited products under a different gas source and with/without hot-filament assist are shown in Figs. 3 and 4, respectively.

When $C_2H_2$ gas was used without hot-filament assist, as shown in Fig. 3(a) and Fig. 4(a), a spring-like coiled fiber, called a carbon nanocoil (CNC) was synthesized. The CNC was mostly amorphous tubular coil with a fine hollow in the center. When $C_2H_2$ gas was used with hot-filament assist, as shown in Fig. 3(b) and Fig. 4(b), a rope-like fiber consisting of two to four fibers twisted together, called carbon nanorope (CNR), was synthesized. In other words, it looked like a nano-drill. The CNR always had a catalyst particle at the top of the fiber. An obvious crystalline structure was not observed, but the TEM image indicated the shape of the comparably fat trunk at the center with thinner skin around the trunk. When $C_2H_4$ gas was used without hot-filament assist, spider egg capsule-like or cocoon-like products were obtained, as shown in Fig. 3(c). When $C_2H_4$ gas was used with hot-filament assist, as shown in Fig. 3(d) and Fig. 4(c), helical twisted fiber without an inner coil space, called carbon nanotwist (CNTw), was synthesized. The outer diameters of CNC and CNTw were thinner than that of CNR. These results indicate that a Ni/Cu catalyst provides various shapes of HCNFs depending on process conditions.

Figure 5 shows the result of EDX analysis of CNTw. It was found that the major deposition material was carbon (C), although the catalyst was composed of Ni and Cu, with the amount of Cu in the catalyst higher than that of Ni.

The growth model of the HCNFs is considered to conform to that of Amelinckx's model [13]. In the model, it is considered that the helix growth is realized due to the imbalance of the extrusion velocity of the carbon on the compound catalytic surface.

### 3.2 Ni/Cu mixture sol-gel film catalyst

In this experiment, $C_2H_2$ gas was used as a carbon source and a hot-filament was not used. The deposition time was 10 min.

Figure 6 shows the dependence of the NiO/CuO ratio on the carbon yield ratio processed at 650°C with a $C_2H_2$ flow rate of 180 ml/min. The carbon yield rate expresses the carbon deposition weight relative to the catalyst weight per unit process time (minute). The range where the HCNF was obtained is indicated in the figure. When the amount of NiO was larger than that of CuO the deposition amount was larger, although the product was mostly nanofibrous without helicity. When the NiO amount was lower, the deposition amount was smaller and the product was mostly HCNFs. The optimum NiO/CuO composition ratio for HCNF synthesis was in the range of 4/6-1/9 and the optimum was 2/8. This ratio

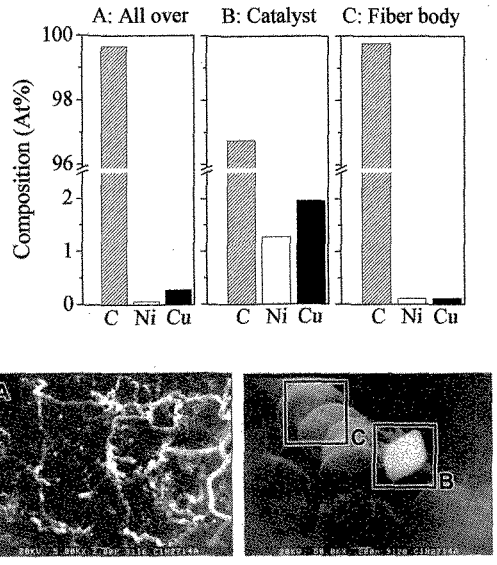



Fig. 5. EDX analysis of CNTw desposition and SEM micrograph of analysis positions.

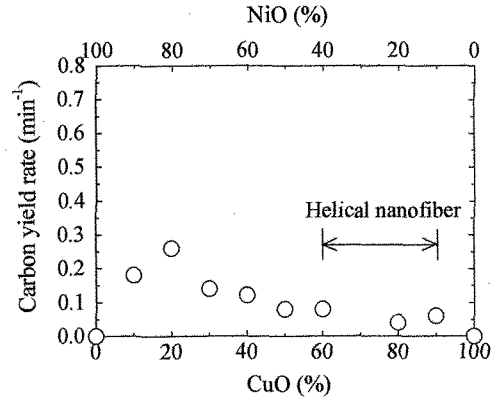



Fig. 6. Dependence of NiO/CuO catalyst composition ratio on carbon yield rate. Process temperature, 650°C; $C_2H_2$ flow rate, 180 ml/min.

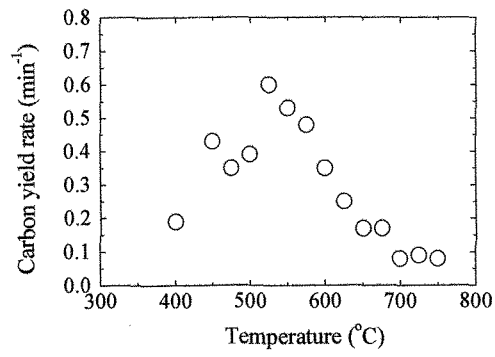



Fig. 7. Dependence of process temperature on carbon yield rate. NiO/CuO ratio, 2/8; $C_2H_2$ flow rate, 180 ml/min.

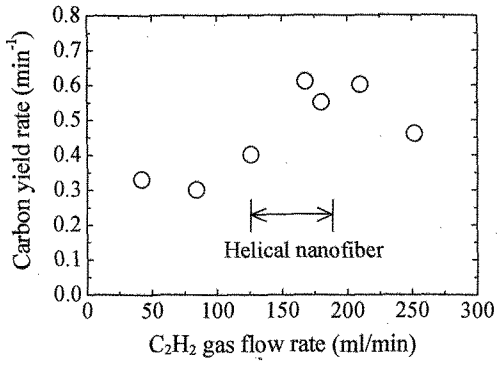



Fig. 8. Dependence of source gas flow rate on carbon yield rate. NiO/CuO ratio, 2/8; process temperature, 550°C.

is very close to a previous report indicating that the ratio Ni/Cu=3/7 provides the helical carbon fibers in the CVD process with $C_2H_4$ gas [7].

Figure 7 shows the temperature dependence of the carbon yield rate. The NiO/CuO ratio was 2/8. When the temperature was 500-600°C, which was the optimum, the carbon yield rate was high, the HCNF product yield was high, and the diameter was 80-100 nm. When the temperature was higher than 600°C, the carbon yield was lower, the HCNF yield was low, and the HCNFs were thick (200-300 nm diameter). It is considered that temperatures above 600°C are too high; thus the carbon deposition is so fast that the catalyst is immediately covered by carbon and is not able to sustain the carbon extruding function. When the temperature was lower than 500°C, the carbon yield was lower and the HCNF yield was low. The temperature obtained in the present work was lower that the optimum temperature 600-700°C for Ni/Cu catalyst and $C_2H_4$ source gas, reported by Kim *et al.* [7]. This implies that $C_2H_2$, which is readily to thermally decomposed, is adequate for the lower temperature process.

The influence of the flow rate of the $C_2H_2$ source gas on the carbon yield rate is shown in Fig. 8. When the $C_2H_2$ gas flow rate was lower than 100 ml/min, carbon yield was low and the product was a nanofiber without helicity. When the flow rate was 125-180 ml/min, the carbon yield rate was high and the HCNF yield was high. When the flow rate was higher, the carbon yield was high and a nanofiber with regular helicity was not obtained. In this experiment, most HCNFs were CNTws. Figure 9 is a micrograph of a CNTw prepared in the optimum condition.

## 4. CONCLUSIONS

The present study revealed that the Ni/Cu composed catalyst provides various shapes of HCNFs, such as CNC, CNR, and CNTw, depending on the conditions of the CVD process. The optimum conditions for CNTw production with a NiO/CuO mixture catalyst film and $C_2H_2$ gas source, were as follows: NiO/CuO ratio, 4/6-1/9; process temperature, 500-600°C; and $C_2H_2$ gas flow rate, 125-180 ml/min against dilute gas flow rate of He 480 ml/min ($C_2H_2$/He flow rate ratio, 3/10-4/10). Further optimization of the catalyst preparation and CVD system development are required to increase yields and enable the mass-production of shape-controlled

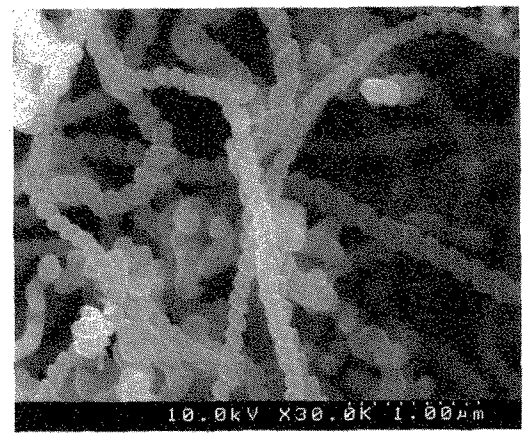



Fig. 9. CNTw obtained at optimum conditions. NiO/CuO ratio, 2/8; process temperature, 550°C; $C_2H_2$ flow rate, 160 ml/min.

CNTws.

## 5. ACKNOWLEDGEMENTS

This work was partly supported by the Excellent Research Project of the Research Center for Future Technology, Toyohashi University of Technology, by the Research Project of the Venture Business Laboratory, Toyohashi University of Technology, by the 21st Century COE Program "Intelligent Human Sensing" from the Ministry of Education, Culture, Sports, Science and Technology, and by a Grant-in-Aid from The Japan Society for the Promotion of Science.

## 6. REFERENCES

[1] W.R. Davis, R.J. Slawson, G.R. Rigby: *Nature*, **171**, 756 (1953)
[2] W.R. Davis, R.J. Slawson, G.R. Rigby: *Trans. Brit. Ceram. Soc.*, **56**, 67 (1957)
[3] S. Motojima, M. Kawaguchi, K. Nozaki, H. Iwanaga: *Appl. Phys. Lett.*, **56**, 321 (1990)
[4] N.M. Rodriguez: *J. Mater. Res.*, **8**, 3233 (1993)
[5] S. Motojima, X. Chen: Review: Nanohelical/Spiral materials, "Encyclopedia for Nanoscience and Nanotechnology", American Science Publisher (in press)
[6] M. Zhang, Y. Nakayama, L. Pan: *Jpn. J. Appl. Phys.*, **39**, L1242 (2000)
[7] M.S. Kim, N.M. Rodriguez, and R.T.K. Baker: *J. Catal.*, **134**, 253 (1992)
[8] C.A. Bernardo, I. Alstrup, J.R. Rosytup-Nielsen: *J. Catal.*, **96**, 517 (1985)
[9] H. Takikawa, M. Yatsuki, R. Miyano, M. Nagayama, T. Sakakibara, S. Itoh, Y. Ando: *Jpn. J. Appl. Phys.*, **39**, 5177 (2000)
[10] W.J. Jong, S.H. Lai, K.H. Hong, H.N. Lin, H.C. Shih: *Dia. Relat. Mater.*, **11**, 1019 (2002)
[11] L. Pan, T. Hayashida, M. Zhang, Y. Nakayama: *Jpn. J. Appl. Phys.*, **40**, L235 (2001)
[12] H. Takikawa, K. Shinsako, T. Sakakibara: *Thin Solid Films*, **316**, 73 (1998)
[13] S. Amelinckx, X.B. Zhang, D. Bernaerts, X.F. Zhang, V. Ivanor, J.B. Nagy: *Science*, **265**, 635 (1994)

(Received October 11, 2003, Accepted December 15, 2003)