Transactions of the Materials Research Society of Japan 25 [3] 873-876 (2000)

Carbon Nanotube Growth at Cathode Spot in Vacuum Arc

Hirofumi Takikawa, Yoshitaka Tao, Ryuichi Miyano, Tateki Sakakibara, Yoshinori Ando*, and Shigeo Itoh**

Department of Electrical and Electronic Engineering, Toyohashi University of Technology
Toyohashi, Aichi 441-8580, Japan
Fax: +81-532-44-6727, e-mail: takikawa@eee.tut.ac.jp
*Department of Physics, Meijo University
Nagoya, Aichi 468-8502, Japan
**Research and Development Center, Futaba Corporation
Chousei, Chiba 299-4395, JAPAN

Multi-wall carbon nanotubes were fabricated in cathodic vacuum arc, in which the pure graphite was used as a cathode and stainless-steel vacuum chamber was used as an anode. First, the arc with a constant current of 50 A was ignited for approximately 0.8 s without magnetic field and the cathode spot motion was recorded by a video. After the discharge, the crater created by the cathode spot was microscopically observed. Numerous carbon nanotubes were observed at the position where the arc might be extinguished. Then the arc was ignited with an external magnetic field parallel to the cathode surface for approximately 1.6 s in order to drive the cathode spot to retrograde direction and to specify the extinguished position of the arc. Again numerous nanotubes were observed at the extinguished position. The nanotubes were hardly observed at other area. These results indicate that two different processes on the nanotube growth in cathodic vacuum arc can be possibly considered.

Keywords: multi-wall carbon nanotube, cathodic vacuum arc, cathode spot, magnetic field

1. INTRODUCTION

Since the carbon nanotube was found in the cathode deposit in arc discharge [1], numerous numbers of researches have been concentrated on the low-pressure arc with homoelectrode system, namely graphite (C) cathode and C anode [2], [3]. However, the formation mechanism of carbon nanotube in the carbon arc method is still unclear.

Recently, the authors have utilized the low-pressure arc with the heteroelectrode system, and shown that the multi-wall carbon nanotubes (MWNT) were synthesized by the cathode spot and that anodic phenomena is not essential to produce MWNT in carbon arc method [4]. Consequently they have employed the cathodic vacuum arc, in which the anode is inert, and it has been found that the cathodic vacuum arc also produces MWNT at the crater that produced by the cathode spot [5], [6]. Moreover, potential of the cathodic arc to produce the macrodroplets having nanotubes, called nanotube sea urchin, and diamond-like carbon (DLC) film embedding MWNT were demonstrated [6]. However, in the previous studies, they have not paid attention on the cathode spot movement.

In the present study, first, the crater produced by the cathode spot in a vacuum arc without magnetic field was more carefully observed than previously. Then the cathode spot crater was created when the magnetic field parallel to the cathode surface was applied in order to drive the cathode spot and to specify the crater site. From these experiments, the position and timing of MWNT growth were identified.

2. EXPERIMENTAL

Experimental setup is shown in Fig.1. A cathode of pure graphite plate (approximately, 10 mm × 15 mm, 1 mm thick) was placed in the cylindrical vacuum chamber (200 mm in diameter, 300 mm in length), which was made of stainless steel (SUS304) and used as an anode. Two permanent magnet plates sandwiched the cathode plate in order to apply the magnetic field parallel to the cathode surface. The chamber was once evacuated down to 0.01 Pa by a turbomolecular and rotary pump, and then helium (He) gas was filled until the pressure became 0.5 Pa. The arc was ignited using a mechanical

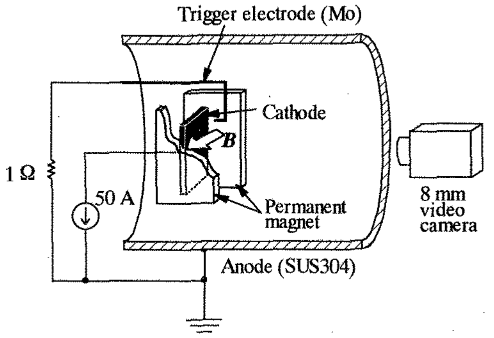


Fig. 1. Schematic diagram of cathodic vacuum arc with applying magnetic field parallel to cathode surface.

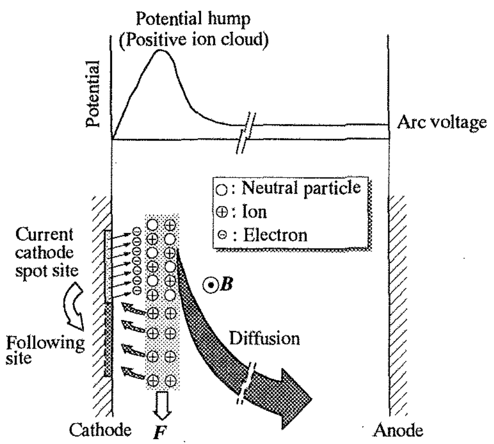


Fig. 2. Illustration of potential hump on cathode spot surface and retrograde motion of cathode spot.

triggering system with a molybdenum (Mo) electrode (3 mm in diameter) and powered by a constant-current DC inverter power supply. Arc current was 50 A. The arc was extinguished after approximately 1 s of ignition by turning the power supply off. Applied magnetic flux density was approximately 4 mT at the arcing position. The cathode spot motion was monitored using a video camera (Sony, CCD-TR1000) with neutral density filters.

When the arc is operated at the pressure more than approximately 1 kPa (namely, so-called high- and low-pressure arc) under applying the parallel magnetic field, the cathode spot was moved to the direction followed by the Laurentzian rule, since the cathode spot was dragged by the motion of the pinched dense arc column. On the other hand, in cathodic vacuum arc, the cathode spot was moved to retrograde direction under

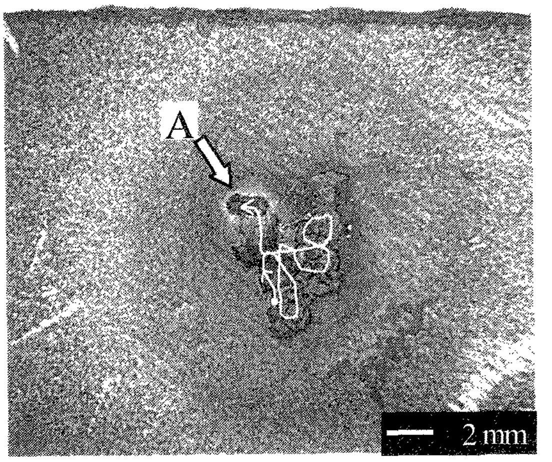
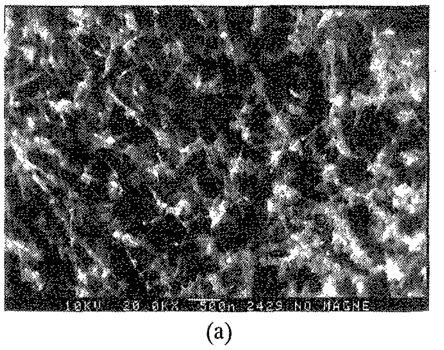
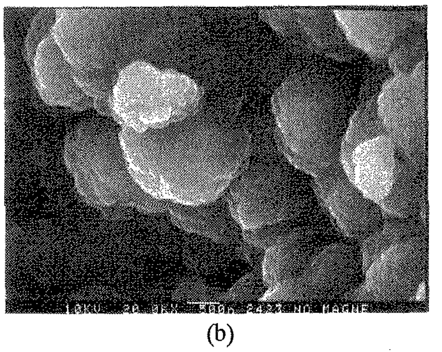


Fig. 3. Micrograph of the cathode spot crater created by the arc without magnetic field and cathode spot motion was overlapped (discharge time: 0.8 s, arc voltage: 24 V).



(a)



(b)

Fig. 4. HR-SEM micrograph of the crater surface of Fig. 3. Fig. (a) shows an enlarged image of the position A in Fig. 3, and (b) shows that of other position.

the magnetic field, since the repetitive creation of new cathode spot occurs at the side where ions bombard from the potential pump of ion cloud, as shown in Fig. 2 [7]-[9]. Such arcs, namely the arc driven by the magnetic field are so-called steered arc or running arc.

After the arc discharge, the cathode surface was

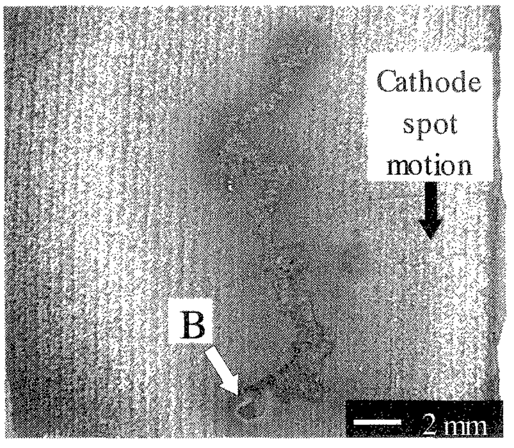
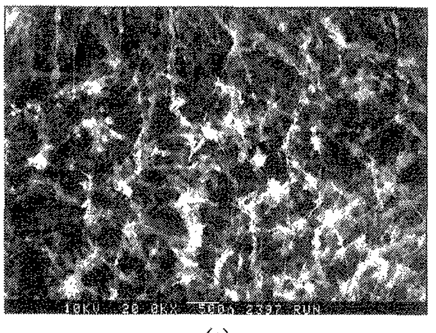
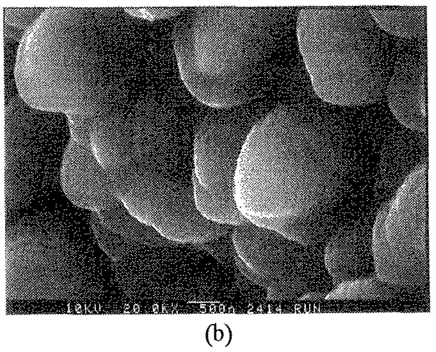


Fig. 5. Micrograph of the cathode spot crater created by the arc with 4-mT magnetic field (discharge time: 1.6 s, arc voltage: 28 V).



(a)



(b)

Fig. 6. HR-SEM micrograph of the crater surface of Fig. 5. Fig. (a) shows an enlarged image of the position B, and (b) shows that of other position.

observed using a digital hi-scope (Hirox Co. Ltd., KH-2400), a scanning electron microscope (SEM; Jeol, JSM-6300) and a high-resolution scanning electron microscope (HR-SEM; Topcon, ABT-150F).

3. RESULTS AND DISCUSSION

3.1 Without magnetic filed (random-walk arc)

Fig. 3 shows the overall view of the crater that was created by the cathode spot of the arc without magnetic field, taken by the digital hi-scope. The cathode spot motion is roughly overlapped, traced from the video recording. The cathode spot moved randomly on the surface. Arrow A shows the crater where the arc might be extinguished. In this crater, numerous nanotubes were observed, as shown in Fig. 4 (a). However, at other position of the cathode spot crater, only globules with ripples on the surface, but no nanotubes, were observed, as shown in Fig. 4 (b).

3.2 With magnetic field (running arc)

In order to specify the position where the arc was extinguished, the magnetic field was applied on the cathode surface, as shown in Fig. 1. The overall image of the cathode spot crater is shown in Fig. 5. The trace of the cathode spot crater was almost straight, and moved to reverse direction against the direction expected from Laurentzian rule [9]. The arc was extinguished at the bottom position, arrowed by B. Numerous nanotubes were again observed only here, as shown in Fig. 6 (a). The typical image of the surface of other crater is shown in Fig. 6 (b). This morphology is just same as the image of Fig. 4 (b).

3.3 Possible nanotube growth process

From above two experiments, obvious fact is that in the cathodic vacuum arc, the nanotubes stay on the surface of cathode spot crater where the arc has been extinguished. This fact brings two different processes on nanotube growth, which can be considered as follows.

First model of the process mechanism is that when the arc was extinguished, the ions in the potential hump region are attracted to the cathode surface and those ions form nanotubes, as shown in Fig. 7 (a). Therefore, the nanotubes were observed only at the position where the arc is extinguished. However, this model is not consistent with the fact that the nanotubes can be observed on the surface of macrodroplets, which are emitted during the arc burning [6].

Second model is that the nanotubes are generated during the creation of new cathode spot site, as shown in Fig 7 (b). When the cathode spot is fully developed, the cathode spot destroys the nanotubes by its high temperature and/or emits the macrodroplets with nanotubes

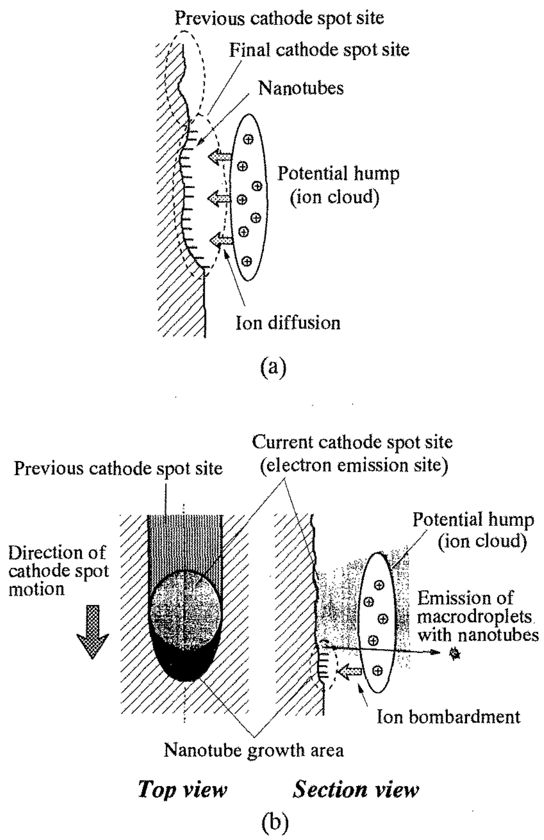


Fig. 7. Possible nanotube-growth processes. Fig. (a) is the model that nanotubes form during the arc-quenching period. Fig. (b) shows the model that nanotubes form during the creation of new cathode spot site.

by its explosive attribute. Thus the nanotubes are mostly observed at final site of the arc. However, this model involves a difficulty to explain the fact that some nanotubes can be observed outside the cathode spot crater of the final position, but not outside the crater of other crater position.

4. CONCLUSIONS

In cathodic vacuum arc using graphite cathode, numerous carbon nanotubes (multi-walled) were observed at the cathode spot crater where the arc was extinguished, for both arcs with and without magnetic field, namely, random-walk arc and running arc. Two possible process models on nanotube growth in cathodic arc were presented. However, both models cannot explain all phenomena. Further investigation is definitely required base on cathodic physics.

ACKNOWLEDGEMENT

The Authors would like to thank Professor Takayoshi Kubono of Shizuoka University for the use of the digital hi-scope. This work was supported in part by Futaba Electronics Memorial Foundation, Japan.

REFERENCES

[1] S. Iijima: *Nature*, **354**, 56-58 (1991).
[2] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund: Science of Fullerene and Carbon Nanotubes, Academic Press (1996).
[3] T. W. Ebbesen, ed.: Carbon nanotubes: Preparation and Properties, CRC Press (1997).
[4] H. Takikawa, O. Kusano, and T. Sakakibara: *J. Phys. D: Appl. Phys.*, **32**, 2433-2437 (1999).
[5] H. Takikawa, M. Yatsuki, O. Kusano, and T. Sakakibara: *Trans. IEE of Japan*, **119-A**, 1156-1157 (1999).
[6] H. Takikawa, M. Yatsuki, and T. Sakakibara: *J. Phys. D: Appl. Phys.*, in print.
[7] J. E. Daalder: *J. Phys. D: Appl. Phys.*, **11**, 1667-1682 (1978).
[8] P. J. Martin, D. R. Mckenzie, R. P. Netterfield, P. Swift, S. W. Filipczuk, K. H. Müller, and B. James: *Thin Solid Films*, **153**, 91-102 (1997).
[9] R. Miyano, H. Takikawa, and T. Sakakibara: "Retrograde motion velocity of graphite cathode spot in vacuum arc deposition apparatus", *Trans. IEE of Japan*, **114-A**, 117-122 (1994) (in Japanese).

(Received December 17, 1999; Accepted March 30, 2000)