Production of Carbon Nanotubes by an Underwater Arc Discharge Method Using a Metal Cathode

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Carbon nanotubes (CNTs) are produced by an arc discharge method, using carbon for both electrodes along with a metal catalyst for the cathode. In this study, we conducted experiments using four kinds of metals (iron, copper, manganin, and nickel) for the cathode and investigated the difference in product and production yield due to the differences in the metals. The greatest quantity of high quality CNTs was produced with nickel as the metal catalyst, with some CNTs as large as 10 microns. Iron produced almost no CNTs, copper produced linear CNTs, and manganin produced a small quantity of very short CNTs. [DOI: 10.1380/ejssnt.2018.343]

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I. INTRODUCTION

Carbon nanotubes (CNTs) are new allotropes of carbon that were discovered by Dr. Sumio Iijima in 1991 [1]. CNTs have superior properties to most other similar materials. For example, the tensile strength is approximately 100 times that of steel, the heat conduction is approximately 10 times that of copper, and the electrical conductivity is approximately 1000 times that of copper. CNTs are expected to have potential applications in a great variety of fields. They are 0.4–5.0 nm in diameter and are created when uniform graphite planes are rolled into tubular shapes after carbon combustion and redeposition processes.

They have a variety of advantages such as lightness, flexibility, high strength, and high conductivity, due to the manner in which the graphite sheets, which have carbon atoms arranged in a hexagon pattern, are wound and overlapped. Consequently, they are expected to have applications not only in biotechnology, but also as next-generation electrode materials [2–5].

In general, CNTs can be synthesized by any of the following techniques: the arc discharge method [6–12], laser-ablation method [13–17], or chemical vapor deposition (CVD) method [18–26]. The arc discharge releases electrons from the carbon in the cathode which collide with carbon on the anode, and the carbon on the anode tip becomes extremely hot and vaporizes. High quality linear CNTs are produced when these carbon atoms recombine. However, the disadvantage of the arc discharge method is that the device configuration for arc discharge in a vacuum is complicated and costly [27].

Therefore, underwater (or liquid) arc discharge has been proposed as a method of synthesizing low cost CNTs (or carbon nanomaterials) using a simple equipment setup, without the need for a vacuum apparatus [28–37]. Unfortunately, there are some disadvantages associated with the underwater arc discharge method. Compared to the vacuum method, the discharge environment, including the discharge intensity and sustainability of the arc discharge, is not suitable for efficient large-scale production of CNTs.

An investigation was performed to ascertain the possibility of synthesizing CNTs using metals as cathodes, in addition to using four types of metals with lower resistances than carbon electrodes as the cathodes to increase the strength and sustainability of the arc discharge under water.

II. EXPERIMENTAL

Figure 1 shows a schematic of the experimental setup. For the arc discharge environment, a 500 mL beaker was filled with 300 mL of distilled water. A regulated DC power supply (PDS20-36, Kenwood TMI Corp.) was used as the direct current power source for the arc discharge.

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FIG. 1. Schematic of the experimental setup. (a) Arc discharge using metal as cathode.
For the arc discharge anodes, carbon rods C ($\phi 4\ mm$ electrolyzer electrodes, Narika Co.) were used. For the cathodes, four types of metal electrodes were used; iron (FE-222624 $\phi 8.0\ mm \times 500\ mm$, 99.5%, manufactured by Nilaco Co.), copper (CU-112624 $\phi 8.0\ mm \times 500\ mm$, 99.9%), manganin Cu-Mn-Ni (661624 $\phi 8.0\ mm \times 500\ mm$, manufactured by Nilaco Co.), and nickel (NI-312624 $\phi 8.0\ mm \times 500\ mm$, 99+%, manufactured by Nilaco Co.). The composition of the manganin was 86% copper, 12% manganese, and 2% nickel.

Carbon and nickel exhibited resistance values of $1.68 \times 10^{-8}\ \Omega\ m$ and $6.99 \times 10^{-8}\ \Omega\ m$, respectively. The resistance of manganin, a composite of copper and nickel, was $4.82 \times 10^{-7}\ \Omega\ m$, which is higher than that of both copper and nickel alone. The resistance of iron was $1.00 \times 10^{-5}\ \Omega\ m$. On the other hand, the resistance of carbon was $1.64 \times 10^{-5}\ \Omega\ m$, a value one or two orders higher than those of the above reported metals.

To separate CNT samples after arc discharge, an ultrasonic separation device (FU-2H manufactured by TGK) was used. For evaluation of CNT samples, a transmission electron microscope (H-9500 manufactured by Hitachi High-Technologies Co.) was used.

The following steps were used in the underwater arc discharge tests:

1. We connected insulated cords to the anode and cathode terminals of the regulated DC power supply and used alligator clips to hold the carbon rod to the anode end of the cable and the metal rod to the cathode end.

2. Using a current of 20 A and voltage of 20 V, we produced an arc discharge for 30 min inside a beaker that was filled with 300 mL of distilled water. During this step, if the electrodes got too close to each other, electric current passed between them and the discharge stopped. We tried, to the extent possible, to sustain discharge by maintaining a fixed distance between electrodes to prevent shorting out, as shown in Fig. 1(a).

3. After discharge, we used an ultrasonic separator for 15 min to separate the samples that were produced inside the beaker.

4. We collected the samples with a dropper from inside the beaker after separation and observed them using transmission electron microscopy (TEM Hitachi H-9500).

III. RESULTS AND DISCUSSION

A. Observation of products using an iron cathode

When iron was used as a cathode, the intensity of the arc discharge was weak, it shorted many times, and the discharge was very difficult to sustain. As a result, evaporation from arc discharge could not be seen on either electrode, and only a trace amount of product was produced. When we observed the product using TEM, we found almost no CNTs.

As shown in Fig. 2(a), most of the observed products were iron particles. A very small amount of CNTs were observed, however, they were covered with iron particles.

As shown in Fig. 2(b), a membranous substance was often observed. Since carbon and iron were the only sample materials used in the experiment, we believe that vaporized carbon is present in Fig. 2(b). It is likely, however, that the carbon did not successfully grow into CNTs.

B. Observation of products using a manganin (Cu-Mn-Ni) cathode

When manganin was used for the cathode, an intense arc discharge was sustained somewhat longer than when iron was used. However, the arc discharge was weak in intensity, and it was very difficult to maintain the electrodes at high temperatures. Thus, there was only a trace amount of vaporization from the arc discharge on both electrodes. After discharge, when the product was observed using TEM, we found almost no CNTs. As shown in Fig. 3(a), a black substance was mostly observed. We believe that the CNT is inside the square in Fig. 3(b).

C. Observation of products using a copper cathode

When copper was used as the cathode, a high intensity arc discharge could be sustained for a long time compared to that produced from iron or manganin. After the arc discharge, the copper rod on the cathode electrode was vaporized and greatly shaved down in addition to the carbon rod on the anode electrode.
FIG. 4. TEM images of products when copper was used as cathode.

The copper electrode vaporized at the same time as the arc discharge. As shown in Fig. 4(a), a relatively large amount of CNTs were produced. Fig. 4(b), many CNTs were 1–5 μm in length with a long, straight, rod-like morphology.

D. Observation of products using a nickel cathode

When nickel was used as the cathode, a greater amount of CNTs were produced compared to iron, manganin, and copper. The arc discharge was intense enough to shoot sparks, and it was easy to sustain for a long period of time. During the arc discharge, the carbon rod turned red. When the discharge continued, sparks scattered to a limited extent and, afterwards, enough heat was generated to ignite it. After discharge, the cathode nickel rod had barely vaporized. However, during the 30 min of the experiment, the anode carbon rod largely vaporized and was reduced almost to the point of being entirely shaved down.

The CNTs had grown in random directions, but a large quantity was produced, and they were linear in shape as shown in Fig. 5(a). As shown in Fig. 5(b), many were between 1 μm and 5 μm in length. The longest observed CNT was 10 μm. Also, we observed almost no vaporized metal. The greatest amount of CNTs with stable shapes were produced using a nickel cathode.

E. Comparison of production quantity of the four metal cathodes

As mentioned above, when arc discharge was carried out using four types of metals as cathodes, we observed differences in the amount of CNTs produced depending on the type of metal. Also, a qualitative assessment of arc discharge excellence (discharge sustainability and intensity) when metals were used as cathodes showed that both nickel and copper had excellent discharge sustainability and intensity.

The amount of CNTs produced and their shape and length when each of the four types of metal was used for arc discharge, Nickel produced the greatest amount of CNTs, followed by copper and manganin. Both nickel and copper produced well-shaped CNTs. When nickel was used as the cathode, particularly long CNTs were produced.

Even though nickel grew CNTs in random directions, they were linear in shape, and we observed some that were 10 μm in length. Furthermore, almost no metal evaporation was observed as cathodes.

Additionally, the quantity of the metal particles contained in CNTs. Very few metals were included in the product synthesized with the nickel cathode.

Copper produced CNTs that were 1–5 μm in length and linear in shape, the same as those produced by nickel. However, a certain amount of vaporized metal was found in the product. Manganin produced a small amount of extremely short CNTs. Moreover, the large amount of vaporized metal poses a big problem for later purification.

On the other hand, a large quantity of metal was contained in the product synthesized with the iron cathode. Therefore, a purification process for removing the metal is required. Also, Iron only produced something resembling carbon that had not succeeded in growing into CNTs.

IV. CONCLUSIONS

The purpose of this study was to produce CNTs with an underwater arc discharge method using metals as the cathode material, focusing on the changes in product and production quantity obtained by changing the type of metal. We performed underwater arc discharge using four types of metals: iron, copper, manganin, and nickel.

Iron group metals that have high catalytic graphitization are often used as metal catalysts for the arc discharge method. In this experiment as well, the greatest quantity of CNTs was produced when nickel was used as a cathode. Compared to iron and cobalt, another iron group metal, nickel grows graphite in a specific direction aligned with the crystal direction and possesses properties that cause CNTs to form easily [9]. Temperature and sustainability of the discharge are important to the arc discharge method. We believe that nickel, with its high conductivity, is capable of producing CNTs with sustained discharge and maintenance of high temperatures.

Iron, which is in the same iron group as nickel, produced the smallest amount of CNTs. Iron tends to form a eutectic mixture with carbon [10]. We believe that when carbon reaches the temperature that exceeds the temperature of the eutectic mixture with iron and vaporizes on its own, the energy sufficient for forming CNTs no longer exists.
Besides nickel, copper produced the next largest amount of CNTs. Like iron, copper is a metal with a tendency to form a eutectic mixture with carbon, but its melting point is lower than iron. Therefore, we believe that copper and carbon are sufficiently active to exceed the temperature of the eutectic mixture and form CNTs. Manganin is an alloy whose principal component is copper. Unlike copper, it produced few CNTs and many lumps of metal were observed.

Therefore, the effect of the metal purity on CNT formation is an issue to be addressed in the future. Also, the production quantity as a function of voltage, current, and/or length of discharge time, along with discharge environment, should also be investigated in the future.

Additionally, the size and yield of the CNTs must be investigated further using measurements such as X-ray diffraction, Raman spectroscopy, and EDX to perform compositional analysis of the CNTs produced by using the above metal cathodes.