THE CRYSTALIZATION OF CARBON NANOTUBES IN LIQUID HELIUM

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The arc in liquid method has been developed as a cost-effective technique to fabricate various kinds of carbon nanomaterials. In liquid nitrogen, especially high-quality multi-walled carbon nanotubes were observed. So, our research aims at creating carbon nanomaterials using contact arc method in liquid helium. For this research, a special evaporation cryostat, which has moving parts at low temperature part, is prepared. Experiments in liquid helium were carried out at current density 10kA/cm^2 and 12kA/cm^2, based on the results of discharged experiments in liquid nitrogen. The results of these experiments, some fibrous carbon nanomaterilas could be obtained at current density 10kA/cm^2. Using TEM Imaging, it turn out that these clusters were multi-walled carbon nano-tubes. Unfortunately, formation efficiency and plasticity are not so good.

This is the first observation of creating carbon nanotubes in liquid helium.

Keywords: Low temperature liquid, CNT, Contact arc discharge

1. Introduction

In the past few years, researches on carbon nano-tubes have been developed remarkably [1]-[4]. Among those, researches on the characteristics of carbon nanotube (CNT) have been done, so that the electronic conditions and electrical characteristics have been cleared [5]. As effective production method to synthesize nanotube stably and abundantly, contact arc method, laser ablation method, and chemical vapor deposition method have been proposed. The disadvantage of these methods, however, is to require expensive machinery. Recently, as simplified carbon arc nanotube synthesis method, it has been demonstrated that carbon nanomaterials can be synthesized by arc discharge generated in liquid water [6] or in liquid nitrogen [7]. Not only this method is easy to operate but also it allows to produce high-quality multi-walled carbon nanotubes at high production rates [7] and to produce some new type of nanomaterials (nanoonion) [6]. Here, Shigematsu et al. shows that in low temperature liquid carbon atoms emitted by discharge are cooled down quickly and start to combine with some amount of energy, it is possible to create carbon nano materials with basic structures [8], [9]. Then, in order to challenge to find some new carbon nanomaterials and to create high-quality carbon nanomaterials, the aim of this research is to investigate the effectiveness and possibility of the production of carbon nanomaterials using arc discharge in low temperature liquid, such as liquid helium. As the pre-stage experiment, so as to find out the creation condition, discharged experiments were carried out in liquid nitrogen.

2. Experimental Setup

In our present experiment, contact arc method is adopted, and original instruments are designed and produced. Fig. 1 shows the outline of our experimental system. The target carbon rod is set in low temperature liquid and it is high charged by an outside electric source. Then, the charged carbon rod can be controlled its discharge period by electromagnetic coil at room temperature. The process of creation is observed through investigating combine spectrum of carbon materials. An ICCD camera (HAMAMATSU C5909) for analyzing spectrum is set at room temperature.

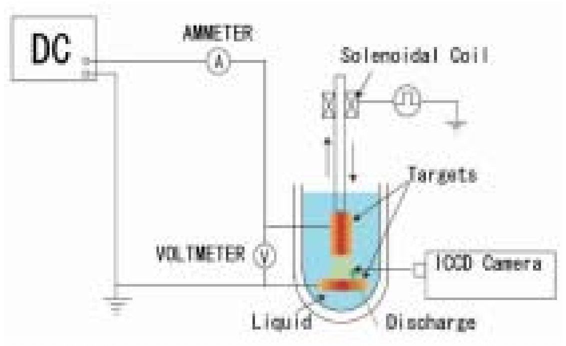

Fig.1 Schematic diagram of contact arc method

Fig. 2 shows our experimental instruments. This instrument is vacuum-jacketed structure, and has an

author's e-mail:shige@post.cc.sasebo.ac.jp evaporation cryostat, which consists of liquid nitrogen dower and liquid helium dower in order to prevent evaporation of liquid. So as to remove experimental cells easily, quick coupling method is utilized for the instrument's top plate. Because most of arc energy is absorbed by the liquid and it causes extraordinary evaporation, the instrument has a leak valve of 10 lit./sec as a solution.

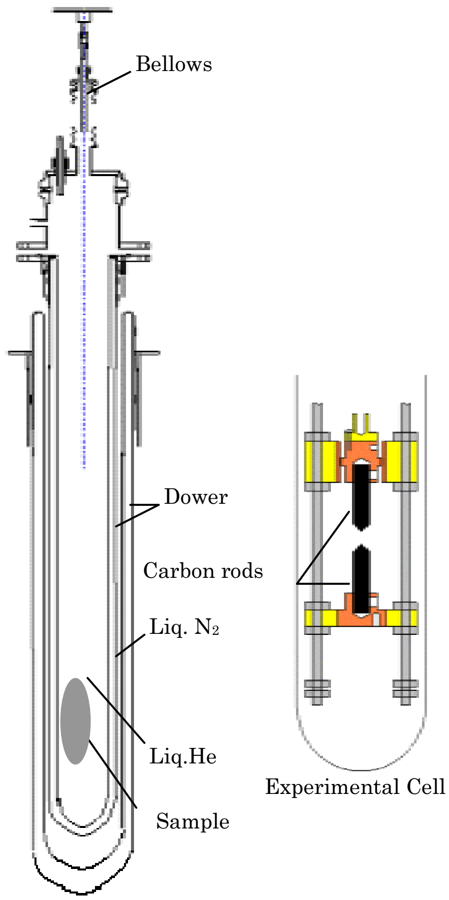

Fig.2 Our original experimental instrument and experimental cell for contact arc method in liquid experimental instrument.

The dielectric breakdown voltage in liquid helium is approximately 20kV at 1mm [10], and it discharges 20 more percent [11]. That's why, for contact arc method, it is necessary to let carbon rod electrodes approach carefully. Considering this, a system which allows electrode to move slowly is prepared using bellows and isolators (see Fig.2).

An experimental cell used in contact arc method is shown in Fig.3. The upper carbon rod is made to move up and down. Two carbon rod electrodes, which are purchased from Nilaco Coro., Japan: 99.99% purity, 10mm diameter and 30mm long) are perpendicularly placed in liquid helium.

As for the confirmation of product after arc experiment, SEM and TEM observations are carried out analyzing the collector located at the lower part of experimental cell.

3. Experimental Results

3-1. Experiment in liquid nitrogen

The experiments were carried out at current density $8kA/cm^2$, $10kA/cm^2$, $12kA/cm^2$ and $14kA/cm^2$. The time of arc was 1 second. Every time arc was done, the resultant product was collected. Fig. 3 shows the result of spectroscopic analysis of discharged experiments in liquid nitrogen. In Fig. 3, when current density is $8kA/cm^2$, every experiment shows almost the same result. As for spectroscopic analysis, all lights in discharged experiments are integrated. Because C2 swan band can be observed, it turns out that carbon ions emitted by discharge combines and form carbon nano clusters. In Fig. 4 to Fig. 5, each of SEM pictures is shown. When current density was less than $8kA/cm^2$, ample carbon nanomaterials were not obtained. On the other hand, when current density was $10kA/cm^2$ and $12kA/cm^2$, many fibrous carbons were obtained. Then, when current density was $14kA/cm^2$, the production rate seemed to decrease.

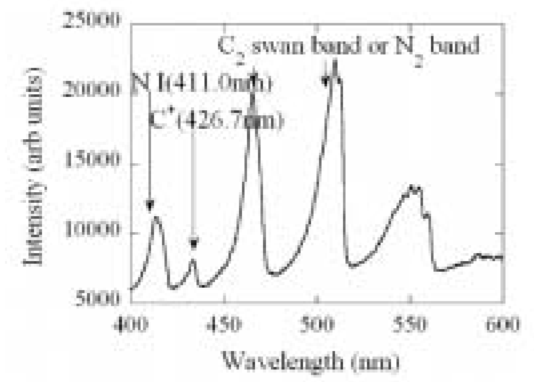

Fig.3 The result of spectroscopic analysis of discharge experiments in liquid nitrogen. Evaporations of carbon and C_2 swan band of clusters are observed.

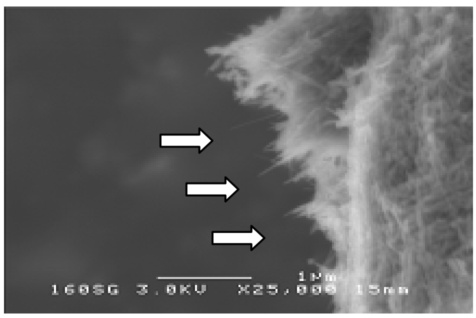

Fig.4 SEM image of arc in liquid nitrogen, current density $12kA/cm^2$. Many fibrous carbons were obtained. Same results at the current density $12kA/cm^2$. Arrow heads in Figures point out fibers.

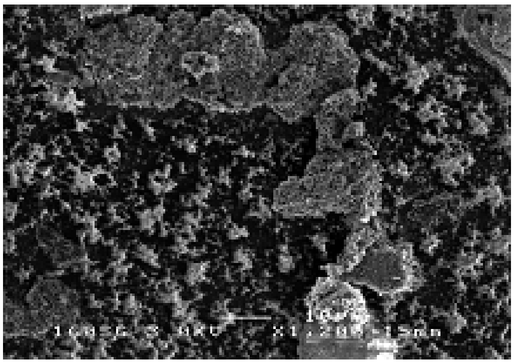

Fig.5 SEM image of arc in liquid nitrogen, current density 14kA/cm^2.
Carbon nanomaterials were not obtained.

At low electric density (8kA/cm^2), the small amount of carbon evaporations can be one of the reasons why clusters were not observed. On the other hand, at high electric density (14kA/cm^2), most of energy caused by discharge is used for the brittle fracture at low temperature region and it prevents carbon from evaporating. Arrow heads in Figure 4 point out fibers, which can be carbon materials. In Figures, the foundation, on which carbon fibers are planted, is thought to be some mixture of broken graphite pieces caused by arc.

3-2. Experiment in liquid helium

Experiments in liquid helium were carried out at current density 10kA/cm^2 and 12kA/cm^2, based on the results of discharged experiments in liquid nitrogen. Unfortunately, discharge experiment at 12kA/cm^2 was not carried on the crystallized carbon. The cause is not clear. Fig. 6 to Fig. 7 show spectroscopic analysis and SEM images of contact arc experiments in liquid helium under the condition that a current was 10kA/cm^2.

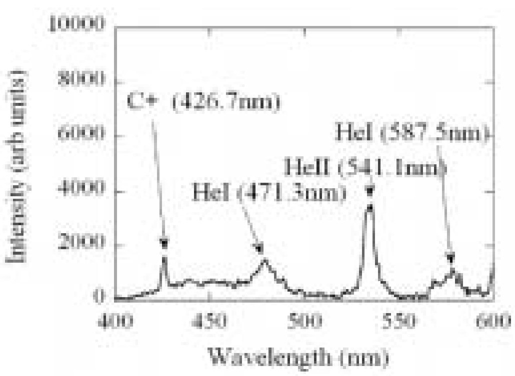

Fig.6 Representative result of spectroscopic analysis in liquid helium

Because the spectrums of carbon ion, HeI, and HeII were observed at the time of this experiment, it is clear that emitted carbon atoms lost their energy due to Ionization loss process. It is also clear that carbons were undoubtedly

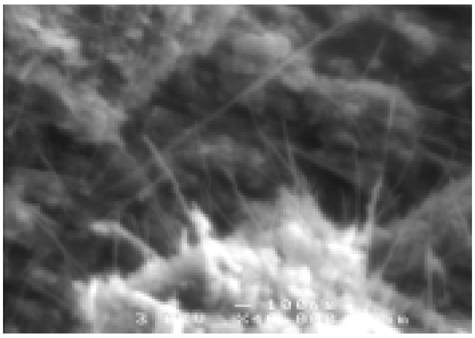

Fig.7 SEM images of the nano-material products using contact arc experiment in liquid helium. Ample needle-shape carbon nanomaterials were observed. Current density is 10kA/cm^2.

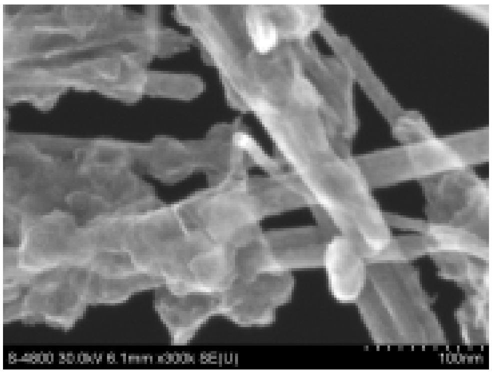

Fig.8 FESEM images of the nano-material products using contact arc experiment in liquid helium.

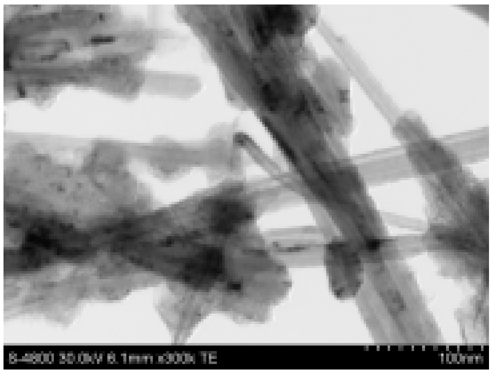

Fig.9 TEM images of the nano-material products using contact arc experiment in liquid helium.

emitted into liquid by discharge. However, C2 swan band was not observed. This shows that carbon clusters were little and spectrums were not strong enough for the ICCD camera to observe them. Fig.7 and Fig.8 show the result of SEM observation of discharge experiment in liquid helium. In them, needle-shape carbon clusters can be observed. Their diameters range approximately from 10nm to 30nm and some of them are longer than 1μm. Then, Fig.9 shows the TEM images of Fig.8. The images show that needle-shape carbon clusters are tube and have multi-walls.

Though the difference of diameter is related to the number of walls, it is not possible to find out how may walls these clusters have because of the low sensitivity of TEM imaging. Though its inside diameter is 2～4nm, its outside diameter is approximately 20nm. This shows that it has multi-walls.

4. Conclusions

In this research, discharge experiments have been carried out in low temperature liquid. In liquid nitrogen, fibrous carbon nanomaterials were obtained at current density 10kA/cm^2 and 12kA/cm^2. As for arc in liquid helium method at current density 10kA/cm^2, carbon nanomaterials could be obtained for the first time. The TEM imaging shows that they were multi-wall carbon nanotubes. It also shows that the top has a ball-shape as if fullerene were attached. Unfortunately, it seems that formation efficiency has been weak, and also reproduction rate has been not so good. The following is thought about as the reason. 1. By arc in low temperature liquid, generation conditions (current density, electric discharge time etc) is severe. 2. Evaporation of helium gas after discharge experiment is an intense phenomenon. Therefore the generated materials may run away with evaporation gas.

5. References

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