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Experiments of Creating Carbon Nanomaterials in Low Temperature Liquid

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In the latest few years, "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-wall carbon nanotubes were observed. So, our research aims at creating carbon nanomaterials using contact arc method in liquid nitrogen and in liquid helium. For this research, a special evaporation cryostat, which has moving parts at low temperature part, is prepared. Experiments in liquid nitrogen were carried out at current density $8kA/cm^2$, $10kA/cm^2$, $12kA/cm^2$ and $14kA/cm^2$. At current density 10 and $12kA/cm^2$ ample fibrous carbon nanomaterilas could be obtained. As for contact arc experiments in liquid helium, however, any carbon nanomaterials were not still obtained at current density $10kA/cm^2$.

Key words: Low temperature liquid, CNT, Contact arc method

1. INTRODUCTION

Since carbon nanotube was discovered by Iijima et al. in 1991[1], basic and applied researches have been actively carried out by numerous researchers[2]-[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]. Under such circumstances, in order to challenge to find some new carbon nanomaterials and to produce 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 nitrogen or liquid helium.

2.ESTIMATE OF CNT CREATION

In this chapter, the discussion is on whether it is possible to create carbon nano -materials in liquid helium and if so, what energy conditions will be at the time of creation and whether it happens in the middle of or after the freezing process.

2-1 Possibility of CNT creation

Whether carbons combine with others or not depends on the level of their energy. If their energy is higher than necessary activation energy, the combinations occur. On the other hand, if not, the combinations don't occur. Fig.1 shows schematic of CNT creation.

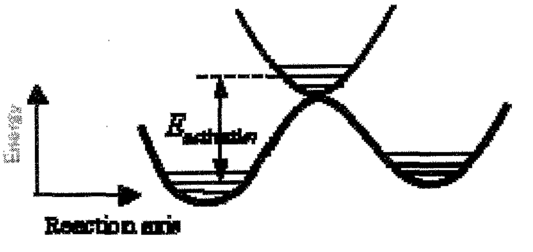


Fig.1 Schematic of carbon nanomatelial creation

Suppose, carbon atoms, which are emitted by discharge in liquid, are the same temperature (T=4.2K) as liquid helium.

Using Arrhenius equation, activation energy at the temperature of liquid helium can be shown as follows.

$$E_{activation} = k_B T^2 \frac{d}{dt}\left(\ln\frac{k}{A}\right)$$

$$k = \frac{k_B T}{h} K$$

Here, k is rate constant, A is frequency factor, and K is the hypothetical constant at the start and transition. As for carbon, these figures can be calculated as follows.

$$100 \quad kJ/mole \leq \frac{k}{A} \leq 500 \quad kJ/mole$$

So, $E_{activation}$ at 4.2K can be obtained as follows.

$$2.4K \leq E_{activation}(T = 4.2K) \leq 11.8K$$

These results shows that carbon atoms with 4.2K energy can create clusters and it is meaningful to carry out experiments at the temperature.

2-2.Estimate of energy loss process in liquid helium

Then, the discussion is on how carbon atoms, which are emitted with high velocity by discharge, lose their energy and under what energy condition they combine with each other.

It can be thought that, in liquid helium, carbon atoms lose their energy in the following two steps till they have the temperature of 4.2K.

1: Ionization loss process (from emission to 24.6eV.)

2: Elastic scattering (from 24.6eV to 4.2K)

While, the possibility whether carbon atoms combine with each other or not can be investigated through observing their mean free paths.

Considering these, the discussion can be carried out to find out in which energy condition carbon atoms combine with each other.

2-2-1. Ionization loss process

It is reported that, by arc discharge, the ratio of the energy which is given to carbon and to liquid helium is about 2 to 8[8]. After the emission, the velocity is high. So, carbon atoms can be thought to lose their energy because of Ionization loss with relativistic effect. The process can be shown as follows as Bethe-Bloch formula.

$$-\frac{dE}{dx} = \frac{4\pi z^2 e^4}{mV^2} nZ \left[\ln\frac{2m\,V^2}{I} - \ln\left\{1-\left(\frac{V}{c}\right)^2\right\} - \left(\frac{V}{c}\right)^2 \right]$$

Here, e, ze, V, m and Z are electric charge, charge of carbon atom, velocity, mass of electron and atomic number respectively. And n is the number of atoms per $1cm^3$ and I is atoms' average ionization voltage. In this process, carbon atoms lose it energy till 24.6eV, which is Ionization potential of helium atoms. Thus, transit length is approximately 40 μ m.

2-2-2. Elastic scattering process

The next energy loss is elastic scattering in the case that an atom is considered as a hard core.

$$-\frac{dE}{dx} = \left(\frac{N_A\rho}{4}\right)^{\frac{1}{3}} \left[\left(1-\frac{m_{He}}{m_c}\right)\left(1+\frac{m_{He}}{m_c}\right)^{-1} \right]^2$$

Here, N_A, ρ, m_c, m_{He} are Avogadro constant, density of helium, the mass of carbon and the mass of helium respectively. Using this formula, as for elastic scattering, transit length can be calculated 0.6 μ m.

Thus, when carbon atoms emitted by discharge move approximately 41 μ m, they have 4.2K, which is the same amount of energy as liquid has.

2-2-3. Estimate of mean free path

According to our experiment, 0.1mmol of carbon atoms is emitted into liquid by one discharge[8]. So, when the volume of carbon atoms is V,

$$\frac{\sqrt[3]{Na \times 10^{-3}}}{V} \sim 200\mu m$$

Considering these calculations, our conclusion is that carbon atoms emitted by discharge lose their energy in the process of interaction with helium atoms, and after carbon atoms become 4.2K energy condition, they combine with each other, resulting in creation of some clusters. Fig.2 shows this process.

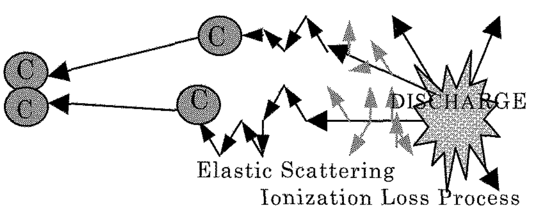


Fig.2 Energy loss images of carbon atoms after discharged in liquid helium

3. EXPERIMENTAL SETUP

Our present experiment adopts contact arc method, and designs and produces necessary instruments. Fig.3 shows the outline of our experimental system. And Fig.4 shows our experimental instruments. This instrument is vacuum-jacketed structure, and has 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 10lit./sec as a solution.

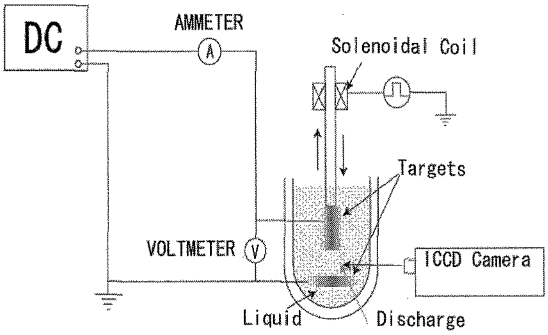
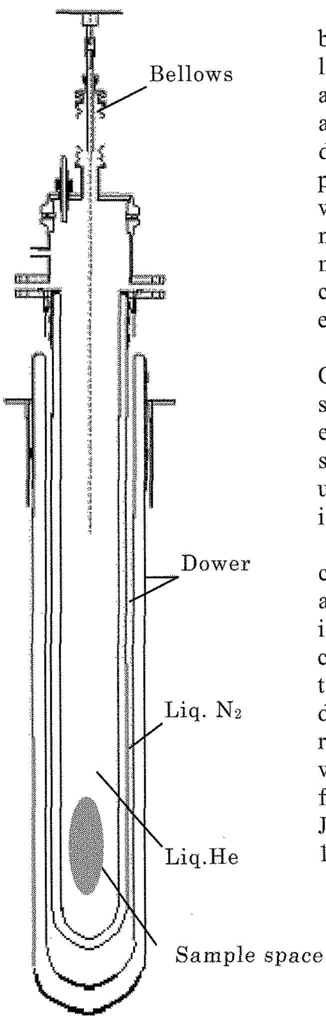


Fig.3 Schematic diagram of contact arc method



The dielectric breakdown voltage in liquid helium is approximately 20kV at 1mm[9], and it discharge 20 more percentage[10]. That's why, for contact arc method, it is necessary to let carbon rod electrodes approach carefully. Considering this, a system which allows electrode move slowly is prepared using bellows and isolator (see Fig.4).

An experimental cell used in contact arc method is shown in Fig.5. 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) were perpendicularly placed in liquid helium.

Fig.4 Our special experimental instrument.

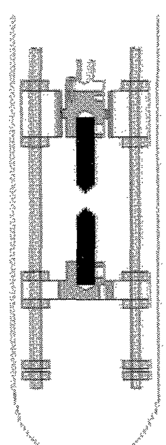


Fig.5 Experimental cell for contact arc method in liquid.

As for the confirmation of product after arc experiment, SEM observation is carried out collecting the collector located at the lower part of experimental cell.

4.EXPERIMENTAL RESULTS

4-1. 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 1second. Every time arc was done, the resultant product was collected. Each of SEM pictures is shown in Fig.6 to Fig.9.

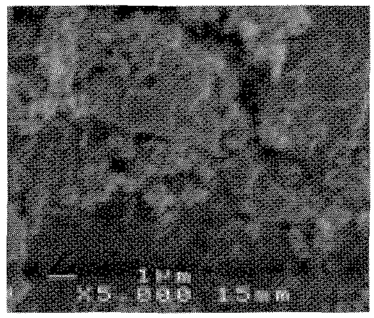


Fig.6 SEM image of arc in liquid nitrogen, current density $8kA/cm^2$. Carbon nanomaterials were not obtained.

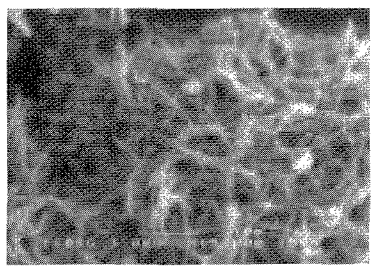


Fig.7 SEM image of arc in liquid nitrogen, current density $10kA/cm^2$. Many fibrous carbons were obtained.

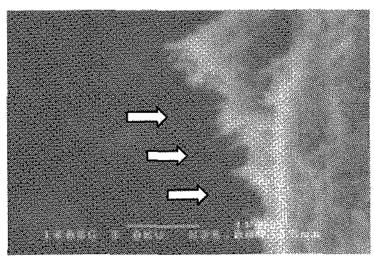


Fig.8 SEM image of arc in liquid nitrogen, current density $12kA/cm^2$. Many fibrous carbons were obtained. Arrow heads in Figures point out fibers

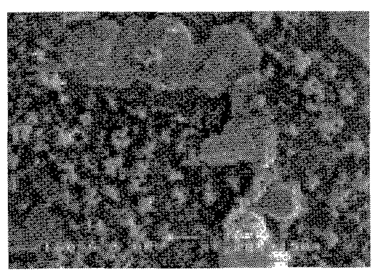


Fig.9 SEM image of arc in liquid nitrogen, current density $14kA/cm^2$. Carbon nanomaterials were not obtained.

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. Arrow heads in Figures 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) .

To confirm these resultant products were carbon materials or not, analysis with energy dispersive X-ray spectroscopy was performed. Then, this analysis proved that resultant products were carbon materials.

4-2. Experiment in liquid helium

Fig.10 and Fig.11 show SEM image of contact arc experiment in liquid helium and spectroscopic analysis under the condition that current density was 10kA/cm^2.

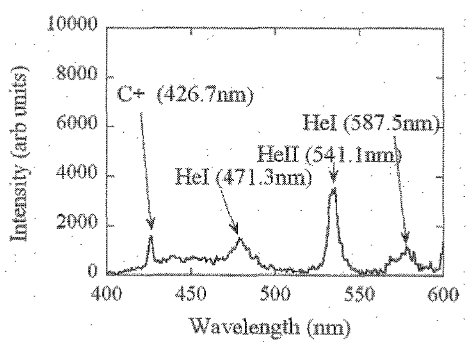


Fig.10 Representative result of spectroscopic analysis in liquid helium

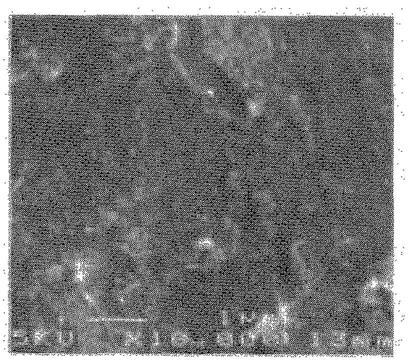


Fig.11 FESEM images of the nano-material products using contact arc experiment in liquid helium. Carbon nanomaterials were not obtained.

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 emitted into liquid by discharge. However, fibrous carbon materials, which were obtained in liquid nitrogen, could not be observed. The possible reasons for this are as follows: (1)Comparing with the case of contact arc experiment in liquid nitrogen, density of carbons was much smaller than that of contact arc experiment in liquid helium. So, resultant carbon clusters were too small to observe. (2)As for discharge in liquid helium and that in liquid nitrogen, each latent heat was different, and the amount of evaporated liquid was 10 times more in discharge experiment in liquid helium than in discharge experiment in liquid nitrogen. This evaporated helium gas might take carbon compositions away from the container. (3)Creating conditions were different between in liquid nitrogen and in liquid helium, so the current density was sifted. These first and second possible reasons have clearly to do with the effectiveness of collecting method. In the following researches, one of our tasks is to improve the performance of our collecting method. At the same time, our future plans are to carry out discharge experiments in liquid helium under various conditions and find out what resultant product can be.

5. CONCLUSIONS

In this research, discharge experiments have 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, however, carbon nanomaterials could not be obtained. In the following experiments, the aims of our researches are to keep carrying out arc in liquid helium experiments with various conditions, and to find effective collecting method for resultant products.

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7. References

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