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Production of fullerenes by high-temperature pulsed arc discharge

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Abstract. We have developed a high-temperature pulsed arc discharge apparatus, which can operate in a buffer gas heated up to 1000 °C, and have succeeded in producing fullerenes for the first time with this method. We have quantitatively analyzed the products, using high-performance liquid chromatography (HPLC), to estimate the concentration of fullerenes in soot. The results show that fullerenes are produced not at room temperature but at much higher temperatures such as 1000 °C for Ar. The concentration of fullerenes C_{70} and higher increases as the pulse width of the discharge increases. In the pulsed arc discharge, the negative electrode is consumed by the sputtering of buffer gas ions.

PACS. 81.05.Tp Fullerenes and related materials; diamonds, graphite – 36.40.Ei Phase transitions in clusters – 82.30.-b Specific chemical reactions; reaction mechanisms

1 Introduction

Fullerenes were originally discovered as magic number species of carbon clusters [1]. However, Boweres and coworkers have found that these carbon clusters are not actually fullerenes; they evolve from carbon clusters to fullerenes by annealing [2, 3]. We have also found that the annealing process is essential for production of fullerenes and other clusters that should have perfect structures [4–8].

So far, resistive heating [9], steady arc discharge [10], and laser furnace methods [11, 12] have been used to macroscopically produce fullerenes. In these methods, carbon is vaporized, aggregated, and subsequently annealed.

The growth mechanism of fullerenes is not yet fully understood. Each production method has merits and drawbacks. For example, the steady arc discharge and the resistive heating methods can control vaporization processes to a certain extent by changing discharge currents and voltages [13, 14], but cannot control the buffer gas temperature. The laser furnace method, on the other hand, can vary annealing processes by changing the buffer gas temperature [11, 12]. The vaporization processes can be varied only through the laser power, since the duration of laser ablation is normally extremely short (~ 10 ns). To obtain quantitative information on the growth mechanisms of fullerenes, we have developed a high-temperature pulsed arc discharge method, which enables us to control arc discharge conditions as well as cooling gas temperatures.

Room-temperature pulsed arc discharge methods have already been applied to produce gas phase clusters, such as metal, sulfur, and carbon clusters [15–20]. The pulsed arc discharge may normally produce relatively small clusters ($n \sim 30$). Mass distribution of the so-produced clusters is almost the same as that of clusters produced by laser vaporization. However, in the pulsed arc discharge, a negative rod is consumed, whereas a positive rod is vaporized in the steady arc discharge [10, 13, 14]. In both arc methods, the cluster distribution is also different, in that small clusters are produced and that C_{60} and C_{70} are not special magic number species in the pulsed arc [20].

In this study, we have developed a high-temperature pulsed arc discharge method in which the pulsed arc operates in high-temperature flowing buffer gas. By using this method, we have succeeded in producing fullerenes for the first time. We have studied the mechanisms of the pulsed arc discharge, and obtained information on the growth mechanism of fullerenes.

2 Experiment

The high-temperature pulsed arc discharge apparatus consisted of a furnace, a quartz tube (ϕ25 mm), electric feed-throughs with insulation quartz tubes, carbon electrodes, a water-cooled trap, and a pulsed HV power supply (Fig. 1). A buffer gas (He, Ar, or Kr) was passed through the quartz tube so that the produced carbon clusters could be annealed. The temperature of the tube was controlled to between 25 °C and 1000 °C by the furnace. The flow and pressure of the buffer gas were regulated to 300 cm^3/s and 500 Torr, respectively. The power supply, which produces pulsed arc discharges between the electrodes, provided

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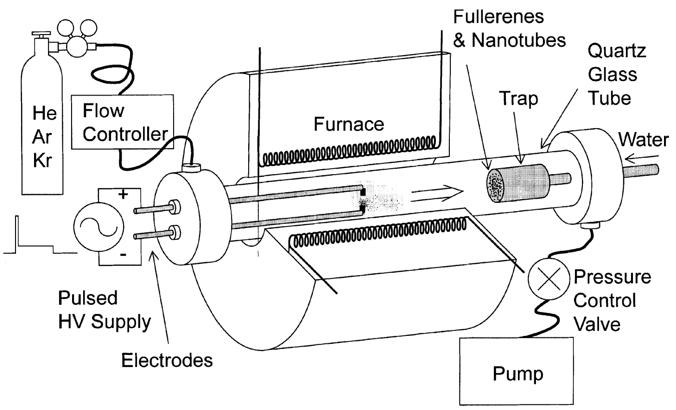

Fig. 1. A schematic diagram of a high-temperature pulsed arc discharge apparatus.

pulsed HV voltages of 1.1 kV, 22 A, and 50 ∼ 3000 μs duration. The repetition rate was normally 3 ∼ 300 Hz with a constant duty factor (1/100). For example, the repetition rate was set to 100 Hz when the duration was 100 μs. The negative electrode was found to be consumed by the pulsed arc discharge. The carbon vapor was condensed and annealed into fullerenes in a high-temperature buffer gas. The fullerenes and other types of carbon particles drifted within the tube by the gas flow and were collected on the water-cooled copper trap.

The trapped soot was extracted by carbon disulfide. Fullerenes were analyzed by high-performance liquid chromatography (HPLC). The HPLC analysis was performed on a Buckyprep column (Nacalai Tesque, 4.6 mm diameter, 250 mm length) with toluene as an eluent. The present HPLC system can detect fullerenes at concentrations as low as 100 ng/ml. The concentration of fullerenes in the soot was estimated by the use of an HPLC peak area at 313 nm. We measured dependencies of fullerene concentration on temperature (25 °C and 1000 °C), HV pulse duration (50 μs to 3 ms), and buffer gas species (He, Ar, and Kr).

3 Results and discussion

In Fig. 2 can be seen HPLC chromatograms of the extracts showing dependencies of peak areas on the temperature and discharge duration time. The HPLC peak intensity is normalized by soot weight and thus corresponds to the concentration of fullerenes in the soot. The results show that C_{60} and C_{70} are not produced at 25 °C but at 1000 °C, and that the concentration increases as the pulse duration increases. Peaks located at 3 min are attributed to the contaminant carbon disulfide.

The absolute concentration of C_{60} in the soot is shown in Fig. 3. The yield (3.54%) of C_{60} at 3 ms duration is comparable to that of the steady arc discharge (5 ∼ 10%) [13, 14]. It can be seen that the production of higher fullerenes such as C_{76}, C_{78}, and C_{84} is much more sensitive to the pulse duration of the discharge (cf. Fig. 2). The C_{60} production in the high-temperature pulsed arc also shows apparent dependence on the buffer gas species. At the duration time of 1 ms, the concentrations of C_{60} in the soot are 0%, 1.54%, and 1.12% in He, Ar, and Kr, respectively. These buffer gas dependencies show that Ar and Kr are much more effective than He for fullerene production.

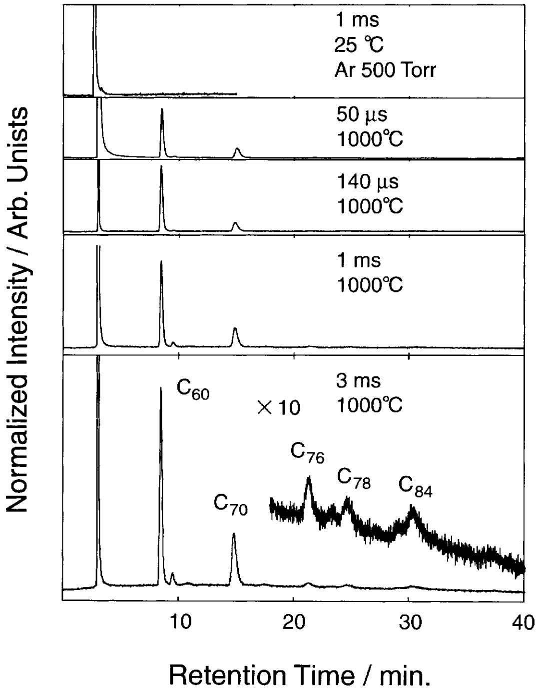

Fig. 2. HPLC chromatograms of CS_2 extracts of the produced soot. Intensities correspond to the concentration in the primary soot.

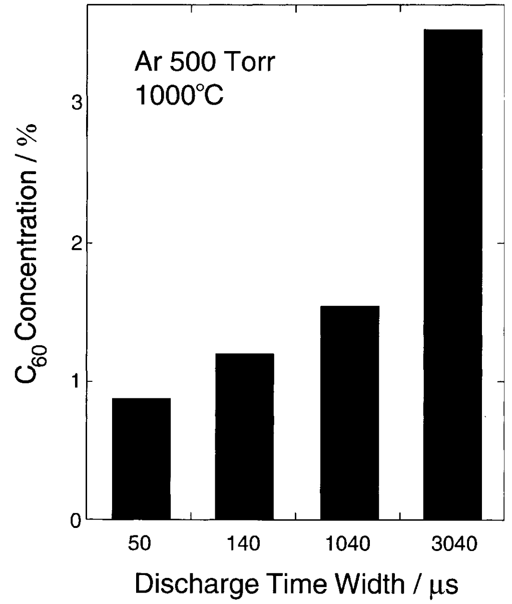

Fig. 3. C_{60} concentration dependencies on temperature and pulse duration time.

The temperature and buffer gas dependencies are similar to those of the laser furnace experiments [11,12] and are different from those of the steady arc discharge experiments [13,14]. The previous laser furnace experiments have shown that there is a threshold at about 800 °C for the production of fullerenes [11,12]. The temperature dependence shows that nascent products of the laser vaporization and of the pulsed arc discharge are not fullerenes; high-temperature thermal annealing is necessary to transform the nascent cluster products to fullerenes.

In apparent contrast to the above conclusion, fullerenes seem to be directly produced in the steady arc discharge with room temperature buffer gas. But in this case, carbon vapors are subjected to enough annealing to produce fullerenes because of the hot buffer gas heated by the steady arc discharge *per sé*.

The annealing mechanism is also supported by the observed vaporization time profile of the rod (Fig. 4). The results show that the vaporization rate decreases as the discharge pulse width increases. The vaporization rate also depends on the buffer gas. The average vaporization rates with 1 ms duration are 11, 109, and 169 μg/s in He, Ar, and Kr respectively. The vaporization rate increases as the atomic mass of the buffer gas increases. This distinct dependence on the buffer gas suggests that the evaporation of the negative electrode occurs not by discharge electrons in the arc plasma because the total current consumed was kept constant.

Based on the production conditions of fullerenes, the observed evaporation rate, and the consumption of the negative electrode, we think the following series of events take place: At first, the power supply provides 1.1 kV high voltages between the electrodes and produces electron discharges. The buffer gas is then ionized by the discharge electrons. The so-produced Ar^+ or He^+ ions are accelerated toward the negative electrodes by the strong electric field between the electrodes. The accelerated ions sputter and vaporize the surface of the negative electrode. The sputter efficiency of Ar and Kr is much greater than that of He, because of the masses and lower ionization potentials of Ar and Kr. During the vaporization, various carbonaceous ions and concomitant electrons are also produced in plasma, which give rise to a decrease in impedance (R) between the electrodes. The impedance decrease brings about a decrease in voltage difference (ΔV) between the electrodes, because ΔV is given by the equation $\Delta\mathrm{V} = R/(R + R_0)$, where R_0 is the output impedance of the pulsed HV pulse power supply (50 Ω). The voltage difference (ΔV) between the electrode decreases from 1.1 kV to about 20 V in about 10 μs. The decrease of the voltage difference results in the rapid decrease of the evaporation rate (Fig. 4) since the kinetic energy of the sputtering ions is determined by the voltage difference. After the rapid decrease of the voltage difference, the pulsed arc reaches a steady state similar to the steady arc discharge with a voltage difference of about 20 V [13,14]. In this quasi-steady arc discharge state, the vaporization rate doesn't change rapidly (Fig. 4).

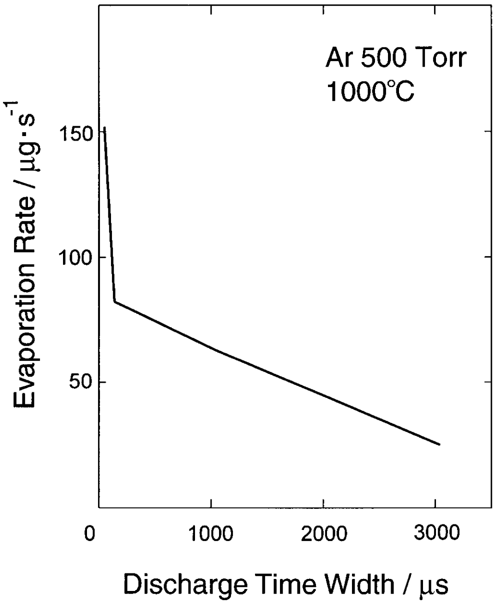

Fig. 4. A vaporization profile of a negative electrode.

The carbon clusters so produced are thermally annealed by the buffer gas and subsequently transform into fullerenes. The annealing process and the production efficiencies of fullerenes are enhanced in longer discharges, because the vapor is heated by the successive discharges. As described above, the discharge processes are separated in two stages: vaporization and successive annealing.

The present pulsed arc experiments have amply demonstrated the importance of the thermal annealing process by the hot buffer gas in the early stage of fullerene formation. The method has a lot of advantages over other production methods. For example, the apparatus is inexpensive, easy to build, and expandable to mass-scale production system. The system can be applied in connection with high vacuum systems, such as time-of-flight mass spectrometers and scanning probe microscopes.

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