Yield of fullerenes generated by contact arc method under He and Ar: dependence on gas pressure

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The yields of toluene-soluble material from carbon soot depend on the buffer gas as well as the pressure. Helium was more effective for yielding fullerenes than argon, and the optimum pressure was 20 Torr, under which a maximum yield of about 13 wt% was obtained. C_{60} showed a maximum abundance at 20 Torr, while C_{70} and higher fullerenes (C_{76} , C_{78} and C_{84}) at a slightly higher pressure between 20 and 50 Torr. Raw soot was also studied by electron microscopy. The pressure dependence of the fullerene yield is discussed in terms of the cooling rate and diffusion of carbon vapor around the evaporation source.

1. Introduction

The fullerenes, C_{60} and C_{70} , were first observed in a mass spectrum of carbon clusters formed by laser ablation of graphite [1], and later discovered in carbon soot prepared by vaporization of graphite with resistive heating under low-pressure helium gas [2,3]. The method to prepare the soot is essentially the same as the so-called gas evaporation technique [4] used to produce small particles of various materials ranging from metals to insulating compounds.

Krätschmer et al. reported in their early paper [2] that the abundance of C_{60} was of the order of 1% of the soot. The estimation was based on the absorption strength in infrared lines. After the discovery that the fullerenes can be extracted from the soot by using an appropriate solvent, benzene or toluene, the yields of fullerenes were measured by weighing the extracts. The soluble material is mostly C_{60} and C_{70} , but it also contains larger fullerenes such as C_{76} , C_{78}

and C_{84} . Taylor et al. [5] reported 8% yield of benzene-soluble material from soot synthesized with resistive heating under Ar between 38 and 75 Torr. Ajie et al. [6] reported a yield of 14% benzene-soluble material from soot prepared with resistive heating under He at 225 Torr. An exceptionally high yield of 25%-35% was also reported later [7]. The reason for this improved yield is not clear, but the authors attributed it to continual optimization of the technique and other factors such as the quality of graphite, optimal He pressure, and the efficiency of extraction in boiling toluene.

An arc discharge between graphite rods is now widely employed to produce raw soot since the arc heating can evaporate graphite efficiently and conveniently. This procedure, called "contact arc" vaporization [8], requires a small gap (less than a few mm) between the two electrodes to be maintained. The yields reported with this method range from 5 to 15 wt% [8-10] comparable to those with resistive heating.

Solvents with higher boiling temperatures such as 1,2,3,5-tetramethylbenzene, quinoline and pyridine

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can extract higher molecular weight fullerenes up to nearly C_{300} from the residue left after toluene extraction [11,12]. A successive extraction with toluene (or benzene) and these solvents have brought about soluble material with yields as high as 44% [11] and 32% [12].

In the present study, the solvent used in the extraction procedure was limited to toluene, and we investigated the effects of buffer gas type (He and Ar) and pressure on the fullerene yield. A study of Yamamoto et al. [13] on the yield of soot prepared under 50-500 Torr He showed that the yield decreased monotonically with the pressure. This pressure dependence is consistent with ours in the same pressure range, but we found a maximum yield at a lower pressure than that employed ordinarily (around 100 Torr). The presence of an optimum pressure for fullerene production, limited to He gas, is also found independently by Achiba et al. [14].

We have also examined the raw soot by transmission electron microscopy to study the pressure dependence of the fullerene yield. It has been found that C_{60} and C_{70} crystallize and form a fcc (face-centered cubic) lattice even in the raw soot when the soot is prepared near the optimum pressure of He.

2. Experimental

The fullerene generator used in the present study is similar to those reported previously [8–10], but two graphite electrodes were held vertically [15]. The evaporator was contained in a water-cooled stainless steel cylinder (30 cm in diameter and 40 cm in height). The chamber was pumped by an oil diffusion pump to a base pressure of 10^{-5} Torr. After the chamber was isolated from the pump, He or Ar was introduced into the chamber up to a desired pressure ranging from 10 to 400 Torr.

A thick graphite rod (13 mm in diameter and 50 mm in length) was press-fitted into a lower carbon holder, which was connected to the positive lead of a power supply. A thin graphite rod (10 mm in diameter and 70–80 mm in length) was screw-fitted to an upper carbon holder. The purity of the graphite electrodes was 99.995% (H-grade, EGF-264 of Nihon Carbon), and the density was 1.85 g/cm³. The upper graphite electrode was movable downwards

and upwards for adjustment of a gap between the electrodes.

The power supply used to generate the arc was an ordinary welding power supply (Hitachi super ADR-300) operated in the direct current mode at a range of 220–250 A. The positively biased electrode was consumed by evaporation. The spacing of the arc gap was maintained to be a few mm during the operation.

Carbon soot deposited on the ceiling and the side wall of the chamber was collected by gentle scratching with a brush. The soot deposited on the baseplate of the chamber was not used for the present study because graphite fragments splashed during the arc discharge were scattered on the bottom.

The raw soot obtained was subjected to soxhlet extraction by refluxing toluene. The extraction was continued until the brown color of the solution was completely faded. The solution was dried in vacuum, and a mixture of fullerenes was obtained. The ¹H NMR spectra of these fullerene mixtures suggested that only negligible amounts of hydrocarbon impurities were present.

The mixture of fullerenes was fractionated by HPLC (stationary phase, Develosil ODS-5, 4.6 $mm \times 25$ cm) with a *n*-hexane mobile phase. The extracts were injected as a cyclohexane solution [16]. The chromatogram was monitored by a UV detector $(\lambda = 350 \text{ nm})$. A typical chromatogram is shown in fig. 1. Besides dominant C₆₀ and C₇₀ peaks, three peaks (HF1, HF2 and HF3) due to higher fullerenes are observed. Mass and UV spectra from these fractions showed that C_{76} , C_{78} and C_{84} were the main constituents of HF1, HF2 and HF3, respectively. However, at present the constituents of HF1 to HF3 are not as well defined as C₆₀ and C₇₀, and the accuracy of the intensity is not as high as the dominant fullerenes. For this reason, the abundances of HF1, HF2 and HF3 cannot be presented individually. Instead, their total abundance is presented as that of higher fullerenes. The ratios of the peak areas in the chromatogram were used to derive the relative abundances of (1) C_{60} , (2) C_{70} and (3) higher fullerenes composed of C₇₆, C₇₈ and C₈₄.

The optical absorbance of C_{70} at $\lambda = 350$ nm is slightly larger (1.07 times) than that of C_{60} [17]. We have not made this minor correction because this correction is smaller than the scatter of data points and does not modify the general profiles of pressure



Fig. 1. HPLC profile of the carbon material extracted from the soot. The peaks marked HF1, HF2 and HF3 are due to the higher fullerenes C_{76} , C_{78} and C_{84} , respectively.

dependences. The actual abundance cannot be derived for the higher fullerenes, because no absolute absorbance is known.

A specimen for electron microscopy was prepared by direct deposition of raw soot on copper grids covered with a perforated (holey) carbon film. The copper grids were placed near the upper electrode by using a soot collection device [18] and were exposed to smoke of carbon soot emanating from the arc gap.

3. Results and discussion

3.1. Extraction and HPCL

Fig. 2 shows the yields of toluene-soluble material plotted as a function of gas pressure for He and Ar. Firstly, He gas is found to be more efficient to produce fullerene-rich soot than Ar gas. Secondly, the pressure dependences of the fullerene yield are clearly observed for these buffer gases. The dependences for He and Ar are similar; the yield has a maximum value (about 13 wt% for He, 6 wt% for Ar) at 20 Torr. Al-



Fig. 2. Yields of toluene-soluble material plotted against the gas pressure for He (\bigcirc) and Ar (\triangle) . Each mark represents an independent production lot.

though most of the fullerene productions have been performed at about 100 Torr He, no singularity such as a yield maximum is found at 100 Torr.

The abundances of the three fractions, $(1) C_{60}$, (2) C_{70} and (3) the higher fullerenes, also vary with the gas pressure as shown in fig. 3a for He gas. Since the soot prepared under Ar gas exhibited a similar trend. we restrict our description to the case of He gas. As is well known, C_{60} is the predominating fullerene in a toluene extract. Its abundance in raw soot has a maximum at 20 Torr and decreases at higher pressures. C₇₀ also shows a maximum of abundance but at a slightly higher pressure (20-50 Torr). On the other hand, for the higher fullerenes whose abundance is lower than 0.3%, it is difficult to draw from fig. 3a systematic changes in their abundance against the gas pressure. When the abundance of the higher fullerenes is plotted against that of C70, a clear correlation is revealed as shown in fig. 3b. The abundance of the higher fullerenes seems to change linearly with that of C_{70} .

3.2. Electron microscopy of raw soot

Fig. 4 shows an electron micrograph and the corresponding diffraction pattern of the soot produced under 20 Torr He, where fullerenes were synthesized with the highest yield. The soot is made of small particles, most of which are coagulated with each other and form chains. The coagulation is presumably



Fig. 3. (a) The abundances of C_{50} (\bigcirc), C_{70} (\triangle) and the higher fullerenes (\square) in soot plotted against the pressure of He. (b) Correlation of the abundances of C_{70} and the higher fullerenes. (\bigcirc) and (\triangle) represent the soots produced under He and Ar gas, respectively.

brought about in the gas phase by coalescence of particles after their nucleation. The coalescence in the gas phase has often been observed from early studies using the gas evaporation technique [18].

In the inset of fig. 4a, a highly magnified image of an isolated soot particle is shown. Lattice images of 0.82 nm spacing are observed in a few places within the particle. As shown in fig. 4b, the diffraction pattern from soot particles exhibits Debye-Scherrer rings, which give interplanar spacings of 0.82, 0.50, 0.43 and 0.32 nm for the four innermost rings. These spacings are assigned respectively to the (111), (220), (311) and (331) planes of an fcc lattice with a lattice constant $a=1.43\pm0.03$ nm. It should be mentioned that reflections of 200 and 400 planes are



Fig. 4. (a) Electron micrograph of the raw soot prepared under 20 Torr He. A highly magnified picture of a soot particle in the inset exhibits a lattice image. (b) Powder diffraction pattern from the soot. Debye-Scherrer rings are observed.

absent, which is characteristic of C_{60} and C_{60}/C_{70} crystals. Moreover, it has been shown by the sublimation technique that C_{70} dissolves into solid C_{60} and forms a solid solution with a slight increase in

the lattice constant [19]. The lattice constant of the solid solution $(C_{60})_{1-x}(C_{70})_x$ $(x \le 1)$ is estimated to be

$$a_x = (1 - x)a_{60} + xa_{70} \tag{1}$$

on the basis of Vegard's laws [20] using the lattice constants of pure C_{60} , $a_{50} = 1.417$ nm [21], and C_{70} , $a_{70} = 1.501$ nm [22]. For x = 0.2, which is close to the actual ratio of C_{70} to (C_{60} plus C_{70}) for the soot shown in fig. 4, the solid solution is expected to have a lattice constant of 1.434 nm, in agreement with the experimental value. Thus, we attribute the crystal-line material to a mixture of C_{60} and C_{70} (and other higher fullerenes with much lower concentrations).

The Debye-Scherrer rings were frequently observed for the soot produced under 20-50 Torr He, under which the highest yield of C_{60} was obtained. Other raw soot prepared at pressures higher than 100 Torr did not show sharp rings but gave only diffuse halos in their diffraction patterns. The halo patterns are indicative of highly disordered structures, i.e. for carbon, network structures possessing trigonally and tetrahedrally coordinated atoms with no translational periodicity. Graphite crystallites were absent in the soot, which is consistent with the results obtained by Krätschmer et al. [2], who carried out infrared absorption experiments. In their infrared spectra, broad features originating from highly distorted graphites were observed besides the sharp lines due to C_{60} . Therefore, the residue of the soot after extracting primary fullerenes (C_{60} and C_{70}) might be mostly giant fullerenes.

The present study suggests that primary fullerenes come together in the gas phase and form a lattice by themselves when their concentration is high enough, whereas when the concentration is low their regular arrangement is prohibited by the presence of giant fullerenes which have sizes and shapes different from those of C_{60} and C_{70} .

The sizes of individual soot particles making up chains range from 30 to 50 nm in diameter for 20 Torr He. The size increases with the increase in the gas pressure, e.g., between 50 and 70 nm for 200 Torr He. The pressure dependence of the particle size has been observed commonly in smoke particles of other elements produced by the gas evaporation technique [18]. According to a preliminary measurement of the temperature gradient around the evaporation source, which was performed for the ordinary gas evaporation to produce metal fine particles, the higher the buffer gas pressure, the more rapidly is the vapor cooled, e.g., 1.5×10^5 K/s for 50 Torr He, and 8×10^5 K/s for 150 Torr He, as estimated by Yatsuya et al. [23]. When the gas pressure is higher, the vapor is quenched more rapidly due to frequent collisions with the buffer gas, and attains higher supersaturation. This brings about nucleation of many small clusters with high spatial density. Coalescence between these clusters is believed to be a key process of the formation of larger particles obtained under high pressures.

The cooling rate of the carbon vapor is presumably responsible for the pressure dependence of the fullerene yield found in the present experiment. Like the ordinary small metal particles mentioned above, the higher the gas pressure, the more abundantly are the embryos formed. The sizes of these embryos range from C_2 [24] to probably around C_{10} [25], and the structure of C_n with *n* less than 10 may be a linear chain, and that of C_{10} a monocyclic ring [26]. At any rate, coalescence between them occurs. The higher the pressure of the buffer gas, the more frequently occurs coalescence because of the higher density of the embryos. Furthermore, the carbon clusters themselves are cooled rapidly. Therefore, when the pressure is too high, the carbon clusters do not have sufficient time to release the structural strains left after the coalescence, and therefore it is hard to attain the closed structure with high symmetry, C_{60} . On the contrary, when the pressure is too low, the carbon vapor diffuses far away from the evaporation source like vacuum deposition. In such a case, since the nucleation occurs in a region where the gas temperature is low, the cluster formed may not be annealed enough to form thermodynamically stable structures. Therefore, the yield of C₆₀ declines again at low pressure. Eventually, there appears an optimum pressure to produce C_{60} .

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