The Carbonization and Structural Analysis of Fullerene Related Materials

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THE CARBONIZATION AND STRUCTURAL ANALYSIS OF FULLERENE RELATED MATERIALS

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1-1. The Overall Features of Fullerene
1-1-1. Fullerene; noble all sp² carbon molecules

It has been believed for a long time that carbon has only two kinds of allotrope, sp³-combined diamond and sp²-combined graphite. In 1970s, a linear sp carbon molecule, so called carbine, was claimed to exist. However, carbine is a rather unstable molecule and difficult to be synthesized[1]. The possibility of a spherical shape all-carbon molecule was described by Osawa in 1970[2]. In 1985, Kroto found a unique C⁶₀ molecule in the space radiospectroscopy. Kroto and Smalley vaporized graphite by laser ablation under lower pressure of He and detected the products of carbon clusters by in situ TOF-mass spectra. Among a number of short-lived carbon clusters, a molecule of 60 carbon atoms seemed most stable[3]. They speculated that the stability of C⁶₀ cluster came from their spherical, closed shape consisting of 20 six-membered and 12 five-membered rings with no dangling bond as shown in Figure 1-1. Because of analogical shape of the cluster with a dome-building designed by Buckminster Fuller, Kroto named C⁶₀ buckminsterfullerene. In 1990, Kratchmer et al. found a large amount of C⁶₀ formed in the soot produced by resistive heating of graphite electrode[4,5]. They succeeded to isolate C⁶₀ and C⁷₀ fullerenes from the soot, using Soxhlet extraction with nonpolar organic solvent such as benzene and toluene[5]. C⁶₀ and larger fullerenes were separated by liquid chromatography. Such a series of investigations stimulated a large number of research on fullerenes in their synthesis, reactivity, and application.

1-1-2. Preparation Methods of Fullerene

So far the five methods have been reported to synthesized fullerene: vaporization of high purity graphite by using resistive heating[6-8]; AC or DC arc discharge of graphite[9-18]; production of soot in flame through carefully controlled combustion of benzene[19-21]; laser ablation of a rotating carbon disc under flowing argon[10]; and a high frequency inductive heating[22]. All methods produce "soot", from which the fullerenes are extracted by appropriate solvents. Table 1-1 summarizes some of the experimental conditions reported in the
literatures for the synthesis of fullerene-containing soot by the arc discharge and resistive heating methods[23]. The arc discharge process appears to be more efficient than the resistive heating method[9,24]. Typically 10wt% of toluene-soluble yield was reported by a wide range of experimental conditions as shown in Table 1-1.

Separation and purification of the fullerene is typically performed by extracting the soot first with benzene or toluene as shown in Table 1-1. The extracted fullerenes of C₆₀ to C₉₆ are further purified by column chromatograph[6,7], HPLC[26-32] and GPC[33] by adjusting the packing materials and solvent. Other procedures such recrystallization[34], fractal crystallization[35], and sublimation[36,37] are also reported.

In spite of extensive research, yield of C₆₀ is still low and its tedious purification is far from satisfaction for its application as a functional material.

1-1-3. Structure and Physical Properties

Sixty carbon atoms in C₆₀ are located at the vertices of a regular truncated icosahedron where every site is all equivalent, being consistent with a single sharp line in NMR spectrum[6,38]. The average nearest neighbor carbon-carbon distance a_C-C in C₆₀ is 1.44Å, almost identical to that in graphite (1.42Å). Therefore, C₆₀ molecule can be regarded as a "rolled-up" graphene sheet. The diameter of the C₆₀ molecule is 6.83Å treating the atoms as points[39], while the outer diameter of the C₆₀ molecule becomes 10.18Å[40], including the π-electron cloud.

Although all carbon atoms in C₆₀ are equivalent, the three bonds emanating from each atom are not equivalent, two being electron-poor single bonds, and one being an electron-rich double bond. The single bonds that define the pentagon are longer than the average bond length of 1.44Å, while the double bond are shortened to 1.40Å[39,41-43].

Since valences of carbon atom in C₆₀ are fully satisfied, the molecules are expected to form a molecular crystal associated through van der Waals force being an insulator (or semiconductor). Reflecting the Iₜₜ symmetry of C₆₀ molecule, it has 46 molecular mode frequencies, including 4 of infrared-active (all with T₁g symmetry) and 10 of Raman-active (2 with A₈ symmetry and 8 with H₈ symmetry). The Raman-active A₈ breathing mode at 1469cm⁻¹ corresponds to tangential displacements of the 5 carbon atoms around each of the 12 pentagons[44,45] which is called the "pentagonal-pinch" mode. C₇₀ was found to exhibit a rugby ball shape and the lower symmetry D₅ₗ and lacks inversion symmetry.
In the solid state, the C\textsubscript{60} molecules crystallize into a cubic structure with a lattice constant of 14.17Å, a nearest neighbor C\textsubscript{60}-C\textsubscript{60} distance of 10.02Å, and a density of 1.72g/cm\textsuperscript{3}[39]. The balls are rotating rapidly with three degrees of rotational freedom with their centers arranged on a face-centered cubic (fcc) lattice with one C\textsubscript{60} ball per primitive fcc unit cell. The rotation of C\textsubscript{60} ball is frozen in two of their three degrees of rotational freedom below 255K, and the anisotropic orientation among balls appears in the crystal[46,47,48].

Fullerenes give molecular solids. Thus, their electronic structures are expected to be closely related to the electronic levels of the isolated molecules. If two single bonds along adjacent sides of a pentagon and one double bond between two adjoining hexagons were coplanar, they would be very similar to the sp\textsuperscript{2} trigonal bonding in graphite. Moreover, the curvature of the C\textsubscript{60} surface causes the planar-derived trigonal orbitals to hybridize, thereby admixing some sp\textsuperscript{3} character to the sp\textsuperscript{2} bonding. The shortening of the double bonds and lengthening of the single bonds in the Kekulé arrangement of the C\textsubscript{60} molecule also strongly influence the electronic structure[49].

1-1-4. Formation Mechanism

Several basic and more detail growing models of fullerene framework under the severe conditions such as arc discharge were proposed. Smalley et al. proposed pentagon road model on which only pentagon and hexagon are structural units and as many pentagons as possible are framed by avoiding the adjacent pentagon (isolated pentagon rule; IPR) [50]. The importance of intermediate circular clusters during fullerene formation was proved[51]. The models based on the formation and rearrangement of circular clusters were also proposed[52,53].

1-1-5. Application

Fullerenes and fullerene-related compounds are known to show unique properties, and expected to their unique application.

As described in Section 1-1-3, C\textsubscript{60} exhibits narrow HOMO-LUMO gap. This electronic structure provides some unique optical properties[54,55], for instance, photo-induced activation effect of oxygen molecule to singlet states[54]. Some A\textsubscript{3}C\textsubscript{60} compounds (A ; alkali metals such as K, Rb and Cs) have been known to show the high-temperature superconductivity[56]. Rb\textsubscript{x}Cs\textsubscript{y}C\textsubscript{60} reached 33K of the critical temperature[57]. Such complexes attracted many researchers by indicating...
a new concept of organic superconductor.

Fullerenes doped with hetero atoms have been investigated, such as endohedral fulleroids M₆@C₈₂[50,58,59], harogenated fullerenes C₆₀Fₓ[60,61], and many other organic derivatives being reported. These doping can functionalize fullerenes for their applications.

Carbon nanotube, regarded as a tubular-shape higher fullerene, is also expected to carry potentials of their unique application especially for the electronic use. Since the discovery by Iijima[62], numerous investigations have made it possible to synthesize and purify it in large amount[63,64,65]. Some interested properties of this material have been calculated[66,67] and measured[68,69,70]. Nanotube seems to be useful as catalyst support[71] to provide its nanoscale hole for chemical reactions in the restricted space[72].

1-2. The Chemical Reactivities of Fullerenes

1-2-1. Additional Reactions

Fullerenes have much higher chemical reactivity than normal graphitic plane due to their bent sp² orbitals and π-cloud orienting to exohedral. The natures of their double bonds are relatively closer to those of the conjugated poly-alkene. Besides, their narrow HOMO-LUMO gap provides them relatively high addition reactivities towards both electrophilic and nucleophilic agents[73]. Especially, C₆₀ has a low reduction potential (-0.36V vs SCE ; in benzene) and shows electron-accepting property[74].

Fluorine molecule easily reacts with C₆₀ even at room temperature and provides adducts in broad distribution of the addition degree[60]. Hydrogen can be also added to C₆₀ by the Birch reduction and provides adducts upto C₆₀H₃₆[75]. The additions of several agent, especially nucleophile, to C₆₀[73] and higher fullerenes[76] were reviewed by Hirsch and Diederich et al., respectively.

1-2-2. The Thermal and Oxidation Reactivities

C₆₀ is known to sublime at high temperatures. Krätchmer et al. have reported that C₆₀ sublimes in a vacuum at ~400°C[5]. Milliken et al. measured thermal gravimetric analysis (TGA) of C₆₀ under N₂ flow on ambient pressure and observed that C₆₀ commenced to lose its weight at ~600°C where a very small weight loss of graphite was compared as shown in Figure 1-2(A)[77]. Using Knudsen effusion mass spectrometric measurements, Pan et al. have determined the heat of sublimation of C₆₀
and C\textsubscript{70} from their polycrystalline mixture to be 40.1 and 43.0kcal/mol at average temperatures of 707 and 739K, respectively\cite{78}. The heat of sublimation of fcc C\textsubscript{60} powder was also measured by Chen \textit{et al.} to be $\geq$39kcal/mol\cite{79}. On the TGA of C\textsubscript{60} measured by Ismail \textit{et al.}\cite{80}, the major C\textsubscript{60} sublimed, leaving behind a small amount of non-volatile carbon residue, whose weight ranged 5-22% dependent on sample preparation. They proposed two possible origins of the residue: a by-product formed during the sublimation of C\textsubscript{60} by polymerization, or soot or particles that were occluded the aggregates.

Milliken \textit{et al.} also measured TGA of C\textsubscript{60} in air as shown in Figure 1-2(B)\cite{77}. C\textsubscript{60} began to lose its weight at $\sim$480°C and completed the weight loss by $\sim$650°C while graphite commenced losing weight at 700°C. Weight uptake data under various conditions\cite{77,79,81} clearly indicate that C\textsubscript{60} is reactive towards molecular oxygen. The reactivity of C\textsubscript{60} at ambient pressure and temperature with molecular oxygen to form an epoxide has been reported in a photoemission IR\cite{82}. Werner \textit{et al.} analyzed the reactivity of C\textsubscript{60} solid towards O\textsubscript{2} using several spectroscopies at the temperature range of 300-600K\cite{83}, and concluded that O\textsubscript{2} molecule first intercalates at room temperature and reacts with C\textsubscript{60} molecule to form C=O bond, deforming the framework of C\textsubscript{60} through the formation of peroxide and epoxide at 600K. Scanlon \textit{et al.} reported that the residual soot after the extraction of fullerene soot was more reactive than C\textsubscript{60} so that 80wt\% of this material burned out by the heat-treatment at 400°C\cite{84}. Chibante \textit{et al.} reveal rather carbonaceous nature of oxidation product of toluene soluble fullerenes\cite{85}.

There are some researches to use C\textsubscript{60} as the catalysts for high temperature reactions. Malhotra \textit{et al.} reported that C\textsubscript{60} effectively catalyzed a hydrogen-transfer reaction of 1,2'-dinaphthylmethane at 400°C\cite{86}. Hirschon \textit{et al.} used fullerene soot and the residual soot after the extraction of fullerene as the catalyst of the dehydrogenative coupling of methane\cite{87}. These fullerene-related materials can accelerate at lower temperature than other carbon materials. The rate-determining step was changed to the dehydrogenation of C\textsubscript{2} by the presence of fullerene soot, indicating catalytic effect of this material. Sakanishi \textit{et al.} applied the soot for the catalyst support of the liquefaction of coal\cite{88}.

Thus, the reactivity of fullerenes widely attracts researchers, thermal reactivity of fullerene is not yet clarified under non-sublimation conditions.
1-3. The Structural Studies of Soot

As described in Section 1-1-2, under the major preparation processes of fullerene, arc discharge of graphite and combustion of hydrocarbon, the main product is carbonaceous soot which is insoluble in solvents. It is impossible to know its precise structure, and its similarity is postulated to much common amorphous carbonaceous soot such as PAH and carbon blacks.

Kroto suggested the icospiral growth model of soot which started from the corannulene-like cluster[89] (described in Figure 1-3). According to this model, fullerenes are the by-product in the growth process of soot. He conjectured that the presence of hydrogen atom stabilized opened clusters, accelerating the formation of soot. This model indicates the structural relationship of soot and fullerene molecule, supported by Gerhardt et al., who found C_{60}^+ as a dominant ion in a flame[90].

Weber et al. produced toluene soluble fullerenes, especially significant percentage of C_{84}, by the heat-treatment of the residual fullerene-soot after the extraction with toluene[91]. This result cannot be fully explained by Kroto's model. More research is necessary to understand the problem.

Iijima first observed the closed-shell carbon bodies in an amorphous structure[92] (Figure 1-4). The observed carbon bodies were multi-shelled, so called "carbon onion". The carbon onion was reported by Ugarte et al.[93], Smallay et al.[94], Endo and Kroto[95], and many other researchers[96,97].

Ugarte et al. synthesized carbon onions and nanocapsules by the heat-treatment of residual fullerene soot after the extraction with toluene[98,99]. Under the observation of high-resolution TEM(Figure 1-5), the amorphous soot is converted to the material resembling glass-like carbon after annealed at 1700°C for 18h. This material is further converted to onion-like particles of 2-3 shells at 2100°C, and then to those of 4-8 shells at 2250°C. Such a unique structure stimulates its unique application.

1-4. Conversions of Pentagonal Ring to Hexagon

Stone and Wales reported that photochemically-allowed transformations between two pyracylene units can occur according to SCF calculations[100]. This transformation makes it possible for the intermediates of fullerenes to grow, satisfying to the isolated pentagon
rule (IPR). Although the energy level of 150-200 kcal/mol had been thought to be necessary for Stone-Wales transformation, Osawa et al. proved that less level of energy allow this transformation[101]. Thus, the conversion of pentagon to hexagon is rather facile. Murry et al. applied this fact to the fragmentation of \( C_{60} \) through 7-membered ring by laser annealing[102].

Previous studies of conversion from pentagon in aromatic hydrocarbons containing pentagon to hexagon were made by Mochida et al.[103] and Otani et al.[104]. Figure 1-6 shows the change of Raman spectra during the heat-treatment of decacyclene[104]. The 1420 cm\(^{-1}\) peak assigned for the "pentagonal pinch" of pentagonal ring disappeared by the heat-treatment at 750°C. The author concerns the deformation of pentagons in fullerenes and the structure of the product.

1-6. Outline of the Present Thesis

The application of fullerene is limited because of its high cost due to the low yield. To find a way is to clarify the thermal reactivity of fullerene. The thermal reactivity of \( C_{60} \) and its homologue fullerenes has been rarely discussed because of the sublimation of such fullerene molecules, although extensive researches have been performed in many organic reactions. The present author believes that the fullerenes \( C_{60} \) and \( C_{70} \) can be converted by the heat treatment to amorphous carbon materials which may have similar structure to that of the residual soot, to prove that the soot is produced consecutively by thermal polymerization of fullerenes. The carbonization in the solid phase may be influenced very much by the crystal structure of fullerenes.

Through the arc discharge of graphite electrode, the products from the anode are collected as soot, which are further fractionated into toluene-soluble \( C_{60}, C_{70} \) and some large fullerenes, toluene-insoluble but quinoline-soluble giant fullerenes, and insoluble amorphous carbon particle. The author attempted to reveal through the structural analysis and heat treatment of each fraction whether each fraction has similarity in their structure which will be thermally converted each other, as fullerenes to soot and giant fullerenes to toluene-soluble fullerenes, respectively, for example. Such a series of study will clarify the reactivity of fullerene as an intermediate. The author expects to be able to propose ways to increase the yield of fullerenes in the arc discharge.

The author examines a noble use of soot as well as fullerenes as the sources of noble carbon artifacts in the present study. Although the
carbonization of fullerenes is competitive with the sublimation, their carbonization yield will be enhanced by moulding into disk and inhibiting the sublimation. The residual soot is expected to provide similar carbon artifact by moulding into disk. After the graphitization, fullerenes and residual soot may provide unique carbon of spherical turbostratic layer and extremely low bulk density. The point is to clarify whether the fullerene or soot can give the artifact through the moulded carbonization.

The author also co-carbonizes fullerene with the synthesized isotropic pitch. Fullerenes is expected to react with hydrogen derived from components in the isotropic pitch at lower temperatures to modify the carbonization behavior of the isotropic pitch. Fullerene can affect effectively the carbonization of pitch through its dehydrogenating ability.

The content of the present thesis is summarized as follows.

Chapter 1. Introduction
The background/scopes of recent fullerene research and objectives of the present study are summarized.

Chapter 2. The carbonization of C$_{60}$ and C$_{70}$ fullerenes to fullerene soot
The author examined the carbonization of C$_{60}$, C$_{70}$, and toluene-soluble component obtained from the fullerene soot by solvent extraction. Such a study may clarify the consecutive natures of a series of reactions to form first C$_{60}$ and then soot.

Chapter 3. Carbonization of the toluene-soluble fraction of fullerene soot into a disk
Some attempts were made to increase the carbon yield from the fullerene, based on the observation that its sublimation took place around 1000°C, in competition with its carbonization.

Chapter 4. Structural changes of fullerene by heat-treatment up to graphitization temperature
The structural changes of the fullerene were studied from the molecular crystal to the amorphous carbon and then to the spherical hollow structure through successive analysis with X-ray, Raman, FE-SEM, TEM and STM/AFM techniques.
Chapter 5. *Carbon frameworks produced in the fullerene related materials*

The products in the preparation of C₆₀ from graphite through arc discharge were separated and analyzed to clarify the correlation in their structure and their successive conversions.

Chapter 6. *Some properties of carbon disk prepared from toluene insoluble fraction in fullerene soot*

The carbonization of toluene insoluble fraction in the fullerene soot was studied by moulding to prepare the carbon artifact of unique properties and strength. Adhesion and fusion of the toluene-insoluble particles were particularly interested to develop the strength. Some properties of artifact due to the microhollow spheres were measured to suggest some application.

Chapter 7. *Effects of fullerene addition on the carbonization of synthetic naphthalene isotropic pitch*

Fullerenes were co-carbonized with synthesized isotropic pitch derived from naphthalene. This chapter describes the carbonization process of the mixture and how the chemical states of fullerene change during the carbonization with pitch.

Chapter 8. *Conclusions*

Conclusions of the thesis are summarized.
Figure 1-1. The Structure of C₆₀ Molecule.[3]
### Table 1-1. Summary of Some Fullerene Synthesis Methods[23].

<table>
<thead>
<tr>
<th>Discharge method &amp; Yield</th>
<th>unknown %</th>
<th>DC %</th>
<th>AC %</th>
<th>Current (A)</th>
<th>Voltage (V)</th>
<th>He Pressure (Torr)</th>
<th>Contact Method</th>
<th>Extraction Method</th>
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<tr>
<td>8(3†)</td>
<td>100</td>
<td>50</td>
<td>37-75</td>
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<td>Soxhlet</td>
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<td>225</td>
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<td>100</td>
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<td>Soxhlet</td>
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<td>40-60</td>
<td>200</td>
<td>gravity</td>
<td>Soxhlet</td>
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<tr>
<td>5-10</td>
<td>100-200</td>
<td>150</td>
<td>contact arc</td>
<td>Soxhlet</td>
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<tr>
<td>10</td>
<td>200</td>
<td>20</td>
<td>gravity</td>
<td>Soxhlet</td>
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<td>7.7</td>
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<td>Soxhlet</td>
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<td>3</td>
<td>130</td>
<td>100</td>
<td>gravity</td>
<td>Soxhlet</td>
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<td>24</td>
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<td>200</td>
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<td>Soxhlet</td>
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<td>toluene</td>
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</table>

†3% is the yield of pure C<sub>60</sub>; 8% is the yield of extractable material.
Figure 1-2. TGA Profiles of (a) C\textsubscript{60} and (b) Graphite under N\textsubscript{2} Flow(Top) and Air Flow(Bottom).[77]
Figure 1-3. Icospiral Model for the Growth of Soot[89]
Figure 1-4. TEM Image of Carbon Onion First Observed by Iijima.[92]
Figure 1-5. HRTEM Images of heat treated carbon soot.[98]
(a) crude soot produced in the electric arc
(b) soot annealed at 1700°C, 18h
(c) soot annealed at 1700°C, 1h and 2100°C, 1h
(d) soot annealed at 1700°C, 1h and 2250°C, 1h
Figure 1-6. Raman Spectra of Decacyclene and its heated products.[104]
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Chapter 2

Carbonization of C_{60} and C_{70} Fullerenes to Fullerene Soot

2-1. Introduction

Since C_{60} in a bulk quantity has been produced from the graphite electrode through its electric arc discharge[1], its organic chemistry is now expanding to establish new aromatic concept[2].

The present procedure produces C_{60} at a yield of ca. 10wt% regardless of the production facility. Although a higher yield of C_{60} is strongly desired, any preparation procedure gives a so-called "soot" as the major product which is basically insoluble in any solvent[1]. The soot appears to be similar to a carbon black of large surface area[3-5]. It is an intriguing question whether C_{60} is an intermediate for the soot in the reaction initiated by the arc discharge or an independent product as described in Section 1-3.

In this chapter, the author examined the carbonization of C_{60}, C_{70}, and the toluene soluble component separated from the fullerene soot by solvent extraction. The reactivities of C_{60}, C_{70} fullerenes for carbonization, the structure of carbonized and graphitized product, and the relationship of the structure of these products to that of the residual soot after extraction from fullerene soot are discussed toward the problem described in Section 1-2-2. Such a study will clarify the consecutive natures of a series of reactions to form first C_{60} and then soot.

2-2. Experimental

The fullerene soot (Fs) was produced by arc discharge method using a graphite electrode and was separated into two fractions by Soxhlet extraction with toluene. About 10% of Fs is soluble in toluene. The toluene-soluble fraction (Fs-TS) was then isolated and re-crystallized by evaporating the solvent, and then heated in vacuum at 100°C to remove the residual solvent. The Fs-TS fraction was analyzed by high-performance liquid chromatography. The obtained Fs-TS powder thus obtained was used for the carbonization in the present study. Pure C_{60} (purity 99.9%) and C_{70} (purity 99.5%) were obtained from Shinku Yakin Co.
The heat-treatment of Fs-TS powder was carried out by the following procedures; the sample was put in an alumina boat, placed in the electrical tube furnace and heated under flowing argon (flow rate: 200ml/min) at a heating rate of 4°C/min to the prescribed temperature, where it was held for 1 to 2 h. These temperatures were 200, 400, 500, 800, and 1000°C. The heating behavior was also probed by thermogravimetric analysis (TGA) in flowing N₂. Carbonaceous product at 1000°C was further calcined and graphitized to 2500°C.

The heated materials (called TS-HT) of Fs-TS was extracted by toluene at room temperature. The toluene-soluble fraction in TS-HT (to be called TS-HT-TS) was also analyzed by HPLC. Both the total product and the toluene-insoluble fraction (to be called TS-HT-TI) were characterized by X-ray diffraction, and transmission electron microscopy (TEM).

2.3. Results and Discussion

Figure 2-1 illustrates the TGA profiles of C₆₀, C₇₀, and Fs-TS under N₂ flow of 200 or 100 ml/min and heating rate of 10°C/min. Such substrates of C₆₀, C₇₀, and Fs-TS were found to exhibit sharp weight loss at 800–900°C, 800–900°C, 850–950°C, respectively (as reported by Milliken et al. [7]), leaving some carbonaceous soot-like product in the TG platinum pan. The yield of the soot-like product was trace from C₆₀, 6% from C₇₀, and 10% from Fs-TS under N₂ flow of 200 ml/min. Larger fullerenes appear to give higher yield of soot-like product. C₆₀ and C₇₀ in Fs-TS appear to give more carbonaceous product than their isolated forms. C₇₀ in Fs-TS appears to react together with C₆₀ at a lower temperature of 800°C than that observed with pure C₇₀. The slower flow rate of 100 ml/min increased the yield of carbonaceous product from Fs-TS to 20%. Further slow rate of 50ml/min did not increase the yield.

Table 2-1 summarized the yields of remaining products from Fs-TS heated in an alumina boat. In an electric furnace, a trace amount of TI was formed by the heat treatment at 250°C. It should be noted that 10% of other TS, probably large fullerenes was produced by this temperature. Higher temperature increased TI up to 24% by 1000°C at the sacrifice of toluene soluble fullerenes while a large weight loss was found between 500 and 800°C where C₆₀, C₇₀ and TS might sublime.

Figure 2-2 illustrates the X-ray diffraction patterns of Fs-TS, and its heated products. The starting Fs-TS shows the typical pattern of C₆₀ which was the main component in Fs-TS[1]. There was a broad
background diffraction. The heat-treatment destroyed the crystal completely by 1000 °C. Graphitization at 2500 °C provided a sharp diffraction at 26.0° with a small shoulder at 26.3°. Such X-ray profiles of graphitized Fs-TS were very similar to that of the quinoline insoluble fraction (Fs-QI) in the soot graphitized at 2500 °C[8].

Figure 2-3 illustrates the TEM bright field images of heated Fs-TS and QI. Both Fs-TS heat-treated at 1000 °C and as-extracted QI show grain-assemble forms as observed for soot by Werner et. al.[5] and by the present authors for QI[8]. The each grain carried very small planes randomly oriented. The graphitization at 2500 °C developed very thin graphitic layers of about 1nm thick. The layers in the graphitized Fs-TS appeared spherical, forming a hollow in the inside the grain, while those of graphitized Fs-QI were flake-like with some twists, as reported[9,10].

The present study revealed the successive carbonization of C_{60} and C_{70} through large fullerenes into soot-like substances which are very similar to the soot produced as the major by-product in the preparation of the fullerenes from the graphite electrode by electric-arc discharge. Very similar X-ray profile and TEM image after the graphitization indicate that the spherical surface of C_{60} due to C5 rings is converted into hexagonal planes at elevated temperature above 800 °C which will stack into the graphitic layers within limited range. The interlayer spacing is estimated around 0.3 nm to be called turbostratic. Spherical shape of turbostratic layers forming a hollow should be noted to inherit the grain of the molecular crystals of fullerenes. The yield of carbonaceous product from Fs-TS depends very much on the flow rate during the heat treatment. The competition of sublimation with carbonization is definitely suggested to govern the yield of the soot. Such conclusions indicate a way to increase the yield of C_{60} in its preparation by the rapid run-away of new born C_{60} from the hot zone in the electric arc discharge.

2-4. Conclusion

The toluene soluble fraction of fullerene soot (Fs-TS), containing 76wt% of C_{60}, 22wt% of C_{70} and 2wt% of higher fullerenes, was carbonized and graphitized. Although fullerenes sublimed around 800 °C, ca. 20wt% of the sample remained after heated treated at 1000 °C. The residue was more from higher fullerenes than pure C_{60}. C_{60} and C_{70} in Fs-TS were converted to toluene insoluble matter after heat treated upto 250 °C, via higher fullerenes. The carbonized product of Fs-TS was a
soot-like amorphous carbon and appeared peripheral turbostratic layers after graphitization. The similarity in the carbonization and graphitization behaviors of Fs-TS to that of quinoline insoluble soot (Fs-QI) indicates the consecutive formation of soot from $C_{60}$ and fullerenes in arc discharge chamber, and a way to increase the yield of $C_{60}$ in the preparation by the rapid run-away of new born $C_{60}$ from the hot zone in arc.
Figure 2-1. TG Profiles of Fullerenes in N\textsubscript{2} flow
1) Fs-TS under a N\textsubscript{2} flow rate of 100ml/min
2) Fs-TS under a N\textsubscript{2} flow rate of 200ml/min
3) C\textsubscript{60} under a N\textsubscript{2} flow rate of 200ml/min
4) C\textsubscript{70} under a N\textsubscript{2} flow rate of 200ml/min
**Table 2-1. Compositions of Fs-TS and its Heated Products**

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>C\textsubscript{60}</th>
<th>C\textsubscript{70}</th>
<th>Other TS</th>
<th>Toluene-Insoluble</th>
<th>Loss 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-treated</td>
<td>76</td>
<td>22</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>250°C, 2hrs</td>
<td>69</td>
<td>17</td>
<td>10</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>400°C, 2hrs</td>
<td>64</td>
<td>14</td>
<td>6</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>500°C, 2hrs</td>
<td>63</td>
<td>17</td>
<td>3</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>500°C, 5hrs</td>
<td>63</td>
<td>16</td>
<td>2</td>
<td>14</td>
<td>5</td>
</tr>
<tr>
<td>800°C, 2hrs</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>21</td>
<td>79</td>
</tr>
<tr>
<td>1000°C, 1hr</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>24</td>
<td>76</td>
</tr>
</tbody>
</table>

1) Amount of Fs-TS: 0.10g heated in an alumina boat under Ar
   flow rate 200ml/min, heating rate 4°C/min
2) Sublimed
Figure 2-2. X-ray Diffraction Patterns of Fs-TS and its Heated Products
(a) Fs-TS
(b) Fs-TS heated at 1000°C
(c) Fs-TS heated at 2500°C
(d) detailed profile of (c) in the 2θ range 24° to 28°
Figure 2-3. TEM Bright Field Images of Carbonized Fs-TS, Fs-QI, and their Graphitized Products
(a) Fs-TS heated at 1000°C
(b) graphitized Fs-TS
(c) Fs-QI
(d) graphitized Fs-QI
REFERENCES

Chapter 3

Carbonization of Toluene Soluble Fraction of Fullerene Soot into Disk

3-1. Introduction
Since the discovery of a facile synthetic procedure[1], the fullerene (C₆₀ and C₇₀) has attracted a great deal of research on its physical properties, chemical reactivity and theoretical calculation as a unique highly-conjugated species[2]. The present author[3] has described its thermal reactivity to produce amorphous carbon particulate at 1000°C which were converted at 2400°C into hollow spheres surrounded by turbostratic carbon layers in Chapter 2. Such graphitization behavior appears very similar to that of fullerene soot[3,4] The carbon yield was rather limited as low as 24% by the carbonization of powdered fullerenes in a boat under the helium flow because they sublime around 800°C[5].

In this chapter, some attempts were made to increase the carbon yield from the fullerene based on the observation that its sublimation took place around 1000°C, in competition with its carbonization. Hence the carbonization by placing the fullerene at the bottom of long quartz tube or by press moulding it into a disk was performed to suppress the sublimation before its thermal condensation and carbonization into non-sublimable substances. Some properties of the produced carbon disk were also investigated here for the noble application of fullerenes.

3-2. Experimental
Fullerene soot (Fs) was produced by the arc discharge method using a graphite electrode. The produced soot was separated into two fractions by Soxhlet extraction with toluene. About 10% of Fs was soluble in toluene. The toluene-soluble fraction (TS) was then recovered by evaporation, followed by vacuum drying to remove the residual solvent. The Fs-TS fraction consisted of C₆₀(76%), C₇₀(22%) and 2% of the others (probably higher fullerenes) as determined by HPLC (Hitachi Co.; D-2500) analysis.

About 0.5g (otherwise specified) of the Fs-TS powder obtained in this way was moulded in the disk of 20mm diameter and about 1.2mm height using a pellet press. The moulding pressure was 1.5 or 6 MPa.
The heat-treatment of Fs-TS powders was carried out by the following two procedures as shown in Figure 3-1; (A), the sample was placed in the bottom of a test-tube (200mm high) which was purged with flowing Ar gas through a T-type tube attached at the top of the test-tube, and (B), the sample was placed in an alumina boat and heated in a horizontal tube furnace, being purged with Ar gas at 200ml/min. Heating was programmed at 4°C/min to the prescribed temperature, and held for 1h at that temperature. The temperatures investigated were 250, 500, 700, 800, 900, 1000, 1200 and 1300°C. The carbonaceous product at 1000°C was further calcined and graphitized to 2400°C.

The heated products were observed by FE-SEM (JEOL Co.; JSM-6320F). Bulk densities of the disks were calculated by measuring their volume and weight in the water.

3-3. Results

3-3-1. Sample Forms and Heating Procedures

The yield of carbonaceous material from Fs-TS was markedly influenced by the sample form and heating procedure. Table 3-1 shows the yields obtained with Fs-TS of powder and disk at 900°C or 1000°C in the tube A or boat B, respectively. The moulded disk (6MPa) yielded the largest amount of heated product, the yield reaching 94% when it was heated in the bottom of the tube A, and 54% heated even in a shallow boat B. The disk produced markedly higher yields than the powder by limiting sublimation of C60 molecules. Location in the bottom of a tube was more favorable for higher yields than in a shallow boat, again because of limited sublimation.

Figure 3-2 illustrates the relationship of the carbonization yield to the thickness of the disk (6MPa, heat-treated in the B Type furnace). Thicker disks tended to provide higher yields, while the moulding pressure of 1.5 to 6 MPa appeared not to be as critical in obtaining high yield.

Figure 3-3 illustrates the influence of the heating rate. Rapid heating up to 4°C/min increased the yield, but further increases in the heating rate provided no improvement. Competition of sublimation and carbonization is again suggested.

3-3-2. Appearances of Produced Carbon

Figure 3-4 shows the forms and appearances of the moulded fullerene disks (moulding pressure was 6MPa) after heat-treatment to
1000°C using procedure B at a heating rate of 4°C/min, and final calcination at 2400°C. While there was a small shrinkage, the disk was basically maintained during the heat-treatment. Some cracking and bending of the disks may be observed in the photograph, but this can be avoided by lowering the heating rate and using procedure A which gives higher yield. Figure 3-4 also shows the forms and appearances of the graphitized disks produced at reduced moulding pressures (1.5MPa). When the moulding pressure was 6MPa, the graphitized disk was mechanically strong like commercial hard carbons, while the lower pressure provided disks which were easily broken. The graphitized disk moulded at 1.5MPa appeared much less glossy, probably because of the porosity of the surface.

The apparent and bulk densities of Fs-TS disks and their heated products at the moulding pressures of 1.5 and 6MPa are summarized in Table 3-2. While apparent densities of heated disks were influenced by the densities of the initial disk, their bulk densities appeared independent from the initial moulding pressure. The A type furnace provided a higher apparent density of the disk to almost the same to that of the initial disk reflecting very high carbon yield. Although the bulk densities of the disks heated to 1000°C were similar to those of typical non-graphitizable carbon, those of the disk heated to 2400°C were markedly smaller.

Figure 3-5a and b show FE-SEM photographs of cross-sectioned surface of Fs-TS disk carbonized in A type and B type furnace, respectively. The areas near the surface of the disks showed granular assemble regardless the carbonization procedures of A and B, although the former procedure appeared to give more fused (Boarders of granulars became much less distinct). The inner areas of the two disks were very different. The procedure A gave no trace of granular, allowing a complete fused adhesion of grains to show continuous plate of no boundary, although some pores and cracks were observable under high magnification. In contrast, the procedure B showed again granular assembles in the inside of the disk. Their fusion was emphasized compared to the surface. Such results indicate the very different extent of sublimation according to the carbonization and moulding procedures as well as the location within the disk.

3-4. Discussion

In Chapter 2, the author has reported that the carbonization process of the fullerene molecules competes with their sublimation at 700-800°C.
Therefore the best way to increase the carbon yield is to limit the sublimation by increasing their partial pressure. A type method (placing sample at the bottom of the tube) is the preferable for this purpose. It is found through the present study that their sublimation process was almost completely suppressed when the vapor of the fullerene was filled in the atmosphere at the upper part of the vertical test tube.

Moulding fullerene into the disk is also effective to increase the yield by limiting the sublimation. The smaller outer surface of the disk and diffusion inside the disk limit the sublimation in the competition with the carbonization. Hence a thicker disk gave a higher yield. It is also of value to point out that the bottom of the tube allowed a further higher yield of moulded disk, suggesting the complete suppression of the sublimation pressure. The rapid heating increased the yield, the physical sublimation and chemical carbonization of different activation energies may response differently with the heating rate.

The dense packing of fullerene provided an amorphous carbon disk of high strength. The fullerene grains adhered each other, giving a high density when carbonized in the procedure A. Although the bulk of the disk stayed unchanged by the carbonization, the grains appeared to be fused to adhere at the chemical transformation of spherical structure of C_60 into graphitic planer structure appears to be related to their fusion in the range of 700-800°C. Structural change of the fullerene is now under investigation.

It is also of value to mention that the density decreased by the graphitization. The small loss of weight and no shrinkage in a disk of very high carbon yield gave a hollow grain with graphitic skins, looking close to multi-walled tubular fullerene in Ref.[6], reducing the density as revealed by TEM in Chapter 2, while maintaining the form of the disk.

The high pressure of moulding and carbonization procedure of limiting sublimation can give textureless carbon plate of no boundary in the inside of the disk (60% volume) like the surface of glass-like carbon derived from thermosetting polymers. Complete fusion of the fullerene molecules as well as crystals is suggested during its carbonization. A unique preparation procedure of glass-like carbon artifact can be proposed.

3-5. Conclusion

Carbonization of toluene soluble fraction in the fullerene soot was examined in the disk at the bottom of the test tube. Such a carbonization
was found to increase the carbon yield to 94% by 900°C and 89% by 2400°C. The carbon yield was also found to be influenced by the thickness of the disk and the heating rate. All these results indicate that the carbonization competes the sublimation. The carbon disk thus prepared showed appearance of glass-like carbon and had bulk density of 1.5g/cm³ at 900°C and 1.2g/cm³ at 2400°C. The reduction of the density by the graphitization reflects hollow spheres surrounded by their turbostratic layers in the graphitized disk.
Figure 3-1. The Carbonization Methods of Fs-TS
Table 3-1. Yields of Heat-treatment

<table>
<thead>
<tr>
<th>Forms (Heating System)</th>
<th>Carbon Yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder (Type A)</td>
<td>39</td>
</tr>
<tr>
<td>Powder (Type B)</td>
<td>24</td>
</tr>
<tr>
<td>Disk (Type A)</td>
<td>94</td>
</tr>
<tr>
<td>Disk (Type B)</td>
<td>54</td>
</tr>
</tbody>
</table>

Heating System: Type A - Bottom of Tube
Type B - Boat on Flow

Heating Temp.: Type A - 900°C,
Type B - 1000°C

Disk: 20mmφ, thickness - ca.1.25mm
Figure 3-2. The Carbon Yields vs Thickness of Fs-TS Disk
Disk : 20mmφ
Heating System : ● ; A Type, ○ ; B Type,
Heating Rate : 4°C/min
Figure 3-3. The Carbon Yields vs Heating Rate of Fs-TS Disk
Disk : 20mmf, ca.1.25mm thickness
Heating System : Boat on Flow
Figure 3-4. The Shapes and Appearances of Fs-TS Disk and its Heat-treated Products
(a) Fs-TS Disk    (b) HTT 1000°C   (c) HTT 2400°C
(d) HTT 2400°C
Furnace : B, Moulding Pressure : 6MPa(a, b, c), 1.5MPa(d)
Table 3-2. The Yields and Densities of Fs-TS Disk and its Heating Products

<table>
<thead>
<tr>
<th>Moulding Pressure (MPa)</th>
<th>Type of Furnace</th>
<th>HTT (°C)</th>
<th>Yield (wt%)</th>
<th>Apparent Density (g/cm³)</th>
<th>Bulk Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 B</td>
<td>R.T.</td>
<td>1000</td>
<td>52</td>
<td>0.663</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2400</td>
<td>48</td>
<td>0.644</td>
<td>1.0</td>
</tr>
<tr>
<td>6 B</td>
<td>R.T.</td>
<td>1000</td>
<td>54</td>
<td>0.806</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2400</td>
<td>52</td>
<td>0.763</td>
<td>1.1</td>
</tr>
<tr>
<td>1.5 A</td>
<td></td>
<td>900</td>
<td>94</td>
<td>1.36</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2400</td>
<td>89</td>
<td>1.29</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Figure 3-5a. FE-SEM Photographs of Cross-sections of Carbonized Fs-TS Disk
(Using AType Furnace, Heating Temp.: 900°C)
Figure 3-5b. FE-SEM Photographs of Cross-sections of Carbonized Fs-TS Disk
(Using B Type Furnace, Heating Temp.: 1000°C)
REFERENCES


Chapter 4

Structural Changes of Fullerene by Heat-treatment up to Graphitized Temperature

4-1. Introduction

Fullerenes such as C\textsubscript{60} have attracted many researchers in chemistry and physics regions since their discovery\cite{1}. Fullerene molecules are basically reactive, especially for the addition to the double bonds, such as oxidation\cite{2} and photochemical coupling\cite{3}. The reactivity of fullerenes suggests to be ascribed to the particular bonds in the spherical conjugation.

The high temperature behavior of fullerenes has been neglected due to their sublimation at the temperature range of 700 to 800°C\cite{4}. The present author previously reported that the crude extract of fullerene soot containing C\textsubscript{60} and C\textsubscript{70} was converted to amorphous carbonaceous material at the yield of as high as 90% by moulding into disk form and heating in the sublimation-limiting furnace as described in Chapter 3 \cite{5}. This amorphous carbon changes its structure into hollow spheres with turbostratic skin by further heat-treatment up to 2400°C as described in Chapter 2 \cite{6}. Such products are expected to have some unique properties as new types of carbon materials which are expected useful for some applications.

In this chapter, the structural changes of fullerene by the heat-treatment to the amorphous carbon and to the spherical hollow structure were observed through the successive analysis with X-ray, Raman, FESEM, TEM and STM/AFM. The deformation of molecular framework and conversion of crystal structure of fullerene to amorphous carbon, and the origin of hollow turbostratic spheres are discussed toward the problem described in Section 1-4, based on the successive analysis.

4-2. Experimental

Fullerene soot(Fs) was produced by the arc discharge method using a graphite electrode. The produced soot was separated into two fractions by Soxhlet extraction with toluene. About 10wt% of Fs was soluble in toluene. The toluene-soluble fraction(Fs-TS) was then recovered by evaporation followed by vacuum drying to remove the residual solvent.
Powder form Fs-TS consisted of 76% of C\textsubscript{60} and 22% of C\textsubscript{70} by HPLC analysis.

Powder form Fs-TS was moulded into a disk form using 20mm diameter IR press (Moulding pressure : 6MPa). The sample was heat-treated to 900°C by a heating rate of 4°C/min at the bottom of the quartz tube (20mm long) to suppress the sublimation of fullerenes. Ar gas replaced the air in the tube before heat-treatment and flowed at the top of the tube during heat-treatment. Carbonized disk was heated further to 1300, 1500, 1800, 2000 and 2400°C under Ar flow.

Fs-TS, carbonized, and graphitized disks were analyzed with X-ray diffractometer (Rigaku, Geigerflex) and Laser Raman spectroscopy (Nippon Bunko, NRS-2000, Wavelength : 514nm), and observed under TEM (JEOL, JEX-100CX, Accelerate Voltage : 80kV), FE-SEM (JEOL, JSM-6320F) and AFM/STM (DI, NanoscopeIII). The disk was cut into a thin plate with a diamond microtome to observe under TEM.

4-3. Results
4-3-1. Weight and compositional changes

Figure 4-1 shows the yields of total residue and the toluene insoluble fraction after the heat treatment of Fs-TS disk. When the sublimation was limited by putting the disk in the bottom of the tube, Fs-TS disk was converted into the toluene insoluble product at the yield of as high as 94wt% after the heat-treatment to 900°C. The toluene insoluble fraction markedly increased in a similar temperature range of the sublimation although ca.10% of TI was produced at as low as 300°C. Such reactive components are subjected to be studied in detail.

4-3-2. Changes in the chemical structure

Figure 4-2 shows the Raman spectra of Fs-TS before and after heat-treatment. The spectrum of Fs-TS showed two major peaks at 1420 and 1560cm\textsuperscript{-1} which are assigned to the "pentagonal pinch" vibration of the 5-membered ring (See Section 1-1-3) and to the ring deformation of the 6-membered ring, respectively[7]. The spectrum showed no change below 700°C of heating temperature. The 1420cm\textsuperscript{-1} peak disappeared after the heating to 1200 or 1300°C, suggesting the breakage of 5-membered ring. A peak at 1360cm\textsuperscript{-1}, which is known to be characteristic of non-graphitizable carbon[8], appeared after the heat-treatment to 800°C. Another peak at 1560cm\textsuperscript{-1} disappeared by 800°C, suggesting the loss of spherical structure in C\textsubscript{60}, and another new peak appeared around
1600 cm\(^{-1}\) which is typically ascribed to the graphitic layer structure. The further heat-treatment shifted it to a higher wave number of 1610 cm\(^{-1}\) and sharpened gradually, growth of hexagonal plane being suggested\[9\].

4-3-3. Graphitic change

Figure 4-3 shows the X-ray diffraction patterns of Fs-TS before and after heat-treatment at 500 to 900°C. The pattern of Fs-TS clearly shows the peaks at 10°, 11°, 18° and 21° due to the f.c.c. crystal structure of C\(_60\)[10], and the crystalline size of 12-22 nanometers according to the half-height width. The toluene-insoluble fraction separated from the Fs-TS after the heat-treatment at 500°C also showed clearly the diffraction patterns due to the same f.c.c. crystal, indicating that crystal keeps its molecular location at the transformation from toluene-soluble fullerene to toluene-insoluble species. The toluene-insoluble fraction became amorphous when heat-treated to 1000°C, molecular or crystal forms of the fullerene being deformed completely by this heat-treatment temperature.

Figure 4-4 shows the diffraction patterns after the heat-treatment at 900, 1500, 1800 and 2400°C, respectively. The material stayed amorphous by the heat-treatment upto 1500°C, and then showed a rather sharp peak at 26° which is superimposed on a very broad peak. Appearance of turbostratic stacking of the graphitic planes is indicated[11]. The two peaks were both intensified by the graphitization at 2400°C.

The Raman spectra in Figure 4-2 showed a marked change by the heat-treatment at 1800°C where the two peaks at 1360 and 1610 cm\(^{-1}\) were markedly intensified and sharpened. Both layered and non-stacked hexagonal planes were found present upto 2400°C.

4-3-4. Microscopic observation

TEM images of Fs-TS heated at 900, 1800 and 2400°C are illustrated in Figure 4-5. The photographs showed randomly arranged carbon plates in the product at 900°C. The heat-treatment at 1800°C produced spherically-aligned hexagonal layers of several sheets in the randomly oriented planes. The heat-treatment at 2400°C emphasized the layered stacking of the curved planes at the skin of sphere. The inside of the sphere appeared vacant.

Figure 4-6 illustrates FE-SEM photographs of the surfaces of Fs-TS disk heated at 2400°C. These images are of enough resolution to
indicate that the graphitization at higher temperature induced randomly-shaped grains with several 10nm microdomains.

Figure 4-7 shows low magnification AFM and STM images of the surfaces of Fs-TS disk and its heat-treated ones at 900 and 2400°C, respectively. The fullerene was revealed by AFM to consist of the tens-nanometer grains of fullerene molecules in the disk. Heat-treatment at 900 and 2400°C appeared to maintain the shape and size of the grain unit as observed at the level of magnification although the subunits in the grain appeared to grow by the heat-treatment. Such a size of microdomains is similar to that of micro roughness on the surface observed by FE-SEM. The growth of subunit may reflect the changes in the microstructure of molecular crystal to the hexagonal plane.

Higher magnification of STM in Figure 4-8 indicates superstructure of graphite basal planes in a particular zone the graphitized disk of fullerene at 1800°C.

4-4. Discussion

Figure 4-9 illustrates the scheme of the structural changes of Fs-TS during heat-treatment. While the toluene insoluble fraction appeared to maintain bucky ball structure of C_{60} by the heat-treatment below 800°C, the collapse of molecular structure of fullerene occurred above 800°C. This collapse seems to be initiated by the cracking of 5-membered rings as suggested by reduced intensity of 1360cm\(^{-1}\) peak; X-ray diffraction suggests that the collapse of intermolecular as well as intramolecular structure occurred in the same temperature range.

The carbonaceous products from Fs-TS at 900 or 1000°C have an amorphous structure which consists of small hexagonal carbon planes of several nanometers size with no orientation in their arrangement. The development of stacked layers from this amorphous carbon started above 1800°C to show peripherical layers, the size of spheres appearing to be limited by the crystalline size of the starting fullerene. It should be noted that the graphitized Fs-TS carries similar structure to that of graphitized soot material by the same heat-treatment under TEM[5,10,13].

Both Fs-TS disk and its graphitized product look like the assembly of 5-20nm micrograins. Thermosetting nature of fullerene maintains basically its crystal size and the nanoscopic unit through the carbonization in the solid phase and graphitization up to 2400°C, although some adhesion of the grain and marked changes of chemical as well as crystal forms take
place. The microstructures of the components are completely different in the starting fullerene and graphitized one: the former is the microcrystallite of fullerene whereas the latter is hollow sphere with the periherical turbostratic layers. These periherical turbostratic layers seem to carry the surface with the superstructure of graphitic basal plane as the observed under high magnification STM. The superstructure of the graphitic material is observable under STM only when stacked layers are bent. Such a bent layer can be naturally built, inheriting the C₆₀ crystal form to be transformed in the spherical shape of the turbostratic structure, which is stable enough to survive a high temperature around 2400°C.

4-5. Conclusion

Structural changes of C₆₀ and C₇₀ mixture during the heat-treatment up to 2400°C were studied by observing the carbonized disk of the fullerene with Raman spectra, X-ray diffraction, FE-SEM, TEM and AFM/STM. The fullerene lost its five-membered ring and its fcc crystal structure by the heat-treatment at 800°C, as revealed by Raman spectra and X-ray diffraction, forming hexagonal planes by 1300°C which were randomly arranged. Further heat-treatment allowed some stacking of layer which grows to dominate, reducing the randomly oriented planes. The graphitized temperature up to 2400°C provided a very sharp peak at 26°, suggesting formation of stable turbostratic layer. The TEM characterized turbostratic stacking of 3 to 4 layers. A series of observation under AFM/STM and TEM indicate the crystal of the fullerene, amorphous grain of hexagonal planes, hollow sphere are all in the same range of size around 10-20 nm. Such microdomains induced micro-roughness as observed by FE-SEM on the surface of the carbon disk. Superstructure of hexagonal plane was observed on the surface. A kind of solid state carbonization of the fullerene is suggested to maintain the dimension of its crystal into the spherical microdomain, even if its marked structural changes take place within the unit.
Figure 4-1. The Residual Weight and the Yields of Toluene-insoluble Fraction After the Heat-treatment of Fs-TS Disk
Figure 4-2. Raman Spectra of Fs-TS before and after the Heat-treatment
f.c.c. crystal of C60
Crystalline Size: 12-22 nm

Figure 4-3. X-ray Diffraction Patterns of Fs-TS and Toluene-insoluble Fractions of its Heated Products

*Note: The image contains an X-ray diffraction pattern with peaks at different temperatures (R.T., 500°C, 900°C) showing the crystalline size of C60.*
Figure 4-4. X-ray Diffraction Patterns of Heat-treated Fs-TS

(002) of graphite

2400°C
1800°C
1500°C
900°C

2θ (deg)
Figure 4-5. TEM Bright Field Images of Heattreated Fs-TS Disk
HTT: (a) 900°C    (b) 1800°C    (c) 2400°C
Figure 4-6. FE-SEM Images of the Surface of Heated Fs-TS Disks Heattreated at 2400°C
Figure 4-7. (a) AFM Image of the surface of Fs-TS Disk, (b-d) Low Magnification STM Images of the Surface of the Heat treated Fs-TS Disk

HTT: (b) 900°C, (c) 1800°C, (d) 2400°C
Superstructure of basal plane

ca. 0.25nm

Figure 4-8. High Magnification STM Image of the surface of Fs-TS Disk Heattreated at 1800°C

A : A part to indicate the superstructure of basal plane
B : Model of superstructure observed in STM image
Figure 4-9. The Scheme of Structural Change of Fs-TS Through the Heat-treatment
REFERENCES


5-1. Introduction

Fullerenes of unique sp²-carbon molecules have attracted many researchers to work on their selective production[1] and application[2] as described in Section 1-1. Limited yield of C_{60} and trivial application are now reducing quantity of such study (Section 1-1-2), although their potentials are still large as revealed by carbon nanotube of their homologues[3].

The present author has described the carbonization reactivity of C_{60} and its relatives to clarify the successive reactivity of C_{60} in its preparation[4] and new application as a precursor for unique carbon material of amorphous nature[5,6]. Such a reactivity includes the conversions of pentagon to hexagon of carbon ring and of molecular sphere to graphitic plane.

In this chapter, products in the preparation of C_{60} from graphite through arc discharge were separated and analyzed to clarify the correlation in their structure and their successive conversions.

As described in Section 1-1-2, the products at the anode were collected as soot, which are further fractionated into toluene soluble C_{60}, C_{70} and some large fullerene, toluene insoluble but quinoline soluble giant fullerenes, and insoluble amorphous carbon and graphitic particles[1,7]. Their separation and structural analysis to consider about the problem proposed in Section 1-3 are the objectives of this study to suggest the conversion scheme of carbon clusters and application of amorphous carbon particles of the major product in the arc discharge method.

5-2. Experimental

Fullerene soot was produced by arc discharge method using graphite electrode in an arc chamber (Shinku Yakin Co.; Type II-S). Produced soot was separated into two fractions by Soxhlet extraction with toluene; toluene soluble (Fs-TS) and toluene insoluble (raw Fs-TI). Fs-TS fraction consists of 76wt% of C_{60}, 22wt% of C_{70} and a small amount of higher fullerene(beyond C_{76}).
Raw Fs-TI was separated by a precipitation method in acetone into graphitic carbon and amorphous soot. Amorphous soot was then dispersed in quinoline and separated into soluble (Fs-TIQS) and insoluble (Fs-QI) fractions.

The insoluble fractions were heat treated under following conditions; 5°C/min of heating rate, holding 1 or 2h at prescribed temperatures under N₂ atmosphere in the bottom of T-shape tube.

The oxidation of Fs-QI was observed at 10°C/min of heating rate and holding time of 1h under air flow (N₂/O₂=4/1) at prescribed temperatures, using TG/DTA apparatus (Seiko co.; SSC5200), or in a tube furnace.

Fs-TI, Fs-QI and their heat treated products were characterized by density separation using CsCl/water gradient [8], X-ray diffraction (Rigaku Co.; Geigerflex; target: CuKα), Raman spectroscopy (Nippon Bunko Co.; laser wavelength: 514.8nm) and transmission electron microscope (TEM, JEOL Co.; JEM-100CX, accelerate voltage: 80kV). The soluble fractions were analyzed by high performance liquid chromatograph (HPLC, Hitachi Co.; D-5200, column: ODS, fluent: n-hexane, detector: UV-vis 280nm) and time-of-flight mass spectroscopy (TOF-MS, JEOL Co.; JMS-ELITE II).

5-3. Results

5-3-1. Separation of Fullerene Soot

Fullerene soot was divided into four fractions, using such procedures as the extraction and gravimetric separation; toluene-soluble (Fs-TS), toluene-insoluble and quinoline-soluble (Fs-TIQS), quinoline-insoluble (Fs-QI), and fragment of graphite. Table 5-1 illustrates the yields of these fractions. Figure 5-1a shows the X-ray diffraction pattern of raw Fs-TI and Figure 5-2 shows the density profile of Fs-QI extracted from raw Fs-TI. X-ray pattern clearly shows that Fs-TI contained graphite substance. This graphitic portion occupied ca.15wt%. Major portion of Fs-TI had ca.1.6g/cm³ of density while the graphitic substance had 2.2g/cm³ as shown in Figure 5-2. Figure 5-1b shows the X-ray diffraction profiles of Fs-TI after the density separation in acetone. The peak assigned for graphitic portion (2θ=26.5°) markedly decreased after the separation. The estimated content of graphitic substance in Fs-TI after the separation was ca. 4wt%.
5-3-2. The Structural Analysis of Fs-TI before and after Heat-treatment

Figure 5-3 shows TEM bright field images of Fs-TI and its heated products at 400 to 800°C. Fs-TI appears ultrafine particles of amorphous carbon with the size range of 20-150nm. After the heat-treatment upto 800°C, Fs-TI maintained the same TEM images.

Figure 5-4 shows the X-ray diffraction patterns of Fs-TI and its heat-treated products at various temperature. Fs-TI showed a very broad peak at $2\theta=16^\circ$ in addition to sharp peak ascribed to the remaining graphitic substance, suggesting the atomic distance of approximate 0.55nm. Fs-TI heat-treated below 800°C maintained diffraction patterns except for the appearance of an additional peak at $2\theta=9^\circ (d=0.79\text{nm})$. After heat-treated at 800°C, the peak at $2\theta=16^\circ$ shifted to a higher angle of $2\theta=21^\circ$.

Figure 5-5 shows the Raman spectra of Fs-TI and its heat-treated products. In addition to two peaks being observed with conventional carbon materials (around 1360cm$^{-1}$ and around 1590cm$^{-1}$), Fs-TI before heat-treatment showed an extra peak assigned for 5-membered ring[9] (see Section 1-1-3) around 1420cm$^{-1}$. This peak was observed only when the laser intensity during the measurement of Raman scattering was very low. This peak disappeared by the heat-treatment at 800°C, where significant changes were also observed in X-ray diffraction.

It was reported by Weber et al. that a few wt% of fullerenes was obtained from the residual soot more after heat-treated at 300-600°C[10] (see Section 1-3). Table 5-2 illustrates the extraction yield (by toluene) of Fs-TI and Fs-QI after the heat-treatment at 400°C. Heat-treated Fs-TI provided 0.2-0.3wt% of C$_{60}$ and C$_{70}$, while heat-treated Fs-QI did only 0.02-0.05wt%.

5-3-3. The Structural Analysis of Fs-TIQS

Figure 5-6a shows the TOF-mass spectra of Fs-TIQS. The molecular weight of Fs-TIQS distributed from ca. 700 to ca. 4800, which corresponding to the number of carbon atoms, from ca. 60 to ca. 400. Figure 5-6b shows magnified spectra. The peaks exactly positioned by 24 of m/z (the equivalent of C$_2$ intervals) as reported by Shinohara et al.[7].

Figure 5-7 shows the Raman spectra of Fs-TIQS. Similar to Fs-TI, basically two peaks common to the carbon materials were observed except for a peak at 1420cm$^{-1}$.
5-3-4. The Structural Analysis of Fs-QI

Figure 5-8 shows TEM bright field images of Fs-QI. Fs-QI appears to consist of spherical fine particles which showed similar images to those of Fs-TI; circular walls of graphitic layers were found in the large particles.

Figure 5-9 shows TG profile of Fs-QI in air, comparing with those of Fs-TS and some commercial carbon blacks (MA600 and Ketjen Black). The temperature range of the oxidation of Fs-QI was much lower and wider than those of other carbons, indicating broader variation of graphitic structure.

Figure 5-10 shows the X-ray diffraction patterns of Fs-QI and its residual materials after the combustion at 400 and 500°C in air flow. The weight losses by the combustion at these temperatures were 35wt% and 39wt%, respectively. The residual materials showed a broad peak at 2θ=25° superimposing the sharp peak of typical graphite. A peak at 2θ=15° in Fs-QI disappeared. Figure 5-11 shows the Raman spectra of these materials. The 1420cm⁻¹ peak disappeared in the residual material at 400°C, suggesting the selective combustion of pentagon-containing component.

5-4. Discussion
5-4-1. The separation of Fullerene Soot

The present study clarified that four kinds of materials are present in the fullerene soot produced at the anode of graphite by arc discharge. They are separated by density separation and solvent extraction procedures. Toluene extracted, as extensively reported, C₆₀ and C₇₀ and larger fullerenes (C₇₆-C₁₂₀) whose yields are 76, 22 and 2wt%, respectively. Their molecular weight increased exactly by 24 each, indicating successive growth of carbon atoms in the clusters. Another characteristic is the peak around 1420cm⁻¹ in Raman spectra which is assigned to pentagonal unit[9]. TI-QS consisted of further larger fullerene families, of which molecular weight distributes from 60 to 400. They carry a peak of 1420cm⁻¹ in their Raman spectra, suggesting the presence of pentagon units (Section 1-1-3). They provided a little amounts of C₆₀ and C₇₀ which are produced pyrolysis or included in Fs-TIQS grains not to be extracted by toluene.

Fs-QI consists of two components, amorphous carbon soot and graphitic materials, of which yields are 45 and 15wt%, respectively.
according to X-ray diffraction. Their densities are 1.6 and 2.2g/cm³, respectively, hence they are separated by precipitation according to their densities. The amorphous carbon consists of spherical particles which carries graphene planes randomly stacked as X-ray diffraction suggested average interlayer distance of 0.55nm. Pentagonal unit is still observable in this structure. Heat-treatment does provide very little amount of smaller fullerene molecules. Large particles carry some layers of circular hexagonal planes at their surface wall. Their reactivities for the oxidation is high compared to that of the carbon black, in spite of some similarities in their structures[11,12], more amorphous natures and smaller size of graphene plane. The oxidation divided amorphous carbon Fs-QI into two components: one is oxidized below 400°C and the other stayed unburned by this temperature. The latter fraction did not show pentagon unit.

The origin of the graphite particles found in the soot is basically electrode.

5-4-2. Reactivity of Pentagonal Unit for the Oxidation

Fs-QI is found to consist of three components as described above. Their reactivities in the oxidation is related to the two structural characteristics of 1420cm⁻¹ scattering in Raman spectrum and 2θ=16° in X-ray diffraction. These two characteristics may be mutually related. The presence of pentagon units in the carbon plane may cause such a large interlayer distance of carbon planes. So far the size of carbon plane is not observed, however, larger interlayer distance may indicate the smaller plane. The carbon of smaller plane carries generally larger reactivity for oxidation[13]. At the same time, pentagon units in C₆₀ and C₇₀ have been reported to be more reactive against oxygen to form oxidized product, indicating higher affinity to oxygen molecules[14,15]. The two features may dependently or independently bring about the higher reactivity of the component.

5-4-3. Conversion of pentagon unit into hexagon

The present study revealed that the pentagon unit in Fs-TI is rearranged into hexagon by the heat-treatment at 800°C where large fullerenes (~C₄₀₀) and reactive component in Fs-QI are converted into rather graphitic (hexagonal plane) materials. The conversion of C₆₀ and C₇₀ into graphitic plane has been reported to take place also at 800°C[6]. Hence the pentagon is thermally stable upto 800°C.
Such a conversion is very much related to the low yield of C$_{60}$ and its homologue since they appear to be consecutively converted into soot before quenching in the arc discharge. Further heat-treatment allows the growth of hexagonal plane. However it should be noted that the large particle in Fs-QI carries the circular wall of hexagonal planes. Solid state carbonization may not overcome the restriction defined by the size of the molecular crystal.

5-5. Conclusion

Soot produced from graphite through arc discharge was separated into four fractions to analyze their structure. Toluene-soluble fraction carried C$_{60}$, C$_{70}$, and C$_{76}$-C$_{120}$ fullerenes while toluene-insoluble quinoline-soluble fraction (ca. 1 wt%) consisted of larger clusters of C$_{70}$ to C$_{400}$ which have similar framework to C$_{60}$ or C$_{70}$ fullerenes. Graphitic substances in quinoline insoluble fraction were separated through the precipitation in acetone. Reactivity of the quinoline-insoluble fraction free from graphitic substances (15 wt%) revealed two kinds of carbon frameworks in the combustion; one is pentagon-containing system similar to fullerenes (ca. 30 wt%) and rather graphitic, hexagonal system (ca. 45 wt%). Pentagon-containing system in "soot" particle was more reactive to be burnt at as low temperature as 400°C and thermally converted to hexagonal system by the heat-treatment above 800°C.
according to X-ray diffraction. Their densities are 1.6 and 2.2 g/cm³, respectively, hence they are separated by precipitation according to their densities. The amorphous carbon consists of spherical particles which carries graphene planes randomly stacked as X-ray diffraction suggested average interlayer distance of 0.55 nm. Pentagonal unit is still observable in this structure. Heat-treatment does provide very little amount of smaller fullerene molecules. Large particles carry some layers of circular hexagonal planes at their surface wall. Their reactivities for the oxidation is high compared to that of the carbon black, in spite of some similarities in their structures [11, 12], more amorphous natures and smaller size of graphene plane. The oxidation divided amorphous carbon Fs-QI into two components: one is oxidized below 400°C and the other stayed unburned by this temperature. The latter fraction did not show pentagon unit.

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Such a conversion is very much related to the low yield of C\textsubscript{60} and its homologue since they appear to be consecutively converted into soot before quenching in the arc discharge. Further heat treatment allows the growth of hexagonal plane. However it should be noted that the large particle in Fs-QI carries the circular wall of hexagonal planes. Solid state carbonization may not overcome the restriction defined by the size of the molecular crystal.

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Table 5-1. The Yields of Fractions in Fullerene Soot

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fs-TS</td>
<td>10</td>
</tr>
<tr>
<td>Fs-TIQS</td>
<td>1</td>
</tr>
<tr>
<td>Fs-QI</td>
<td>74</td>
</tr>
<tr>
<td>Graphitic Fragment</td>
<td>15</td>
</tr>
</tbody>
</table>
Figure 5-1. X-ray Diffraction Patterns of Fs-TI with Si Standard
(a) Fs-TI as Extracted
(b) Fs-TI after the Density Separation
Figure 5-2. The Density Distribution Profile of Fs-QI as Extracted
Figure 5-3. TEM Images of Fs-TI and its Heattreated Products
(a) Fs-TI  (b) HTT 400°C  (c) HTT 600°C  (d) HTT 800°C
Figure 5-4. X-ray Diffraction Patterns of Fs-TI and its Heat treated Products
Figure 5-5. Raman Spectra of Fs-TI and its Heattreated Products
<table>
<thead>
<tr>
<th></th>
<th>Yield from Original Soot (wt%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₆₀</td>
<td>C₇₀</td>
</tr>
<tr>
<td>TI-400</td>
<td>0.235</td>
<td>0.295</td>
</tr>
<tr>
<td>QI-400</td>
<td>0.025</td>
<td>0.056</td>
</tr>
</tbody>
</table>

TI-400 : Fs-TI heattreated at 400°C, 1h
QI-400 : Fs-QI heattreated at 400°C, 1h
Figure 5-6. TOF-Mass Spectra of Fs-TIQS
(a) An Overall View
(b) Magnified Spectrum at m/z=2000-3000
(c) Magnified Spectrum at m/z=3000-4000
Figure 5-7. Raman Spectrum of Fs-TIQS
Figure 5-8. TEM Bright Field Image of Fs-QI
Figure 5-9. TGA Profiles of Fs-QI, Fs-TS and Some Carbon Blacks in Air
Figure 5-10. X-ray Diffraction Patterns of Fs-QI and its Oxidized Materials
Figure 5-11. Raman Spectra of Fs-QI and its Oxidized Materials
REFERENCES

Chapter 6

Some Properties of Carbon Disk Prepared from Toluene Insoluble Fraction in Fullerene Soot

6-1. Introduction

Fullerene has attracted broad interests because of its unique structure[1] (see Section 1-1-3). However, practical application has not been achieved due to its low yield and hard purification[2] (Section 1-1-2). Carbon nanotube produced at the same time is now prepared selectively[3,4] and its application is extensively studied[5,6] (see Section 1-1-5). The present author has described that C_{60} and C_{70} provided a unique carbon of hollow spheres (Chapter 2) which can give an artifact of significant strength in a very high yield by moulding and carbonization to suppress their sublimation[7] (Chapter 3). However, 10-15wt% yield of toluene soluble fraction including 76wt% of C_{60} and 22wt% of C_{70} in the fullerene soot is too small for the practical application (Section 1-1-2). The present author[8] and Ugarte[9] also reported that the soot itself provided similar hollow spheres as described in Section 1-3.

In this chapter, the carbonization of toluene insoluble fraction in the fullerene soot was studied by moulding to prepare the carbon artifact of unique properties and strength. The interaction among particles can be discussed here, i.e., adhesion and fusion of the toluene-insoluble particles were particularly interested to develop the strength. Some properties of the artifact due to the nano hollow spheres were measured to suggest some application for this abundant material.

6-2. Experimental

Fullerene soot was produced by arc discharge method using graphite electrode in commercial arc chamber (Shinku Yakin Co.; Type II-S). Produced soot was separated into two fractions by Soxhlet extraction with toluene; toluene soluble (Fs-TS) and toluene insoluble (raw Fs-TI). Fs-TS fraction consists of 76wt% of C_{60}, 22wt% of C_{70} and small amount of higher fullerene (beyond C_{76}). Raw Fs-TI had two fractions, which were isolated by precipitation method in acetone into amorphous soot(Fs-TI) and graphitic substance as described in Chapter 5 [10].
Isolated Fs-TI free from graphitic substance was then moulded into disk by IR press (20mmϕ). Moulding pressure was ca. 6MPa and sample weight was ca. 0.5g (the thickness of disk was ca. 1.8mm). Moulded disk was heattreated at 900°C placing it in the bottom of T-type tube under following conditions; under N₂ atmosphere, 5°C/min of heating rate and 1h of holding time. Some disks were further heattreated at higher temperature (1200, 1500, 1800 and 2400°C) in a tube furnace.

The structure of heattreated disks was analyzed using X-ray diffraction, Raman spectroscopy and transmission electron microscopy (TEM). The samples to be observed by TEM were cut by a diamond knife. The electric conductivity of these disks was measured by four probe method after cut in a rectangular shape.

The specific surface area and pore distribution were measured by BET and Dubinin methods, using the same adsorption apparatus.

6-3. Results

6-3-1. The yield of the Disk Derived from Fs-TI

Table 6-1 summarizes the yield of Fs-TI disk at 900 and 2400°C. The yield of disk carbon from Fs-TI stayed at 900°C as low as 85wt% even in the bottom of T-type tube, while Fs-TS was reported to provide 94wt% of carbonized products at 900°C by inhibiting the sublimation of C₆₀ and C₇₀ fullerenes[7]. Therefore the observed weight loss of Fs-TI may be due to remaining substances such as residual solvent (toluene) or strongly adsorbed water. The graphitization provided a yield of 81wt% based on initial Fs-TI weight, indicating that major component of carbonized product stayed up to the graphitization temperature.

Figure 6-1 shows the appearances of Fs-TI disks heattreated at 900°C(a), and 2400°C(b). After the heat-treatment, the disk basically maintained its shape without any shrinkage. It should be noted that Fs-TI including graphitic substance failed to give a carbon disk of sufficient strength.

6-3-2. The Structure of the Disks Derived from Fs-TI

Figure 6-2 shows the X-ray diffraction patterns of Fs-TI and its derived disks heattreated at 900, 1200, 1500, 1800 and 2400°C, comparing with that of powder Fs-TI heattreated up to 2400°C. The sharp peak at 26.5° observed in the samples regardless of the heat-treatment originates from the residual graphitic substance (4wt%) derived from the electrode. Fs-TI exhibited a broad peak at 16°, which indicates the
extraordinary wide interlayer distance of average 0.55nm, as described in \textit{Chapter 5} [10]. Heat treated disk at 900°C showed gave a shift of the peak to a higher angles of around 20° which was still very broad. The heat-treatment at 1800°C, gave a shoulder peak at 26° which is ascribed to turbostratic layered structure. The heat-treatment at 2400°C sharpened the peak which was still located at 26°. A powder of Fs-TI after the heat-treatment at 2400°C provided a similar peak to that of the disk heat treated at the same temperature, indicating that both carbons have similar turbostratic layers of graphitic planes regardless their forms at the carbonization.

Figure 6-3 shows FE-SEM photographs of the broken surface of Fs-TI disk heat treated at 2400°C. The grains of tens micrometer, and smaller particles of several hundreds nanometer were observed on this surface, the latter particles being located on the boundaries of larger grains. Fs-TI forms the disk as the aggregates of tens micrometer grains with the binder of small particles.

Figure 6-4 shows TEM bright field images of Fs-TI disks heat treated at 900 and 2400°C. The disk heat treated at 900°C appeared clearly as the assembly of amorphous particles, whereas the disk heat treated at 2400°C did not show any boundary of particles while thin turbostratic layers were observable in the wall of hollow spheres of irregular shape as described in \textit{Section 1-3, Chapter 4 and 5} [10,11]. The adhesion of Fs-TI particles may occur between these temperatures and is expected to increase the macroscopic hardness of the disk.

6-3-3. \textit{The Properties of the Disk Derived from Fs-TI}

Table 6-2 summarizes some properties of Fs-TI disk before and after the heat-treatment. The heat-treatment at 900°C increased the surface area of the disk up to as high as 490m²/g and the electric conductivity of the disk to the level of semiconductor. Such properties were maintained up to 1800°C. A drastic change of such properties occurred after the heat-treatment above 1800°C, decreasing its bulk density and surface area. It should be noted that the graphitized disk still carried surface area of 183m²/g. Its conductivity successively increased by the heat-treatment at higher temperatures, indicating closer packing and growth of hexagonal layers of hollow particles. The bulk density of the disk stayed at 1.9g/cm³ by the heat-treatment up to 900°C and then decreased gradually to a very low density of 1.2g/cm³ by the graphitization.
Figure 6-5 shows the pore size distribution profile of Fs-Ti disk after the heat-treatment at 2400°C (a) compared with that of powder Fs-Ti after the heat-treatment at the same temperature (b). In both profiles, a sharp peak at the radius of 20Å was observed. The specific surface area of graphitized Fs-Ti powder was still as large as 169m²/g, being very close to that of graphitized Fs-Ti disk. Any sharp peak did not appear in the profiles of both disk and powder heat-treated at lower temperatures. Therefore, the formation of the mesopore of 20Å is related to the turbostratic layer system which is a characteristic of graphitized Fs-Ti. The moulding of Fs-Ti leads to the adhesion of soot particles during the heat-treatment, however, it did not affect the characteristic of Fs-Ti graphitization process, providing nanopores of 20Å regardless of the forms.

6-4. Discussion

The present study describes the production of a unique carbon artifact from toluene insoluble fraction of fullerene soot (Fs-Ti) free from graphitic substance. Removal of graphitic substance is very essential to prepare the artifact of considerable strength. The infusible graphitic powders may inhibit the adhesion of Fs-Ti by locating on the surface of the latter grains.

The strength of the disk appears to develop through the close packing of the grains at the moulding and adhesion by the heat-treatment up to 2400°C. The Fs-Ti consists of grains and particles, of which diameters range 10-50μm and 20-150nm, respectively. Such size distributions allow the denser packing. The closely packed grains adhere each other above 900°C, where the major structural change in the fullerene soot takes place by converting the pentagon to hexagon carbon plane. Such a change of carbon network may bring about major displacement of carbon atoms, inducing the partial fusion of the grains at least at the contacted boundary of grains. Chapter 5 reported that a portion (30wt%) in Fs-Ti carried pentagon units while the other (45wt%) is free from the pentagon[10]. Hence the portion carrying the pentagon may work as the binder. The small particles may be the fraction.

Rather lower yield of Fs-Ti to carbon than that of Fs-TS to carbon suggests some remaining of extraction solvent, toluene in this study, which may play some roles to give a liquid phase, before its evolution. The growth and rearrangement of hexagonal planes into a turbostratic stacking take place above 900°C according to the calcination and
graphitization temperatures. Such changes may also contribute to the increase of strength and electric conductivity.

The unique characteristics of the present artifact are large surface area, uniform pore size of 20Å, and low density which are maintained after the graphitization. Very random stacking of hexagonal planes at the calcination range and hollow nanospheres of hexagonal layers at the graphitic range are responsible to such characteristics. Unique application can be designed for adsorption and separation.

The basic structure of the present carbon artifact obtained from Fs-TI is same to that from Fs-TS which contains C\textsubscript{60} and C\textsubscript{70}[8]. This fact indicates two significance. Fs-TI yield in the arc discharge is as high as 90wt\% in the anode product while that of Fs-TS is only 10wt\%. Hence the supply of Fs-TI is much more abundant than that of Fs-TS. The carbon yield from Fs-TI is unexpectedly lower than that of Fs-TS. More complete removal of the solvent can be designed. Removal of graphitic substance may not be a problem because density separation in acetone precipitates graphitic substance selectively[10].

Another significance is the consecutive changes of C\textsubscript{60} to soot-like amorphous carbon through the some steps of the thermal process which take place in the arc discharge chamber being reproduced by the slow heating upto the graphitization temperature. Some ideas to moderate the conversions of C\textsubscript{60} may increase its yield in the arc discharge.

6-5. Conclusion

Moulding and successive carbonization of toluene-insoluble fraction in the fullerene soot were studied to prepare carbon disk of unique properties. Separation of graphitic component by precipitation in acetone allows the fraction to be mould and carbonized into a carbon disk of significant strength. The disk was found to consist of large grains and fine particles to be densely packed and adhered each other through partial fusion at their periphery. The disk exhibited density and surface area of 1.9g/cm\(^3\) and 491m\(^2\)/g by the carbonization at 900°C and 1.6g/cm\(^3\) and 183m\(^2\)/g at 2400°C, respectively. The random stacking of hexagonal planes and micro hollow spheres with 2 to 3 layers of planes appear origins of above properties at 900 and 2400°C, respectively. The conversion of pentagon to hexagon around 900°C may cause the partial fusion of small particles. The pore size distributed almost exclusively around 20Å. Some unique application can be designed.
Table 6-1. The Yields of Heat treatments of Fs-TI Disk

<table>
<thead>
<tr>
<th>HTT (°C)</th>
<th>Yield (wt% ; Fs-TI Base)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>85</td>
</tr>
<tr>
<td>2400</td>
<td>81</td>
</tr>
</tbody>
</table>
Figure 6-1. The appearances of heat-treated Fs-Ti disks
(a) HTT : 900°C,   (b) HTT : 2400°C
Figure 6-2. X-ray Diffraction Patterns of Fs-TI Disk and its Heatreated Products
Figure 6-3. FE-SEM Photographs of the Broken Surface of Fs-TI Disk Heattreated at 2400°C
Figure 6-4. TEM Images of Heat treated Fs-Ti Disks
(a)(b) HTT $900^\circ$C, (c)(d) HTT $2400^\circ$C
Table 6-2. Some Properties of Fs-TI Disk and its Heat treated Products

<table>
<thead>
<tr>
<th>HTT (°C)</th>
<th>B.D. (g / cm(^3))</th>
<th>S.S.A. (m(^2)/g)</th>
<th>E.C. (Scm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.T.</td>
<td>1.9</td>
<td>286</td>
<td>&lt;10(^{-3})</td>
</tr>
<tr>
<td>900</td>
<td>1.9</td>
<td>491</td>
<td>2.72</td>
</tr>
<tr>
<td>1500</td>
<td>1.8</td>
<td>446</td>
<td>31.0</td>
</tr>
<tr>
<td>1800</td>
<td>1.6</td>
<td>294</td>
<td>47.5</td>
</tr>
<tr>
<td>2400</td>
<td>1.6</td>
<td>183</td>
<td>58.2</td>
</tr>
</tbody>
</table>

B.D. : Bulk Density  
S.S.A. : Specific Surface Area  
E.C. : Electric Conductivity
Figure 6-5. Pore Size Distributions of Fs-TI Heattreated at 2400°C
(a) Graphitized in disk form
(b) Graphitized in powder form
REFERENCES

9. Ugarte, D., Carbon, 1994, 32, 1245
10. Egashira, M., Koura, H., Korai, Y. and Mochida, I., to be submitted to Carbon
Chapter 7

Effects of Fullerene Addition on the Carbonization of Synthetic Naphthalene Isotropic Pitch

7-1. Introduction

The chemical and physical stabilities of fullerenes have been intensively investigated\[1, 2\] (see Section 1-1 and 1-2) since they were first synthesized in large quantities and isolated\[3\]. Under the irradiation of visible light or thermally at 200–400°C, atmospheric oxygen is added to fullerenes to produce epoxide or peroxide groups\[4\].

On the other hand, fullerenes are known to be stable even at high temperature in inert atmospheres and in absence of light (see Section 1-2). It has been reported that they sublime around 850°C\[1\]. However, the present author previously reported that toluene soluble fraction of fullerene soot (the mixture of C\(_{60}\), C\(_{70}\) and a small amount of higher fullerenes) was carbonized to give very high yield of the amorphous carbon at 900°C and microcellular hollow particles on graphitization\[5,6,7\].

In this chapter, fullerenes were co-carbonized with synthesized isotropic pitch derived from naphthalene. A study of the carbonization process of the mixture, compared with reported acceleration effect towards hydrogenation described in Section 1-2-2, and how the chemical states of fullerene change during the carbonization of pitch were to be discussed in this chapter. Fullerenes have been reported to be hydrogen acceptors from hydrogenated aromatic hydrocarbons around 400°C\[8\] (see Section 1-2). It is our concern whether fullerene can dehydrogenate the synthetic pitch to modify its carbonization and what chemical changes take place with fullerene in such a dehydrogenative step.

7-2. Experimental

An AR isotropic pitch synthesized from naphthalene was provided by Mitsubishi Gas Chemical Corporation(EP-186). Fullerene was obtained as the crude toluene soluble extract from the fullerene...
soot produced by arc discharge method (using conventional arc discharge furnace manufactured by Shinku Yakin Corporation). The conditions of discharge were 450A current, ca. 25V voltage, and He flow at ca. 6kPa. Fullerene-containing soot was then extracted by Soxhlet with toluene. The toluene-soluble fraction consisted of 76wt% of C_{60} and 22wt% of C_{70} by high performance liquid chromatograph (HPLC : Hitachi, D-5200) analysis. The ground pitch and powder fullerenes were mixed in the ball mill, the content of fullerene being 10, 20, 30, 50 and 80wt%.

The mixture of pitch and fullerene (ca. 0.5g, otherwise indicated) was placed in the bottom of the test-tube (25mm diameter) and carbonized at 600°C and ambient pressure under N_{2} flow by 10°C/min of heating rate. The carbonized product was then calcined to 1000°C in an alumina boat under Ar flow. The resultant carbons were observed by polarized optical micrograph (Olympus ; BH2) and analyzed by X-ray diffraction (Rigaku ; Geigerflex) and FT-IR (JEOL ; JIR-5500). The unreacted fullerene in the carbonized product was extracted by Soxhlet with toluene and analyzed by HPLC.

7-3. Results

7-3-1. The Effects of Fullerene on Carbonization of Pitch

Figure 7-1 summarizes the carbon yields from the mixtures after the carbonization at 600 and 1000°C. The AR and fullerene alone gave yields of 75 and 95wt% at 600°C, respectively. The yields from the mixtures were higher than those expected from the yields of their single carbonization, some interaction being suggested between them. The carbon yields of AR and fullerene at 1000°C were 71 and 25wt%, respectively. A major portion of the fullerene sublimed at around 800°C under N_{2} flow as previously reported. A maximum yield of 90wt% was observed for a mixture containing 30wt% fullerene, which was much higher than expected for a linear blending behavior(82wt%). More fullerene in the mixture rapidly decreased the yield, suggesting sublimation of uninteracted fullerene remaining in the carbonized mixture.

Figure 7-2 illustrates the appearances of products from the mixtures in the glass tube after carbonization at 600°C. The addition of fullerene appears to inhibit the expansion of pitch during
solidification. The addition of more fullerene resulted in a little more expansion. The inhibition of swelling was most effective at a content of 10wt% fullerene.

Figure 7-3a-j illustrates the optical micrographs of carbons produced at 600°C from the mixtures of AR and fullerene at variable mixing ratios. The coke from AR appeared to have a very thin wall under low magnification. The wall of coke was thickened and the pores became smaller by addition of 10wt% of fullerene. Larger amount of fullerene produced a similar pore distribution and wall thickness regardless of its content, although the expansion was minimum at 10wt%.

The AR alone provided flow domain texture under higher magnification. Addition of fullerene at 10wt% introduced large mosaic texture with major flow domain. Fullerene at the 20wt% level provided a number of deformed anisotropic spheres dispersed in the major isotropic matrix. More fullerene reduced the number and size of spheres in the isotropic texture.

7-3-2. The Chemical State of Fullerene in the Coke

Table 7-1 summarizes the contents of fullerenes in the carbonized pitch/fullerene mixture at 600°C. Approximately 30wt% of the fullerene in the initial mixture was converted to toluene insoluble materials by the reaction with the pitch when the added fullerene content was between 30wt% and 50wt%. The relative contents of C_{60} and C_{70} in the extracted fractions from the carbonized product remained the same value as their initial ratio, suggesting that their reactivities were similar in the pitch.

Figure 7-4 shows the FT-IR spectra of semi-cokes carbonized at 600°C resulting from AR isotropic pitch - fullerene mixtures at the fullerene contents of 0, 20, 50 and 100wt%. The C_{60} molecule shows only 4 peaks[12] (517cm^{-1}, 552cm^{-1}, 1183cm^{-1} and 1429cm^{-1}) in high sensitivity because of its high symmetry (see Section 1-1-3). When the fullerene content of the mixture was below 20wt%, these peaks did not appear. Fullerene contents higher than 20wt% exhibited such peaks in the product.

Figure 7-5 shows the X-ray diffraction patterns of semi-cokes carbonized at 600°C from AR isotropic pitch - fullerene mixtures at various contents of fullerene. A broad peak appeared around 18° when
20wt% of fullerene was added. Definite peaks of fcc crystal of $C_{60}$ appeared when fullerene was added at levels above 30wt%.

Figure 7-6 shows TEM bright field images of cokes obtained from AR alone and its mixtures with fullerene carbonized at 600°C. Many non-transparent spheres of ca. 10 nm size were observed dispersed in the stacked layers in the semi-cokes of the mixtures. The content of such spheres increase in the semi-coke as the fullerene contents increased from 10 to 30 wt%.

7-3-3. The Intermediate Products

Table 7-2 summarizes the H/C ratios and solubilities of products from AR and mixtures heated at 400, 425 and 450°C. The addition of fullerene decreased hydrogen content and increased the toluene-insoluble fraction in the product above those expected from their individual carbonizations. The toluene-soluble fraction contained very little fullerene when fullerene content was below 30wt%.

Figure 7-7a-i shows the micrographs of intermediate products from AR alone and the mixtures (10wt% and 30wt%) heated at 400°C, 425°C and 450°C, respectively. Heat-treatment at 400°C produced a number of small anisotropic spheres. After heating to 425°C, mesophase spheres were found coalesced in the product from AR alone. In contrast, smaller spheres were still dispersed in the carbonized mixture containing 10wt% fullerene. The mixture of 30wt% of fullerene appeared to complete the carbonization at 425°C where very small anisotropic regions were dispersed in the isotropic matrix. When heated at 450°C, all samples provided similar textures to those of the semi-coke carbonized at 600°C.

7-4. Discussion

The addition of fullerene induced two apparent effects on the carbonization of isotropic pitch; one is the acceleration of the pitch carbonization rate and the other is the inhibition of the expansion during carbonization. These two effects have different optimum contents of fullerene (the former at 30wt% and the latter at 10wt%). According to X-ray diffraction and extraction of carbonized mixtures at 600°C, saturation of the effect of fullerene in the isotropic pitch appeared at around 30wt%. Fullerene appears to disperse uniformly in
the pitch when the content of fullerene is below 30wt%, while the semi-coke yielded a heterogeneous phase when the content was over 30wt%. Fullerene dispersed in the pitch with the spheres of 10-20 nm as shown in TEM images when the content was below 30wt%. The TEM image of the carbonized material from the mixture of pitch and 10wt% fullerene shows that the mixture was poorly dispersed, most likely because there was no stirring. It has been reported that carbonaceous particles, such as carbon black, dispersed in isotropic pitch inhibited the expansion and the coalescence of the mesophase spheres during heat-treatment[13]. The small spheres from fullerene dispersed in the isotropic pitch may play similar role in suppressing the expansion during carbonization while the texture of carbonized product appeared unchanged under the optical microscope.

Fullerene has been reported to have the ability to accelerate the hydrogenation-dehydroygenation of hydrocarbons[11, 14]. Therefore, fullerene may also accelerate the dehydrogenation from the pitch molecules and then increase their viscosities. For example, when heated at 425°C the mesophase spheres from the mixtures containing 10wt% of fullerene never coalesced and remained in spherical form since it provided more mesophase than pitch alone. Figure 8 illustrates the proposal carbonization schemes of pitch alone and the mixtures containing 10 and 30 wt% of fullerene. The fullerene initiates the dehydrogenation of the pitch at lower temperature to complete the reaction at a lower temperature range. Fullerene at a 10wt% level appeared optimum for suppression of the expansion, while maintaining optical texture for the pitch. The addition of more fullerene, up to 30wt%, allowed a little more expansion probably because too much hydrogenation accelerates the increase of viscosity of the pitch matrix before the completion of the hydrogenation.

The experimental results give the different indications about the chemical state of fullerene molecule according to its content with pitch. Fullerene below 30wt% was extracted after heated at 400°C and 600°C, whereas pure fullerene remains stable at the same conditions[1, 8]. FT-IR of the carbonized product shows no sign that fullerene molecule is present in the heated mixtures, even in the toluene-soluble fraction when the fullerene content of the mixture was lower than 30wt%. In contrast, fullerene at more than 30wt% can survive to maintain its structure after the heat-treatment at 600°C in the pitch.
When the content of fullerene is below 30wt%, the framework of the fullerene may be destroyed (probably due to the activation of C-C bonds by the hydrogen addition; see Section 1-3) to some extent through the hydrogenation from the pitch and suspended in the pitch, being separated in the spheres originated from the small crystals of fullerene. Larger amounts of added fullerene did not suffer such reactions and it behaves chemically as if it were in an inert atmosphere. It appears that 30wt% fullerene content is the optimum level for the interaction of fullerene and pitch.

7-5. Conclusion

The toluene soluble fraction of fullerene soot, consisting of C_{60} and C_{70} and other fullerenes, was co-carbonized with synthesized isotropic pitch derived from naphthalene. Mixtures of fullerene and pitch gave carbons in higher yield than expected from their single carbonizations at fullerene contents <30wt%. The fullerenes suppressed the expansion of the pitch during carbonizations, and changed the optical textures of resultant carbons. At levels of addition of fullerenes <30wt%, no fullerenes could be detected in resultant carbons by spectroscopies but they were detected as the spheres of ca.10-20 nm diameter in the carbons by TEM. It is considered that fullerenes remove hydrogen from the naphthenic structures of the pitch and so alter carbonization characteristics. Hydrogenation breaks the spheroidal fullerene framework.
Figure 7-1. The Carbon Yields of the Mixtures of Fullerene and Synthetic Isotropic Pitch after Heattreated at 600 and 1000°C Heating Rate : 10°C/min, Amount of Samples : 0.5g
Figure 7-2. The Appearances after Carbonization of the Mixture of Fullerene and Synthetic Isotropic Pitch at 600°C
Figure 7-3. OM Textures of Cokes from the Mixture of Fullerene and Synthetic Isotropic Pitch (HTT 600°C)
Fullerene Content: 20wt%  

500μm  

Fullerene Content: 30wt%  

500μm  

Figure 7-3 (continued)
Figure 7-3  (continued)
Table 7-1. The Solubilities of the Cokes Derived from the Mixtures of Fullerene and Isotropic Pitch with Toluene

<table>
<thead>
<tr>
<th>Fullerene Content (wt%)</th>
<th>Toluene-soluble (wt%)</th>
<th>C₆₀ (wt% in Toluene-soluble Fraction)</th>
<th>C₇₀ (wt% in Toluene-soluble Fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.3</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>50</td>
<td>19.7</td>
<td>78</td>
<td>22</td>
</tr>
</tbody>
</table>

HTT: 600°C, Heating Rate: 10°C min⁻¹, Extraction: Soxhlet, Quantitative Analysis of C₆₀ and C₇₀: HPLC
Pitch/Fullerene

0/100

50/50

80/20

100/0

WAVENUMBERS (cm⁻¹)

Figure 7-4. FT-IR Spectra of the Cokes Derived From the Mixture of Fullerene and Isotropic Pitch

HTT: 600°C, Heating Rate: 10°C min⁻¹,
IR Measuring Method: KBr Method
Figure 7-5. X-ray Diffraction Patterns of the Cokes Derived from the Mixture of Fullerene and Isotropic Pitch
HTT: 600°C, Heating Rate: 10°C/min,
X-ray Target: CuKα
Figure 7-6. TEM Bright Field Images of the Cokes Derived from the Mixtures of Fullerene and Isotropic Pitch (HTT 600°C)
(a) from Pitch Alone
(b) from the Mixture Containing 10wt% Fullerene
(c) from the Mixture Containing 30wt% Fullerene
Table 7-2. Some Properties of the Heated Materials of the Mixtures of Fullerene and Isotropic Pitch

<table>
<thead>
<tr>
<th>HTT (°C)</th>
<th>Content of Fs-TS (wt%)</th>
<th>H/C</th>
<th>TS (wt%)</th>
<th>TI (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.704</td>
<td>74.2</td>
<td>25.8</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>0.617</td>
<td>41.7</td>
<td>58.3</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.451</td>
<td>39.6 *</td>
<td>60.4</td>
<td></td>
</tr>
<tr>
<td>425</td>
<td>0.571</td>
<td>52.0</td>
<td>48.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>47.4</td>
<td>52.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.447</td>
<td>7.6</td>
<td>92.4</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>0.506</td>
<td>14.5</td>
<td>85.5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>4.1</td>
<td>95.9</td>
<td></td>
</tr>
</tbody>
</table>

*contains 0.91 wt% of (C_{60}+C_{70})
Heating Rate: 10°C min⁻¹, Extraction: Soxhlet,
Quantitative Analysis of C_{60} and C_{70}: HPLC
Figure 7-7. OM Photographs of the Mixtures of Fullerene and Isotropic Pitch Heated at Various Temperature (Heating Rate: 10°C/min)
Figure 7-8. The Scheme of Carbonization Process of the Mixture of Fullerene and Isotropic Pitch
REFERENCES

CONCLUSIONS

8-1. Summary of the Thesis

Fullerenes, spherical carbon clusters represented by \( \text{C}_{60} \), have attracted many researchers because of their unique characteristics, such as their shapes with high symmetry, high abilities as electron-donor and acceptor, anisotropy of their crystals, and relatively high temperature superconductivity of the co-crystal of \( \text{C}_{60} \) and alkali-metal. Most of these characteristics originate from the structure of the molecules, which includes sp\(^2\) carbon network containing 12 of five-membered ring, and from the electric structure derived from the structure.

In this study, \( \text{C}_{60} \) and \( \text{C}_{70} \) fullerenes were carbonized and graphitized under several conditions. Though the sublimation of fullerenes competed with their carbonization, the carbonization yield reached as high as 94wt\% by moulding and limiting the sublimation. The molecular framework of fullerenes was destroyed above 800°C. The carbonaceous product obtained an amorphous structure after the carbonization, and peripherical turbostratic layers of hollow spheres after the graphitization. These turbostratic spheres lead to the relatively low density of the graphitized product.

By the arc discharge process for fullerene production, the product from anode included \( \text{C}_{60} \), \( \text{C}_{70} \) and several higher fullerenes (Fs-TS ; ca. 10wt\%), giant fullerenes of \( \text{C}_{70} \) to \( \text{C}_{400} \) (Fs-TIQS ; ca. 1wt\%), the insoluble soot (Fs-QI ; ca. 75wt\%) and graphitic substance, the most of which is the fragment of the anode. A part of Fs-QI (ca. 30wt\%) contained similar pentagon network of carbon atom to fullerenes which was rearranged to amorphous system upto 800°C, and gave a similar peripherical turbostratic layers by the graphitization. Such similarities of Fs-QI to fullerenes suggest the consecutive production mechanism of Fs-QI of carbon cluster by heat during arc discharge. The author can propose the higher yield of fullerene molecules by the rapid quenching in the arc discharge system.

The toluene-insoluble fraction of fullerene soot (Fs-TI) was also moulded into disk and heat treated upto graphitization temperature. The partial fusion and adhesion of Fs-TI particles increased the strength of the
disk. The graphitized Fs-TI disk had a low density and characteristic pore size distribution at 20Å. This artifact from the abundant source is expected as new molecular sieving system.

Fullerene (Fs-TS) was mixed for the co-carbonization with synthesized isotropic pitch. Fullerene under 30wt% was dispersed into the pitch at high temperature, increased the carbonization yield of pitch, and suppressed the expansion due to the acceleration of dehydrogenation. Fullerene deformed its molecular framework, being converted into toluene-insoluble portion at a lower temperature than that of the heat-treatment by itself.

The fullerene-derived carbon materials described above are expected for the novel carbon artifacts of unique properties.

8-2. Summaries of Chapters

Chapter 1 Introduction

By reviewing literature, the basic properties and some unique features of fullerenes and fullerene-related materials are summarized, and the objective and outline of this thesis are described.

Chapter 2 Carbonization of \( C_{60} \) and \( C_{70} \) fullerenes to fullerene soot

The toluene soluble fraction of fullerene soot (Fs-TS), containing 76wt% of \( C_{60} \), 22wt% of \( C_{70} \) and 2wt% of higher fullerenes, was carbonized and graphitized. Although fullerenes sublimed around 800°C, ca. 20wt% of the sample remained after heat treated at 1000°C. The residue was more from higher fullerenes than pure \( C_{60} \). \( C_{60} \) and \( C_{70} \) in Fs-TS were converted to toluene insoluble matter after heat treated up to 250°C, via higher fullerenes. The carbonized product of Fs-TS was a soot-like amorphous carbon and appeared periherial turbostratic layers after graphitization. The similarity in the carbonization and graphitization behaviors of Fs-TS to that of quinoline insoluble soot (Fs-QI) indicates the consecutive formation of soot from \( C_{60} \) and fullerenes in arc discharge chamber, and a way to increase the yield of \( C_{60} \) in the preparation by the rapid run-away of new born \( C_{60} \) from the hot zone in arc.
Chapter 3 Carbonization of the toluene soluble fraction of fullerene soot into disk

Carbonization of toluene soluble fraction in the fullerene soot was examined in the disk at the bottom of the test tube. Such a carbonization was found to increase the carbon yield to 94% by 900°C and 92% by 2400°C. The carbon yield was also found to be influenced by the thickness of the disk and the heating rate. All these results indicate that the carbonization competes the sublimation. The carbon disk thus prepared showed appearance of glass-like carbon and had bulk density of 1.5g/cm³ at 900°C and 1.2g/cm³ at 2400°C. The reduction of the density by the graphitization reflects hollow spheres surrounded by their turbostratic layers in the graphitized disk.

Chapter 4 Structural changes of fullerene by heat-treatment up to graphitization temperature

Structural changes of C₆₀ and C₇₀ mixture during the heat-treatment up to 2400°C were studied by observing the carbonized disk of the fullerene with Raman spectra, X-ray diffraction, FE-SEM, TEM and AFM/STM. The fullerene lost its five-membered ring and its fcc crystal structure by the heat-treatment at 800°C, as revealed by Raman spectra and X-ray diffraction, forming hexagonal planes by 1300°C which were randomly arranged. Further heat-treatment allowed some stacking of layer which grows to dominate, reducing the randomly oriented planes. The graphitized temperature up to 2400°C provided a very sharp peak at 26°, suggesting formation of stable turbostratic layer. The TEM characterized turbostratic stacking of 3 to 4 layers. A series of observation under AFM/STM and TEM indicate the crystal of the fullerene, amorphous grain of hexagonal planes, hollow sphere are all in the same range of size around 10-20 nm. Such microdomains induced micro-roughness as observed by FE-SEM on the surface of the carbon disk. Superstructure of hexagonal plane was observed on the surface. A kind of solid state carbonization of the fullerene is suggested to maintain the dimension of its crystal into the spherical microdomain, even if its marked structural changes take place within the unit.
Chapter 5 Carbon frameworks produced in the fullerene related materials

Soot produced from graphite through arc discharge was separated into four fractions to analyze their structure. Toluene-soluble fraction carried C$_{60}$, C$_{70}$, and C$_{76}$-C$_{120}$ fullerenes while toluene-insoluble quinoline-soluble fraction (ca. 1wt%) consisted of larger clusters of C$_{70}$ to C$_{400}$ which have similar framework to C$_{60}$ or C$_{70}$ fullerenes. Graphitic substances in quinoline insoluble fraction were separated through the precipitation in acetone. Reactivity of the quinoline-insoluble fraction free from graphitic substances (15wt%) revealed two kinds of carbon frameworks in the combustion; one is pentagon-containing system similar to fullerenes (ca. 30wt%) and rather graphitic, hexagonal system (ca. 45wt%). Pentagon-containing system in "soot" particle was more reactive to be burnt at as low temperature as 400°C and thermally converted to hexagonal system by the heat-treatment above 800°C.

Chapter 6 Some properties of carbon disk prepared from toluene insoluble fraction in fullerene soot

Moulding and successive carbonization of toluene-insoluble fraction in the fullerene soot were studied to prepare carbon disk of unique properties. Separation of graphitic component by precipitation in acetone allows the fraction to be mould and carbonized into a carbon disk of significant strength. The disk was found to consist of large grains and fine particles to be densely packed and adhered each other through partial fusion at their periphery. The disk exhibited density and surface area of 1.9g/cm$^3$ and 491m$^2$/g by the carbonization at 900°C and 1.6g/cm$^3$ and 183m$^2$/g at 2400°C, respectively. The random stacking of hexagonal planes and micro hollow spheres with 2 to 3 layers of planes appear origins of above properties at 900 and 2400°C, respectively. The conversion of pentagon to hexagon around 900°C may cause the partial fusion of small particles. The pore size distributed almost exclusively around 20Å. Some unique application can be designed.
Chapter 7 Effects of fullerene addition on the carbonization of synthetic naphthalene pitch

The toluene soluble fraction of fullerene soot, consisting of C\textsubscript{60} and C\textsubscript{70} and other fullerenes, was co-carbonized with synthesized isotropic pitch derived from naphthalene. Mixtures of fullerene and pitch gave carbons in higher yield than expected from their single carbonizations at fullerene contents <30wt%. The fullerenes suppressed the expansion of the pitch during carbonizations, and changed the optical textures of resultant carbons. At levels of addition of fullerenes <30wt%, no fullerenes could be detected in resultant carbons by spectroscopies but they were detected as the spheres of ca.10-20 nm diameter in the carbons by TEM. It is considered that fullerenes remove hydrogen from the naphthenic structures of the pitch and so alter carbonization characteristics. Hydrogenation breaks the spheroidal fullerene framework.

Chapter 8 Conclusion

The thesis is summarized and concluded in this chapter.
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