Transformation from C_{60} Fullerene into Carbon Spheres by Shock Compression

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Abstract. Here, we report a partially facetted carbon sphere of about 20 \( \mu \)m in diameter on the outer surface of the recovered sample from C_{60} fullerene powder after shock-compression. The sphere has two hexagonal facets locating almost parallel to each other. Spotty contrast is observed on the roundish particle but not on the facetted area. Micro-Raman spectroscopy revealed that the facetted area is in a highly graphitized state but not the roundish area.

1. Introduction
Since the discoveries of fullerene [1] and nanotube [2] which are new carbon allotropes containing pentagons or heptagons in the hexagonal graphitic structure, we have accepted the idea that carbon has a degree of freedom in the sp²-hybridized form. Also, a dynamic transformation from polyhedral particles and tubes into balls with several concentric, nearly spherical shells has been found under electron irradiation condition [3]. Such an experimental result has stimulated theoretical investigations into the structures of graphite and fullerenes, mostly with the emphasis on topology and chemistry [4-9]. To know the morphological stability, it would be a forceful way to investigate the formation of carbon particles from the liquid phase. However, the high melting temperature of carbon materials has made difficult the experimentation.

The shock compression is one of techniques to change the structure of initial carbon specimens instantaneously by giving a high pressure and a high temperature. It has been reported that tapped C_{60} powders, of which initial density is 75 % of bulk crystal, transformed to disordered carbon near 25 GPa and to an amorphous above 50 GPa by shock-compression [10]. Utilizing shock-compression and rapid quenching (SCARQ) technique, on the other hand, transparent amorphous diamond and nanocrystalline diamond ceramics were fabricated from a C_{60} thin film [11-13] and graphite [14] above 50 GPa, indicating that the quenching speed is an important factor to control the products.

Recently, we have found the generation of hollow spheres up to several \( \mu \)m in diameter on an internal hollow surface of the recovered sample from C_{60} fullerene powder after shock-compression up to 57 GPa (Fig. 1) [15-17]. The hollow spheres are significantly larger than the fullerenes reported so far and are revealed to be in a highly graphitized state by Raman spectroscopy. Appearance of the liquid phase of carbon by the shock-compression is assumed in the formation of carbon hollow spheres. This paper reports another type of sphere with characteristic partial facets generated in the shock-compressed specimen.

2. Experimental procedure
C_{60} fullerene powder with the purity of 99.9 % from MER co. is a starting material. It was set into a stainless capsule (10-mm diameter and 4-mm thick) and subjected to shock loading twice using a powder gun. The first shock loading reached 18 GPa (Cu with flyer velocity of 0.92 km/s), of which
pressure is lower than the critical pressure (20 GPa) to collapse C\textsubscript{60} fullerene molecules [18]. The shocked C\textsubscript{60} powder became 97.5\% of the crystal density. The second shock loading reached 57 GPa (W with flyer velocity of 1.72 km/s) [19]. A specimen was recovered and observed by using a scanning electron microscope (SEM). Raman measurements were done with a micro-Raman spectroscope (SPEX Raman-500) using an Ar (488 nm) laser.

3. Results and discussion

3.1. Facets on a spherical particle

Fig. 2 shows a SEM image of particle of about 20 \textmu m in diameter, which is observed on the surface of the recovered sample of C\textsubscript{60} powder after the shock compression. The sphere sits in a large groove and exhibits two hexagonal and one rhombic dark images as denoted by A, B and C respectively. The two hexagonal images locate almost parallel to each other on the surface of particle. The geometry of the particle was obtained by tilting the specimen. The two hexagonal and one rhombic dark images were
revealed to be facets formed on a roundish particle, judging from the linear profiles and the reflections from the area. Then, we designate the areas denoted by $A$, $B$ and $C$ in Fig. 2 as Facet $A$, $B$ and $C$, respectively, hereafter. From the tilted images (Fig. 3), we conclude that Facet $A$ is a dent consisting from sub-grain boundaries, while Facet $B$ is a convex divided by ridges. Also we can find bright spotty image of about 20 nm in the roundish area of sphere. Interestingly, the spotty image is not observed in the faceted area.

Figure 4 schematically draws the configurations of Facets $B$ and $C$ in Fig. 2 and Facet $A$ in a tilted image where Facet $C$ sits in the center of sphere. The lines of grain boundaries and ridges for Facet $A$ and $B$ are also drawn. In Figs. 5a and 5b, all the sides of Facet $A$ and $B$ are overlapped, respectively. The six sides of Facet $C$ and the internal lines in Facet $B$ are also overlapped in Fig. 5c. The lines cross almost at an angle of $60^\circ$ in each set. The sets of line in Figs. 5a and 5b mostly sit in the same geometry. However, the set of lines in Fig. 5c is rotated about $30^\circ$ against those in Figs. 5a and 5b. Anyhow, the close geometrical relationship among the three faceted areas implies a long range order of the faceted sphere. We should note that the images of line in Facet $B$ in Fig. 3 look similar to the ridges running along the so-called arm chair lines of $<10\bar{1}0>$ direction. The ridges were formed by irradiations [20] and are considered to be formed to release the stress induced by the defect formation under irradiation.

In the present experimental condition, the shock state reach to 57 GPa and 3000 K [12], and then the C$_{60}$ fullerene molecules should transform at first to sp$^3$-bonded carbon as the shocked-state is in a diamond phase of the phase diagram [13]. The sp$^3$-bonded carbon structure transforms to sp$^2$-bonded carbon structure due to residual heat after the shock-pressure release. We have reported the formation of hollow spheres in the flaked area, which are observed to be see-through particles (Fig. 1). One should note that the hollow spheres do not exhibit facets although they are in highly graphitized state.

Theoretical study has shown that the fullerene cages should have visible facets in their ground state configurations [4]. Therefore, to explain the formation of spherical surface, the role of thermally generated structural defects of non-classical ring structure was investigated [4-9]. It was proposed that a balance of positive and negative curvature, exerted by five- and seven-membered rings, respectively, may result in an overall roundish shape. In the present case of shock compression, the sphericity of particle originally should have come from the form of carbon droplet, which is strongly affected by the surface tension force. During the crystallization process, faceting should have occurred to reduce the
3.2. Raman spectroscopy for the faceted particle
The partly faceted sphere was investigated by the micro-Raman spectroscopy with a spatial resolution of 2 μm. Fig. 6 shows three Raman spectra for a faceted area and roundish areas, respectively. The Raman spectrum (a) for the faceted area is almost singlet similar to the case of highly oriented pyrolytic graphite (HOPG), while the ones (b) and (c) for the roundish areas are clearly a doublet at around 1580 cm\(^{-1}\) (G peak) and 1360 cm\(^{-1}\) (D peak). Applying a least squares algorithm, the Raman spectra were deconvoluted into two Lorentzian peaks. The intensity ratio of the D peak to the G peak (I(D)/I(G)) for the flat area and the roundish areas are 0.029, 0.46 and 1.03 respectively. Using the formula obtained by Knight and White [21], which gives an inverse linear relationship between the planer crystalline size (La) and the intensity ratio I(D)/I(G), the La for the flat area and the roundish particle are estimated to be 152, 9.6 and 4.3 nm respectively.

The crystalline size La of 152 nm estimated by Raman spectroscopy for the faceted area nearly corresponds to the size of the area divided by the ridge or the boundaries. The values of La for the roundish areas which are less than 10 nm, on the other hand, seems to be too small, because the close
geometrical relationship among the three facets implies a long range order of the particle. The discrepancy can be explained by the formation of small graphitic islands formed on the roundish area, which will reduce the apparent crystalline size observed by Raman spectroscopy.

A question arises; why graphite islands are significantly formed on the roundish area but not on the faceted area? We give a tentative scenario, taking account of the difference in the mobility of carbon ad-atom between the roundish and the flat surfaces, as shown in Fig. 7. If the mobility of carbon ad-atoms on the flat surface is faster than that on the roundish surface (Fig. 7b), the concentration of ad-atoms on the faceted surface area can be too low to nucleate the graphite islands (Fig. 7c). The difference in the mobility of ad-atoms between the roundish and the flat surfaces may be explained by the energy analysis in the case where the bonding of the roundish large fullerene is not exactly the sp² bonding [9]. Such energy difference may induce the difference in the trapping of ad-atoms on the surfaces, thereby affecting the mobility of ad-atoms. Further experimental and theoretical studies are needed to clarify this.

4. Conclusion
A partially facetted carbon sphere formed on the recovered sample from C₆₀ fullerene powder after shock-compression was reported. The faceted area was revealed to be in a highly graphitized state by Raman spectroscopy but not in the roundish area. SEM images of the sphere suggested the formation of small graphitic islands on the roundish area. We gave a tentative scenario, taking account of the difference in the mobility of carbon ad-atom between the roundish and the flat surfaces.

Acknowledgements
This research was partly supported by Collaborative Research Project of Materials and Structures Laboratory, Tokyo Institute of Technology and by JSPS Grant-in Aid (No. 20246094).

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