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Formation of micro-diamond by heat treatment of quenched carbonaceous composite (QCC)

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Abstract: In order to clarify the correlation between the structure and peak position in quenched carbonaceous composite (QCC), which shows an absorbance peak similar to the 217.5 nm feature seen in the interstellar extinction curve, structural changes induced by heating were studied *in situ* using high resolution electron microscopy. As-prepared QCC particles composed of onion-like spherules changed into a structure with well ordered (002) fringes following heating in vacuum. In addition, formation of microdiamond of about 1 nm in diameter took place by heating at 100°C. The metamorphism is discussed based on a specific configuration of sp^3 hybridization existing on the surface of QCC particles.

1. Introduction

The 217.5 nm bump is a well known feature caused by interstellar dust. As candidates of interstellar dust, many types of carbon and other carbonaceous materials have been proposed to explain the 217.5 nm bump, including graphite (Draine and Lee, 1984), hydrogenated amorphous carbon (HAC) (Duley, 1984; Mennella *et al.*, 1995, 1996), graphite onions (Kroto and McKay, 1988; Wright, 1988; Henrard *et al.*, 1993, 1997), diamond-like carbon (Mutschke *et al.*, 1995), a combination of polycyclic aromatic hydrocarbons (PAHs) (Joblin *et al.*, 1992) and quenched carbonaceous composite (QCC) (Sakata *et al.*, 1983, 1994). Although HAC, PAH and QCC are considered to be good candidates of dust analogues: the conclusion is not yet confirmed.

Carbonaceous materials produced by condensation from an ejecta of hydrocarbon plasma show an absorption peak at 220 nm, which was named Quenched Carbonaceous Composite (QCC) by Sakata *et al.* (1983). A brown-black carbonaceous material (dark-QCC) was formed at the center of the ejecta from the plasma. By dissolving organic molecules contained in the dark-QCC with acetone, dark-QCC showed an absorption peak at a wavelength of 220 nm, though the peak was broader than the observed bump. At the center of the dark-QCC, a black circular spot ~5 to 7 mm in diameter was formed. Sakata termed this granular-QCC, which was a thickly condensed carbonaceous material from the ejecta. Sakata *et al.*

measured an absorption spectrum of the granular-QCC and obtained a peak wavelength of ~220 to 224 nm. The peak of the granular-QCC was a little broader than that of the dark-QCC. Though the unheated QCC samples show an absorption peak at a wavelength of ~217 to 224 nm, the absorption peak following heating shifts to longer wavelengths (Wada *et al.*, 1999). After heating at 350°C and 500°C, the absorption peak shifted to 224 nm and 230 nm, respectively. Systematic studies on the correlation between the structure and peak shift are very important for clarifying the reasons why the absorption peak of QCC occurs at 220 nm.

In a previous study using transmission electron microscopy (Sakata *et al.*, 1994), the QCC materials showed a halo-like diffraction pattern that suggested an amorphous structure. High resolution electron microscopic (HREM) observations, carried out by Kaito and Shimizu (1984), have been used in order to make clear the atomic arrangement of other materials that had also been thought to be amorphous materials. In our previous paper, it was elucidated from HREM observations that the fundamental structure of QCC, which shows a 220 nm observation peak, is composed of onion-like spherules (Wada *et al.*, 1999). In order to clarify the correlation between the QCC's structure and a shift in its peak position, structural changes caused by heating were studied *in situ* using HREM. In this experiment, formation of micro-diamond was observed when the QCC was heated at low temperatures in vacuum.

2. Experimental procedure

Figure 1 shows a schematic representation of the experimental apparatus for producing QCC, which was previously described by Sakata *et al.* (1994). QCC is formed from the ejecta of a methane plasma generated by a microwave discharge at 2.45 GHz. The ejecta left the plasma tube through a narrow hole and condensed on a room-temperature substrate under vacuum. A brown-black carbonaceous material (dark-QCC) was formed around the center of the ejecta. At the center of this condensate corresponding to the dark-QCC, a black circular spot (granular-QCC) about 5 to 7 mm in diameter was formed. The QCC samples were collected on

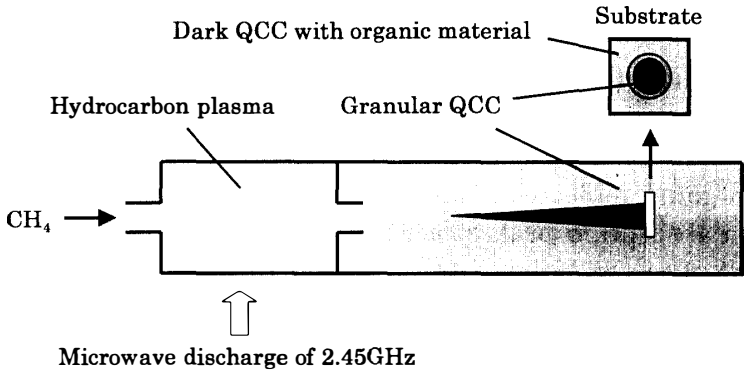

Fig. 1. Schematic representation of the experimental apparatus for producing QCC, which was previously reported by Sakata et al. (1994).

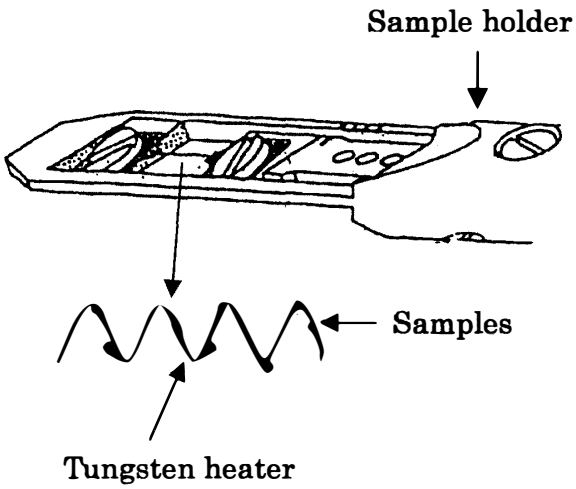

Fig. 2. Schematic representation of the sample holder used in the in-situ observation. QCC samples were directly mounted on the conical tungsten heater. Samples are shown by filled circles.

quartz glass.

Figure 2 shows a schematic representation of the sample holder used for *in-situ* observation of the annealing process. The tip of the sample holder has a sample stage equipped with a conical tungsten heater. For *in-situ* observations, the QCC samples were mounted directly onto the heater and heated to 100°C in a Hitachi H-9000NAR electron microscope. During the heating, the pressure in the vacuum was 3×10^{-6} Pa. The temperature during heating is inferred from the value of the electric current fed to the heating stage. The images were magnified by a factor of twenty using a television system. Structural changes can be observed in the lattice images. These images were recorded on a video tape.

3. Results and discussion

Figure 3 shows HREM images of (a) the granular-QCC and (b) the dark-QCC, which were reported by Wada *et al.* (1999). Onion-like structures exist in both of the QCC images in spite of the amorphous-like electron diffraction pattern. Each particle is composed of concentric shells. The fringe spacing almost corresponds to the (002) lattice spacing of the graphite structure. However, the fringe spacing for the onion-like spherules is not constant but is wider than that of graphite (0.334 nm) in some places. The difference in the fringe spacing may result from some combination of sp^3 hybridization (hereafter sp^3-C) with sp^2 hybridization (hereafter sp^2-C). The onion-like particles in the dark-QCC and the granular-QCC range from 5 to 15 nm in diameter. Particles larger than 10 nm in diameter are found in the granular-QCC. A central vacant core 2 to 3 nm in diameter is often observed in the granular-QCC and dark-QCC, as shown in the top of Figs. 3a and 3b. Some cores are very round, although most QCC cores are highly distorted rather than spherical. No distinct structure could be observed inside the round-shaped core in spite of the 0.18 nm point resolution electron micrograph image. It was concluded that the inside of the core is vacant. The main characteristic of QCC samples is that these carbonaceous onion-like particles are not pure carbon, but are

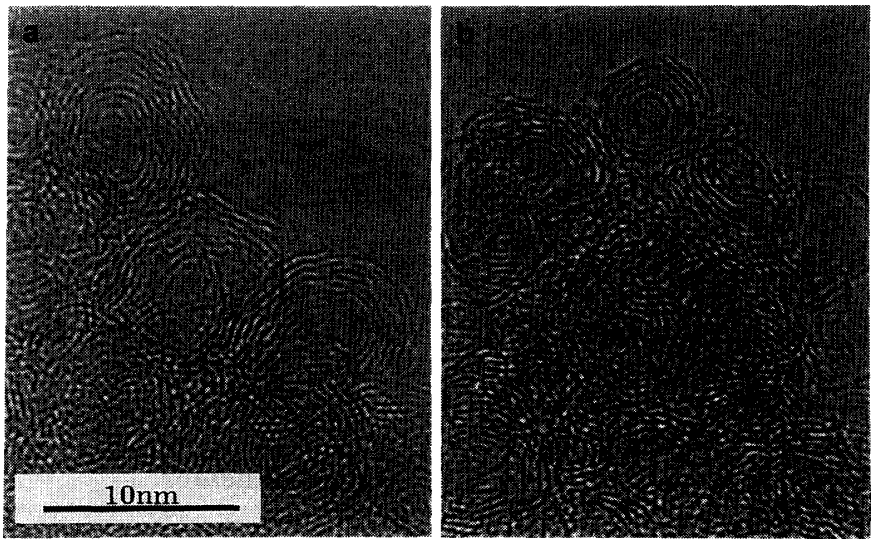

Fig. 3. HREM images of (a) the granular-QCC and (b) the dark-QCC. The materials are an aggregate of onion-like particles. EM images are shown on the same scale.

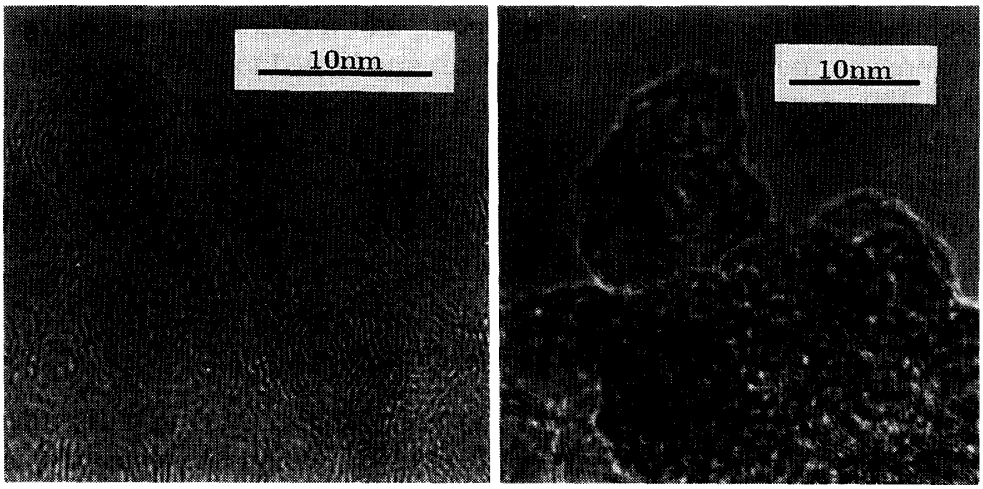

Fig. 4. HREM images of (a) dark-QCC heated for 40 min at 250°C in vacuum and (b) dark-QCC heated for 20 min at 500°C in vacuum. The peak position of sample (a) unchanged, and sample (b) shifted to 228 nm.

composed of carbon and hydrogen, which is different from case of the previously reported carbon onion-like particles (Iijima, 1980; Ugarte, 1992).

Figure 4 shows HREM images of (a) dark-QCC heated for 40 min at 250°C in vacuum and (b) dark-QCC heated for 20 min at 500°C in vacuum. The sample shown in Fig. 4a can be seen as the (002) fringes became a little more distinct as compared with those of as-prepared QCC. However, large changes in the whole structure were not seen. This is consistent with the fact that the absorption peak does not shift in position. When the sample was heated at 500°C, the peak position shifted to 228 nm (Wada *et al.*, 1999). The corresponding QCC is shown in Fig. 4b. Although the particle size hardly changed as compared with as-prepared QCC, we observed that the (002) fringes became much more distinct. The shift of the

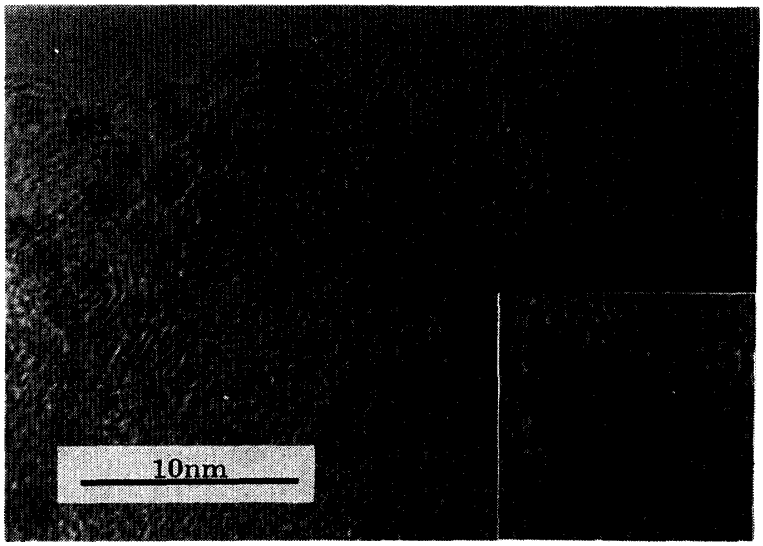

Fig. 5. HREM images of microdiamond appearing on the surface of QCC. The inset is the enlargement of a part of the black spots. The (111) lattice images of 0.206 nm which correspond to diamond can be clearly seen.

absorbance peak to longer wavelengths following low temperature heating suggests that the 220 nm absorbance peak could have two possible origins. First, it may arise from residual organic components in the QCC, which are largely vaporized upon heating. Second, the structural change might occur during the heating of the QCC sample, and cause the shift in the absorbance peak.

In-situ observation of dark-QCC in the electron microscope during heating at 100°C showed that a continuous range of the (002) fringes in the onion region becomes gradually larger; in other words, partial graphitization took place at lower temperatures, as shown in Fig. 4. On heating for about 30 min at 100°C, the appearance of microdiamond grains on the order of one nanometer in diameter took place. These microdiamonds can also be formed by heating at 800°C in vacuum. A typical example of microdiamond, which appears on the surface of QCC, is shown in Fig. 5. The (111) lattice images of 0.206 nm which correspond to diamond can be seen in the dark spots. Since the microdiamonds were not formed in HREM observations without the heat treatment, it is considered that at least the effects of the electron beam can be ignored as far as the formation of microdiamond in the QCC samples is concerned.

Successive pictures of QCC heated at 100°C are shown in Fig. 6. In addition to the graphitization caused by heating at 100°C, a black spot about 1.5 nm in diameter also appeared in the QCC samples, as seen in Fig. 6a. Since the materials are mainly composed of carbon atoms, the strong contrast of the black spot suggests the formation of different crystals. With the passage of time, fringes spaced at 0.206 nm which correspond to the (111) reflection of diamond appeared, as pointed out by the arrow in Fig. 6b. The microdiamond produced in the HREM had a diameter of about 1.5 nm, which is the same size as the microdiamond produced experimentally using the microwave CVD method (Yugo *et al.*, 1995). This is almost equal to the

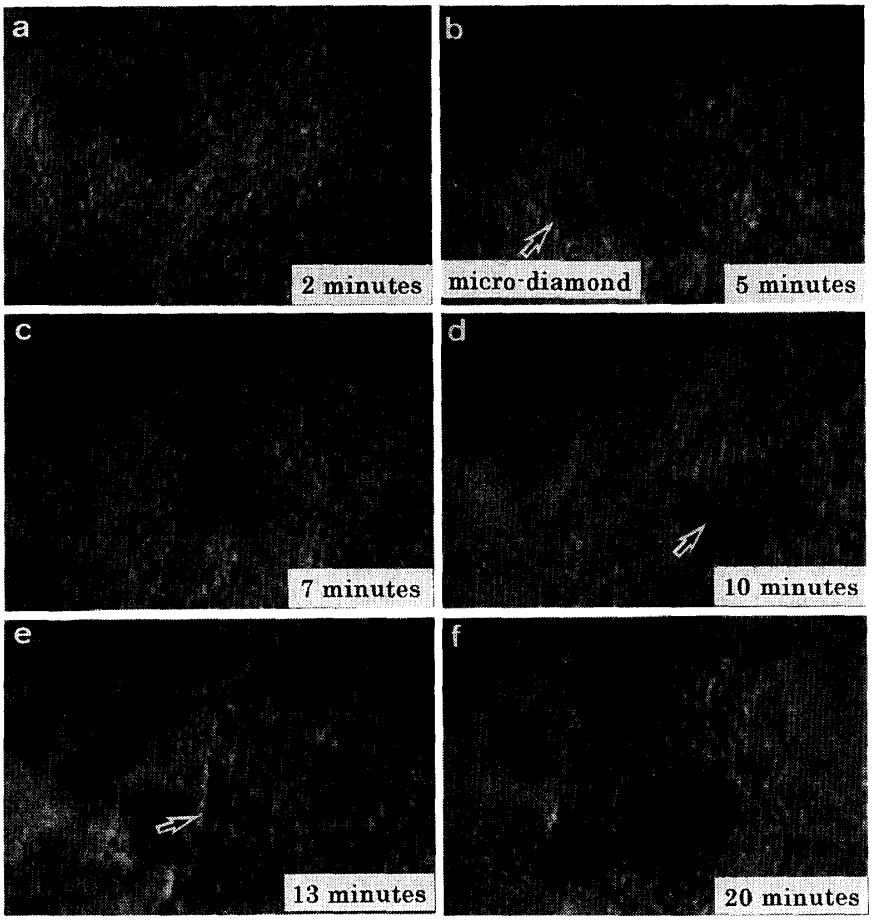

Fig. 6. Successive HREM images of QCC heated at 100°C in vacuum. The passage of time from the appearance of the black spots is shown on the bottom right of each image.

critical size of diamond clusters computed based on the atomistic theory of nucleation and the proposed nucleation mechanisms (Mahalingam *et al.*, 1997). As seen in Fig. 6c, the microdiamond crystals disappear. The lattice images of the (111) reflection of diamond appear again as shown in Fig. 6d. The fringes which correspond to the (111) reflection of diamond can be clearly seen as indicated by the arrow. The diamond becomes larger, as shown in Fig. 6f. The disappearance of the microdiamond in Fig. 6c suggests that the microdiamond might have moved or coalesced with another microdiamond during the heating. It has been shown via X-ray photoelectron spectroscopy that the inner shells of the onion-like spherules of granular- and dark-QCC are composed predominantly of sp^2-C and that most of the sp^3-C is contained in the outer shells of the spherules (Wada *et al.*, 1999). It has been pointed out experimentally and theoretically that the existence of sp^3-C terminated with hydrogen atoms play an important role in the growth of diamond (Yugo *et al.*, 1995; Mahalingam *et al.*, 1997). For surface bonds terminated with hydrogen atoms, it is suggested that diamond clusters smaller than 3 nm in diameter are energetically more stable than graphite of the same H/C ratio (Badziag *et al.*, 1990). In this experiment, the growth of microdiamonds took place not at the inner

shell of the onion-like particle but on the outer shell of the onion-like particles. It can be concluded that a specific configuration of sp^3-C existing on the surface of these particles may be responsible for the nucleation of diamond.

4. Astrophysical implications and conclusions

Among various carbonaceous grains which are expected to be present in space, microdiamond grains have recently received attention. In fact, recent infrared spectroscopic astronomical observations of dense clouds have shown the signature of a 2880 cm^{-1} band which has been tentatively attributed to interstellar diamond (Allamandola *et al.*, 1992). In addition, with the discovery of pre-solar microdiamonds in meteorites by Lewis *et al.* (1987), microdiamond has been proposed to exist in interstellar dust. Clues as to the origin of the microdiamonds come from the diamonds themselves and from their noble-gas components, especially Xe-HL. For example, it is thought that the formation of diamonds takes place in the circumstellar envelope of a carbon star, although Xe-HL requires neutron capture on a fast timescale, *i.e.*, a supernova (Clayton, 1989). There is a problem in that carbon stars are not massive enough to become type II supernovae. A completely satisfactory model for the origin of microdiamonds is not yet available.

It is generally known that carbonaceous materials containing hydrogen are present in interstellar space. It is thought that these materials might experience effects due to heating or ultraviolet ray irradiation. In this experiment, microdiamonds were easily produced by heating QCC (note that QCC shows a spectrum similar to that observed in the interstellar extinction curve). This result suggests that the microdiamonds could possibly be formed in various stellar atmospheres, *i.e.*, under various growth conditions. Since the microdiamonds can be produced from QCC, this material may be a strong candidate for the carbonaceous component of the interstellar dust.

Acknowledgments

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