Antarct. Meteorite Res., **16**, 235–240, 2003

Heating experiments of carbon grains: Implication for the origin of interstellar dust

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Abstract: Amorphous carbonaceous grains produced in a methane gas atmosphere were analyzed by high resolution transmission electron microscope (HRTEM). Structural alteration of the amorphous carbonaceous grains was directly observed by *in situ* HRTEM observation. The specimen was heated to a maximum of 550℃. The HRTEM image of a prepared specimen showed the structure of the onion-like carbon. The onion-like structure distorted at 100℃, which suggested the evaporation of -OH groups included in the grains. Upon heating to 260℃, the centers of the onion-like grains formed holes of the order of 3 nm in size. On further heating to 550℃, the structure of the chained grains with a size of 10 nm changed to graphite sheets with a length of 50 nm by the surface melting coalescence among chained grains. The structural changes at the above temperatures have been observed only in amorphous carbonaceous grains produced in a methane gas atmosphere and have been attributed to the existence of hydrogen in the grains.

key words: amorphous carbonaceous grain, *in situ* observation, high resolution transmission electron microscope, methane gas, hydrogen

1. Introduction

It is known that interstellar carbonaceous material has a characteristic absorption at 217 nm. However, the origin of this feature is not yet understood. So far, many types of carbon and carbonaceous materials have been proposed to be the cause of this absorption, including graphite (Stecher and Donn, 1965; Draine and Lee, 1984), hydrogenated amorphous carbon (HAC) (Duley, 1984; Mennella *et al.*, 1995, 1996), coal-like material (Papoular *et al.*, 1996), fullerenes (Krätschmer *et al.*, 1990), graphite onions (Kroto and McKay, 1988; Wright, 1988; Henrard *et al.*, 1993, 1997; De Heer and Ugarte, 1993), diamond-like carbon (Mutschke *et al.*, 1995), a mixture of polycyclic aromatic hydrocarbons (PAHs) (Joblin *et al.*, 1992), molecular aggregates with aromatic double-ring structures (Beegle *et al.*, 1997) and quenched carbonaceous composite (QCC) (Sakata *et al.*, 1983, 1994). Carbon atoms can form three types of bonds with other carbon atoms. The first type is formed *via* sp^3 hybridization (sp^3-C), the second type *via* sp^2 hybridization (sp^2-C), and the third type *via* sp hybridization (sp-C). A π bond and a σ bond (sp^2-C) form a carbon double bond, and two π bonds with a σ bond (sp-C) form a carbon triple bond. The π electrons are essential in these π bonds. The fundamental structure of QCC was elucidated by HRTEM. The structure was onion-like with a hole at the center. The electron diffraction pattern of the QCC displayed halo-like rings that suggested an amorphous structure, as well as other carbonaceous material such as HAC and PAHs. Recent HRTEM image clearly revealed the short range atomic structure of the QCC (Wada *et al.*, 1999). The HRTEM image also can be used as the analysis of nanostructure in natural sample (Bernatowicz *et al.*, 1991, 1996) and other amorphous samples (Kaito and Shimizu, 1984; Suzuki *et al.*, 2000). Furthermore, Kimura *et al.* (2000) found that nanodiamond can be produced by heating at 100°C. The nanodiamond appeared on the surface of QCC grains; its formation was observed at low temperature. It was found that the HRTEM *in situ* observation can be used in documenting the nanostructure change in amorphous grain by heating. However, the thermal alteration of carbonaceous material is depended on the growth condition.

In the present work, two types of carbon grains were produced by carbon arc-discharge in an argon gas atmosphere and in a methane gas atmosphere. Morphological change of carbon grains predominantly took place in the carbonaceous grains produced in a methane gas atmosphere.

2. Experimental

The vacuum chamber used for sample preparation was a glass cylinder 17 cm in diameter and 33 cm high. The chamber was evacuated to 10^{-4} Pa. Then, the system was closed and methane gas was introduced into the glass chamber. Carbon was evaporated by the conventional carbon arc-discharge method (Kaito *et al.*, 1995) at a methane gas pressure of 10^4 Pa. The carbonaceous grains collected were studied using Hitachi H-7100R and 9000NAR electron microscopes. The dynamic behavior of carbonaceous grains was examined at high temperatures using the H-9000NAR electron microscope, equipped with a real-time video recording system. The carbonaceous grains collected were directly mounted on a conical tungsten heater (Kimura *et al.*, 2000). During heating, the pressure was 3×10^{-4} Pa. The process of structural change of the carbonaceous grains was recorded on video tape.

3. Results and discussion

Figure 1 shows the electron microscopic (EM) image and electron diffraction (ED) pattern of carbonaceous grains produced in a methane gas atmosphere. The diameter of the carbonaceous grains was approximately 30 nm. The ED pattern displays diffuse halos, which suggest the production of amorphous carbonaceous grains. Figure 2a shows the HRTEM image of the amorphous carbonaceous grains. Crystallites of 5 nm size with the (002) plane of graphite are clearly observed. These crystallites are arranged spherically in a manner similar to that of the onion-like carbon. The HRTEM images of QCC and carbon grains produced by using the same method in argon gas are also displayed in Figs. 2b and c, respectively. QCC is formed from the ejecta of methane plasma generated by a microwave discharge at 2.45 GHz (Sakata *et al.*, 1994). The structures of the grains are different depending on the fabrication method. The characteristic central hole structure of the QCC is not observed in the image in Fig. 2a.

As can be seen in the video images of the grains shown in Fig. 3, the carbonaceous grains that were produced in methane gas in the present study showed a considerably different structure as they were heated to successively higher temperatures. The curved graphite structure is distorted by heating at 100°C for 30 min, as indicated in Fig. 3a. The nanodiamond grown from QCC at 100°C (Kimura *et al.*, 2000) was rarely observed in the present specimen. This may be due to the difference in the grain formation

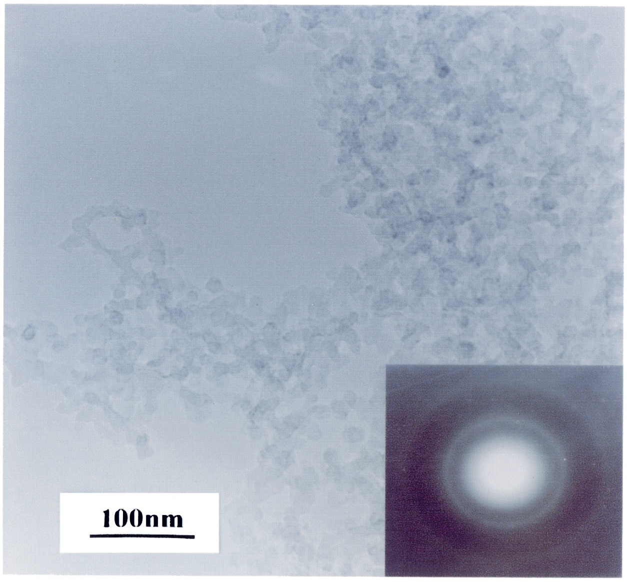

Fig. 1. EM image and ED pattern of carbon grains produced in methane gas atmosphere.

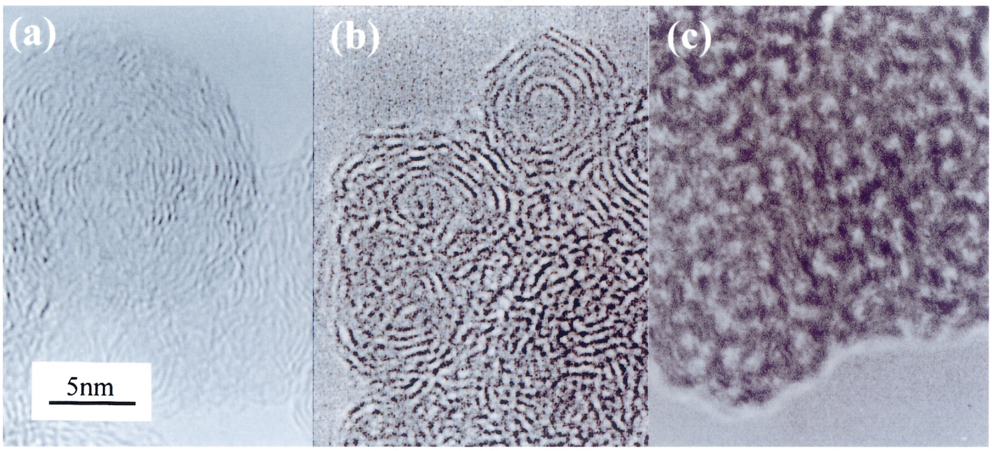

Fig. 2. HREM images of carbon grains produced by various methods: (a) The carbonaceous grains produced in this study, (b) QCC grain, (c) carbon grain produced in Ar gas atmosphere.

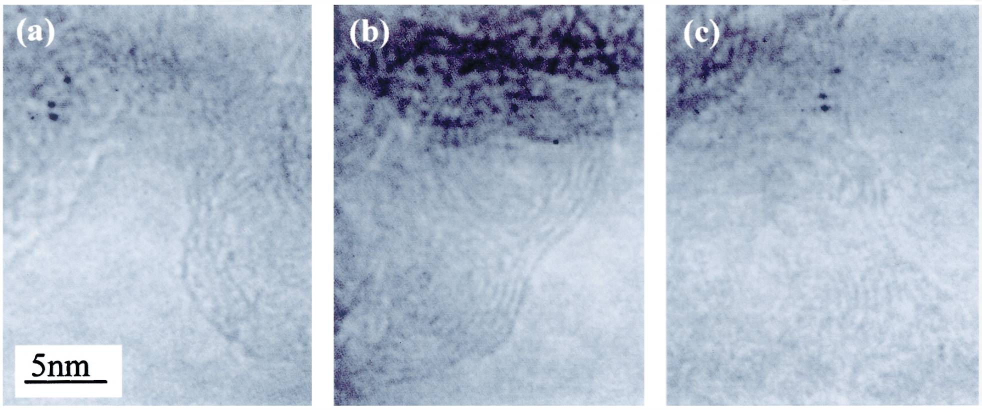

Fig. 3. Structural changes of the QCC-like grains upon heating in vacuum at (a) 100°C, (b) 260°C and (c) 550°C.

method, and the number of sp^3-C terminated with hydrogen atoms may be less than in QCC produced in the plasma (Wada *et al.*, 1999). The distortion in the graphitic structure upon heating to 100°C is thought to be due to the elimination of a functional group, such as -OH, into vacuum, because the -OH group is released by heating at 100–150°C (Allamandola *et al.*, 1992). Upon increasing the temperature to about 260°C, a well-developed onion-like structure appeared, as seen in Fig. 3b. The curved graphite layer of each grain became high contrast graphite image from the surface of each grain. The central parts of each grain became transparent to the electron beam, which suggests the formation of a central hole with a size of 3 nm. Graphitization took place on the surface of each grain and the density change due to graphitization appears to cause the formation of the spherical hole in the center of the grains. This suggests that the development of graphitic structure at the relatively low temperature of 260°C may be responsible for the growth of the QCC structure seen in Fig. 2b. The direct formation of the QCC (Sakata *et al.*, 1983, 1994) may be temperature increment during the formation of the QCC may be due to influenced on the ultraviolet radiation during the growth. Upon further heating to 550°C, the grains combined into sheets according to the graphite lattice relation, as shown in Fig. 3c. Carbon grains produced in inert gases such as argon and helium, as shown in Fig. 2c, did not change upon heating to the previously mentioned temperatures. Therefore, the incorporation of hydrogen into carbonaceous grains is important for the occurrence of structural change at low temperature. The results of this study suggest that the fundamental structures of carbonaceous grains can be significantly changed upon heating, depending upon the composition of the atmosphere from which they were produced.

4. Summary

The development of QCC and graphitic sheets from carbonaceous grains produced in methane gas has been observed using the HRTEM system. The temperature annealing phenomena in the present study were only seen in carbonaceous grains produced in methane gas, *i.e.*, the carbon grains produced in argon or helium gas did not change even upon heating at 500°C. Therefore, it can be concluded that hydrogen incorporated into such grains during their initial formation may be important for the growth of QCC, onion-like structure and graphitic structure. These three characteristic structures are dependent on heating temperature.

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(Received July 18, 2002; Revised manuscript accepted February 3, 2003)