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Communications

Formation of Carbon Onion from Heavily Shocked SiC

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In systems of microscopic scale, it has been suggested that graphite is not always the most stable allotrope of carbon under ambient conditions.[1−5] Fullerenes and carbon onions appear to be more stable than graphite-like flat sheets of hexagonal arrayed carbon atoms.[6,7] Typically, fullerenes have a few tens to several hundreds of carbon atoms and carbon onions have 10^5 to 10^6 carbon atoms; corresponding diameters are roughly 1−3 and 10−100 nm, respectively. Onion structure of carbon shells was first discovered by Iijima in amorphous carbon films prepared by vacuum deposition of carbon vapor.[8] Ugarte generated larger (a few tens of nanometers in diameter) and more spherical carbon onions by intense electron-beam heating of carbon soot particles.[6] In either case, carbon onions were formed under extreme high-temperature conditions. At high pressures, diamond is considered the most stable form of carbon thermodynamically. However, the stability of diamond nanoparticles relative to carbon onions at high temperature and high pressure is not well-known; that is, carbon onions may be stable up to relatively high pressures in the high-temperature regime (in the following, abbreviations such as HT and LP for high temperature and low pressure, respectively, are used throughout the text). In this report, we describe the formation and the structure of unique carbon onions produced from polycrystalline silicon carbide powder under plate-impact-induced heavy shock conditions.

In graphite, the flat planes of hexagonal arrayed carbon atoms (sp^2 state) are weakly bound by van der Waals force, while in diamond the tetrahedral sp^3 hybrid orbitals form rigid cubic structure. This explains why diamond is still stable in nanometer size but graphite is not. Carbon particles with diameters between several and several tens of nanometers can exist as diamond under LT, LP and LT, HP conditions. They can also exist in the form of carbon onions under HT, LP and LT, LP conditions, but graphite with similar particle size is not stable under any T, P conditions. Transformation of shock-formed diamond particles into spheroidal shells under heating at ∼1800 K is reported.[9] Carbon onions are expected to be less stable than diamond particles under LT, HP conditions because diamond cores are formed at the center of carbon onions when they are irradiated with electrons (∼700 °C), where the pressure inside onions is supposed to be much higher than the graphite/diamond equilibrium pressure.[10] Here HT and HP are not precisely defined but roughly HT means 2000 K or higher, depending on the

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(1) Prawer, S.; Peng, J. L.; Orwa, J. O.; McCallum, J. C.; Jamieson, D. N.; Bursill, L. *Phys. Rev.* **2000**, *B62*, R16360.
(2) Jiang, Q.; Li, J. C.; Wilde, G. *J. Phys.: Condens. Matter* **2000**, *12*, 5623.
(3) Gamarnik, M. Y. *Phys. Rev.* **1996**, *B54*, 2150.
(4) Zerilli, F. J.; Jones, H. D. *Proc. Shock Compression Condens. Matter* **1995**, 1663.
(5) Badziag, P.; Verwoerd, W. S.; Ellis, W. P.; Greiner, N. R. *Nature* **1990**, *343*, 244.
(6) Ugarte, D. *Nature* **1992**, *359*, 707.
(7) Kroto, H. W. *Nature* **1992**, *359*, 670.
(8) Iijima, S. *J. Cryst. Growth* **1980**, *50*, 675.
(9) Kuznetsov, V. L.; Chuvilin, A. L.; Moroz, E. M.; Kolomichuk, V. N.; Shaikhutdinov, Sh. K.; Butenko, Yu. V. *Carbon* **1994**, *32*, 873.
(10) Banhart, F.; Ajayan, P. M. *Nature* **1996**, *382*, 433.

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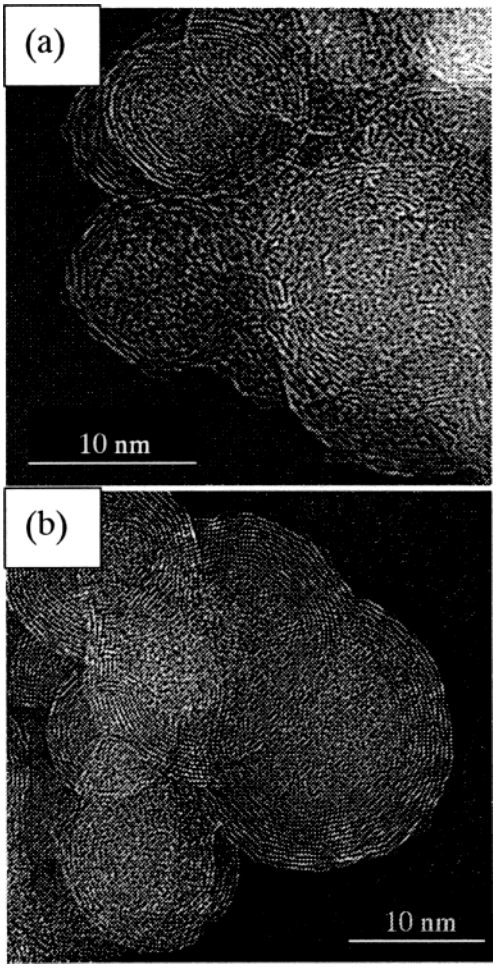

Figure 1. TEM images of shock-recovered sample from SiC polycrystalline powder subjected to strong shock conditions: (a) ~5500 K, ~1.4 Mbar and (b) ~6800 K, ~1.2 Mbar.

pressure, where carbon onions are expected to be formed from carbon soot. HP means diamond stable pressure region (roughly several tens of kbar or higher).

Shock compression is a good experimental technique to provide HT, HP conditions over 1 Mbar and several thousand K that are not easily obtained by other conventional methods. Shock compression provides a harsh environment which prevents substantially any crystal growth and usually only fine (nanoscale) particles are generated. Usual static high-pressure experiments at elevated temperature would not be suitable for the synthesis of carbon onions or for the investigation of the stability of carbon nanoparticles because fine carbon particles would grow to form larger diamond crystals.

Formation of carbon onions under shock conditions using explosives has been reported.[9,11] In plate-impact experiments, however, it is reported that carbon precursors (furfural resin: carbon ~ 90%, oxygen ~ 7%, hydrogen ~ 3%) mixed with copper powder was transformed into only diamond with no trace of carbon onions in the recovered samples.[12] In either case, the starting carbon materials are considered decomposed or melted. We conducted a plate-impact shock experiment with similar shock conditions as in ref 12, but used SiC

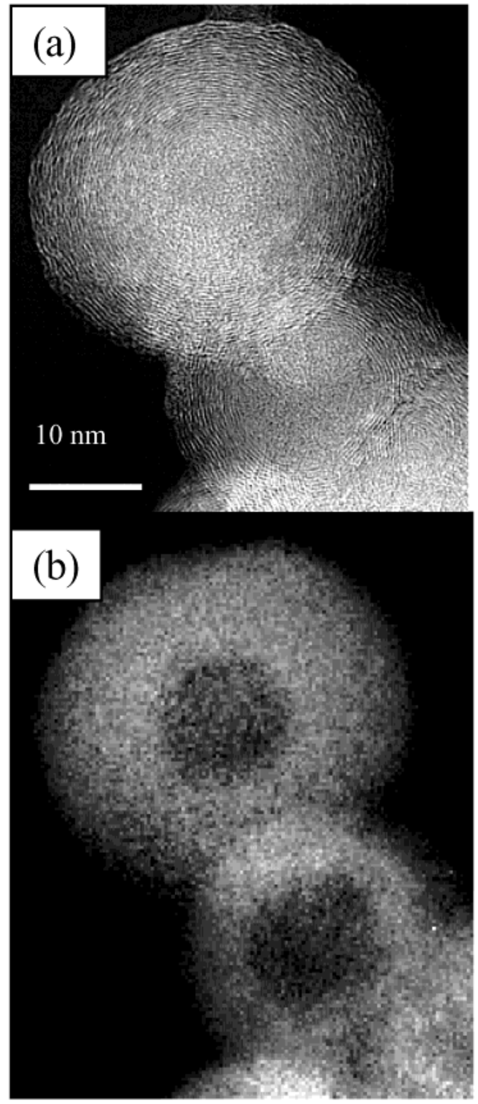

Figure 2. (a) TEM image of shock-recovered sample from SiC polycrystalline powder subjected to strong shock compression (~6800 K, ~1.2 Mbar) and (b) its elemental mapping of carbon by EELS.

(almost pure 6H type) as a source of carbon instead of carbon soot because SiC decomposes under strong shock conditions.[11] The SiC polycrystalline powder (5 wt %) mixed with copper powder (95 wt %) was pressed into a stainless steel capsule and used as a sample. The SiC powder was mixed with copper powder for several reasons: (1) to obtain higher first shock pressure and temperature, (2) to obtain quasi-hydrostatic conditions under shock compression, and (3) for rapid quenching of the postshock sample. No reaction between SiC and copper was observed. A projectile with a 3-mm-thick stainless steel plate impacted the capsule with the impact velocity of ~4.7 km/s to generate shock pressures over 1 Mbar in the sample. Recovered samples were treated with acids to remove metal components and examined by high-resolution transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), and energy-dispersive X-ray analysis (EDX). Shock pressure was estimated using the impedance matching method and shock temperature was estimated using the Hugoniot for copper powder, assuming that

(11) Yamada, K.; Tobisawa, S. *Philos. Mag.* **1990**, *61*, 943.
(12) Setaka, N.; Sekikawa, Y. *J. Mater. Sci.* **1981**, *16*, 1728.

the thermal equilibrium is reached within the sample mixture.

Present shock experiments were performed under two different shock conditions: (1) ~5500 K, ~1.4 Mbar and (2) ~6800 K, ~1.2 Mbar. Representative TEM images of recovered samples from shock conditions (1) and (2) are shown in Figure 1. A more detailed TEM image of carbon onions and its carbon-mapping image are shown in Figure 2. Many particles with onion structure were found, but diamond particles were not found in the recovered samples. Onion diameters are mostly 10−30 nm. At the center of onions is an amorphous-like core and several to 20 layers of nearly concentric spherical carbon shells surround the core. EELS and EDX results indicate that onion shells consist of almost pure carbon atoms, which indicates the decomposition of SiC under present shock conditions. The amorphous-like cores contain mainly carbon and silicon atoms with some inclusion of oxygen atoms. Figure 1b displays clearly that carbon content at the cores of the two carbon onions is significantly less than that of the carbon shells. The spacing between layers in the carbon onions decreases toward the center due to high-pressure effect.[10] SiC particles with reduced crystallite size were also found in the recovered samples.

The production efficiency of carbon onions is significantly higher under shock condition (2) than under shock condition (1). Although it is quite difficult to estimate the production efficiency of carbon onions from TEM images, it appears that the relative production efficiency for shock condition (2) is roughly an order of magnitude higher than that for (1). It is seen in Figure 1 that the carbon onions obtained under shock condition (1) have fewer carbon shells than those obtained under shock condition (2). These facts suggest that higher shock temperature favors the formation of carbon onions. In the experiments of ref 12, similar shock conditions were used (the shock pressure, they claimed, was 1.0 Mbar and the shock temperature, we estimated using their experimental conditions, is ~5500 K), but the carbon precursor was transformed to diamond particles. In the case of our experiments, however, SiC was decomposed under extreme shock compression, and only carbon atoms were selectively combined to form numerous carbon onions when a mixture of decomposed carbon and silicon atoms was rapidly quenched to ambient conditions. In the present experiment, SiC fine particles generated under shock compression might have acted as a kind of nucleus and an onion structure was preferentially formed around the SiC cores. Also, the possible role of Si produced from the decomposition of SiC cannot be ignored. These possibilities mentioned here are merely speculations and further experiments are necessary to obtain more conclusive evidence on the formation mechanism of carbon onions under strong shock compression.

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