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Balloon-shaped graphitic-carbon material induced by shock-compression of dehydrochlorinated poly(vinylidene chloride)

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Shock-compression of dehydrochlorinated poly(vinylidene chloride) at 15 GPa and 6500 K produced a small portion of balloon-shaped graphitic-carbon material mixed with a large proportion of graphite and diamond. The size and thickness of the various balloon particles were *ca.* 40–300 nm and 4–6 nm, respectively. The balloon-shaped material is presumably a by-product from a carbon source fragmented under shock-compression and would not be related to the high yield of diamond.

Carbon forms fundamentally three types of allotropes resulting from its available three bond modes, sp, sp^2 and sp^3. In nature, only the sp^2-type allotrope (graphite) and sp^3-type (diamond) exist. The search for a sp-type has originated from a discovery of two resonance hybrids, α-carbyne[1] (polyyne form) prepared by high temperature treatment of oxidative condensates of copper acetylide and β-carbyne[2] (polycumulene form) derived by coupling of carbon suboxide and sodium acetylide, which was made by a Russian group between 1961 and 1967. This was followed by the preparation of eight or more polymorphs of carbon from vaporized carbon,[3] de(hydro)halogenated polymers having long polyyne segments (carbynoids),[4–6] and a coil form of polyyne by laser vaporization of graphite.[7] However, the presence of carbyne as a high temperature material is unusual considering the fragility of conjugated polyyne compounds.[8]

The world of carbon allotropes seemed to have been completed with diamond, graphite and carbyne. However, between 1985 and 1992, an outstanding discovery of carbon clusters by Kroto *et al.*,[9] Iijima,[10] and Ugarte,[11] the so-called fullerenes, nanotubes and carbon onions, which form topologically closed-shell sp^2-carbon networks completely different from planner graphite networks, were synthesized upon high energy irradiation of graphite such as laser vaporization, arc evaporation, and electron irradiation. This finding along with the recent prediction of an unexpected variety of carbon isomers[12] like *cyclo*-C_{18} and graphyne, *etc.* has encouraged the search for other new carbon-based substances. On the other hand, the carbon clusters including carbyne were found to show surprisingly high diamond conversions under much milder physical conditions in comparison with the graphite-to-diamond transformation, for example, C_{60}-to-diamond (90 mass%) conversion occurs under a non-hydrostatic pressure of 20 ± 5 GPa at room temperature,[13] and carbyne-to-diamond (99 mass%) occurs under a static pressure of 8 GPa at 1400–1700 °C without catalyst.[14]

Knowledge of the isomerisation between two carbon allotropes suggests the possibility of producing hitherto unknown carbon allotropes with or from diamond. Shock-compression[15] used for diamond synthesis owing to the extremely high dense energy supply by shockwaves and successive rapid cooling in microseconds is expected to be a very useful method to search for new metastable carbon-based substances. We studied previously shock-compression of dehydrochlorinated poly(vinylidene chloride) (a carbynoid) under several GPa for the preparation of carbyne and found a trace of a new crystalline carbon mixed with diamond and graphite.[16] The new carbon was assigned to the hexagonal crystal system with cell dimension $a_0 = 0.338$ nm and was compared with carbyne in terms of the carbon geometry projected onto the ⟨001⟩ plane. Here, we further investigate the possibility of producing unknown carbon-based substances under a shock pressure of 15 GPa, the medium pressure required for the shock-induced graphite-to-diamond transformation, using the same starting material as previously.

Experimental

Sample preparation

The starting material was prepared by dehydrochlorination of poly(vinylidene chloride) (Asahi Chemical Industry Co. Ltd., Saran polymer $MW = 10^5$) using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base and *N*,*N*-dimethylacetamide as solvent. Determination of the chemical structure using elemental analysis, IR, Raman, UV–VIS, and NMR spectroscopy was carried out in the same way as described previously.[16] The material which was obtained as a fine black powder was an amorphous block polymer linked with conjugated polyene and polyyne segments, $-(CH{=}CH)_n-(C{\equiv}C)_m-$, containing small amounts of carbonyl and nitrogen and trace amounts of chlorine, and this structure was confirmed to be the same as previously.

A homogeneous mixture of the starting material (2 equiv.) and coarse-grained copper balls (98 equiv.) was filled in a steel sample holder of 30 mm diameter and 15.5 mm depth, and pressed at 28 MPa for 30 min. The product was then dried at 80 °C for 20 min under ordinary pressure, and vacuum-dried at 120 °C for 2 h. The packing density of the starting material in the pressed sample was 0.44 g cm^{-3} (20% of the theoretical density of graphite). Shock-compression of this sample was carried out using the plane shock-compression apparatus shown in Fig. 1. The apparatus was constructed with a detonator, an explosive lens composed of a set charge of hydrazine nitrate (63.5 mass%)–hydrazine hydrate (36.5 mass%) and nitromethane, a high melting point explosive (HMX, detonation speed 9.1 km s^{-1}), a copper flyer, a brass vessel containing the sample holder, and a steel momentum trap surrounding the brass vessel. The average shock pressure applied to the sample was estimated to be 15 GPa. The recovered sample was machined, immersed in 10% HNO_3 to remove the copper matrix, washed with distilled water, and vacuum-dried at 200 °C. A fine black powder was obtained in a yield of *ca.* 25%.

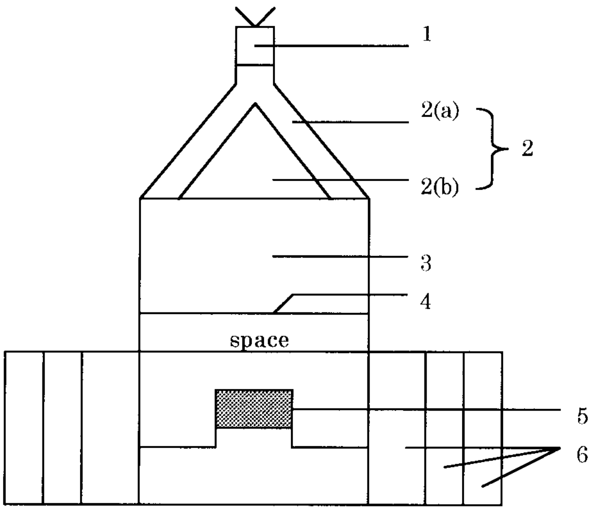

Fig. 1 Section of the plane shock-compression apparatus: 1, detonator; 2, explosive lens consisting of (a) hydrazine nitrate–hydrazine hydrate and (b) nitromethane; 3, high melting point explosive; 4, copper-flyer; 5, brass vessel containing the sample; 6, steel momentum trap.

Measurements

The C, H, N contents of the sample were determined on a Holiba CHN analyzer. Raman spectra were measured at an excitation wavelength of 514.5 nm generated with a 1.0 mW argon laser using a MST foundation Ga-505 spectrometer. The crystal structures were investigated using a Rigaku RINT-2500 X-ray powder diffractometer equipped with a position-sensitive proportional counter and a graphite monochromator on the detector. Ni-filtered Cu-Kα radiation generated at 50 kV and 200 mA was used as the X-ray source. The microscopic morphologies were observed using a JEOL JEM-4000FX high-resolution transmission electron microscope (HRTEM) equipped with an energy-dispersive X-ray analyzer (EDX), an electron energy-loss spectrometer (EELS) and an electron diffractometer (ED). The nanoscaled observation was complemented using a Hitachi HF-2000 instrument for field emission transmission electron microscopy (FETEM) equipped with an ED, a parallel electron energy-loss spectrometer (PEELS) and an EDX. The sample powder was diffused supersonically in a methanol–distilled water (1 : 1) solution for 5 min, a drop of the solution was then placed on a microgrid coated with a carbon–collodion membrane, air-dried, and measured at 400 kV accelerating voltage.

Results and discussion

Elemental analysis and Raman spectrum

The C/H/N content of the shock compacted sample was 98.1% C, 0.3% H and 0.3% N. The elements of the same sample detected by EDX were almost entirely carbon except for oxygen and silicone impurities due to the carbon–collodion membrane and copper due to the microgrid used for the TEM measurement. Fig. 2 shows the Raman spectra of the starting material and the shock-compacted sample. The spectra indicate that the starting material was entirely transformed into different materials. The bands at 1592 and 1352 cm^{-1} of the shock-compacted sample were similar to those of glassy carbon[17] in terms of the peak position, and were assigned to G- and D-bands of the graphite structure, respectively. A broad line width and a relatively comparable intensity of the peaks indicate the material is coagulated with poorly crystalline fine grains.

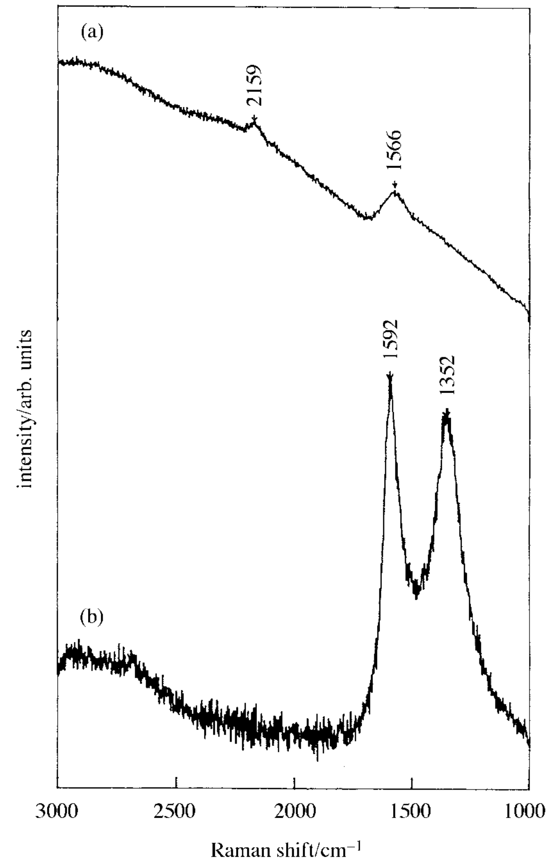

Fig. 2 Raman spectra of the starting material and the shock-compacted sample: (a) the starting material; (b) the shock-compacted sample.

X-Ray diffraction

Fig. 3 shows the X-ray powder diffraction of the shock-compacted sample. The diffraction consisted of two patterns. The observed *d*-values, intensities, and lattice constants of the patterns are given in Table 1 in addition to the data of the known carbon materials. Pattern 1, a cubic structure with $a = 0.35597$ nm, agreed with that of diamond (JCPDS 06-0676) except for a broad FWHM ($2\theta = 1.664°$ for the ⟨111⟩ peak). Pattern 2, a hexagonal structure with the

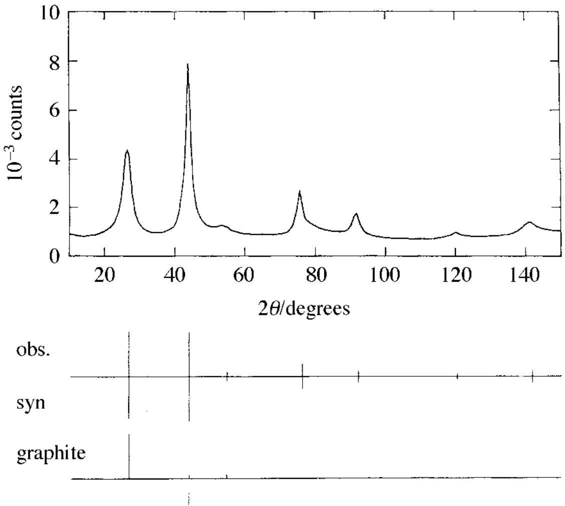

Fig. 3 X-Ray powder diffraction of the shock-compacted sample. For comparison, the standard patterns of graphite (JCPDS 25-0284) and diamond (JCPDS 06-0676) are shown together with their superposition (syn).

Table 1 X-Ray diffraction pattern of the shock-compacted sample and assignment of the structures by comparison with patterns of standard references

Pattern 1

Cubic $a=0.35597$ nm					Diamond (JCPDS 06-0676) $a=0.35667$ nm		
2θ/degrees	d_{obs}/nm	d_{calc}/nm	$100\ I/I_0$	*hkl*	d/nm	$100\ I/I_0$	*hkl*
44.022	0.20553	0.20552	100	111	0.20600	100	111
75.479	0.12585	0.12585	24	220	0.12610	26	220
91.734	0.10733	0.10733	13	311	0.10754	16	311
120.416	0.08876	0.08899	4	400	0.08916	8	400
141.221	0.08166	0.08166	8	331	0.08182	16	331

Pattern 2

Hexagonal $c=0.6683$ nm					Graphite (JCPDS 25-0284) $a=0.2458$ nm, $c=0.6696$ nm		
2θ/degrees	d_{obs}/nm	d_{calc}/nm	$100\ I/I_0$	*hkl*	d/nm	$100\ I/I_0$	*hkl*
26.657	0.33413	0.33413	100	002	0.33480	100	002
					0.21270	3	100
					0.20270	15	101
					0.17950	3	102
53.953	0.16981	0.16707	5	004	0.16740	6	004

lattice constant $c=0.6683$ nm, fitted well with that of graphite (JCPDS 25-0284). The ⟨100⟩ peak of pattern 2 was apparently absent because of overlapping with the ⟨111⟩ peak of pattern 1. As a guide to indexing, the standard patterns of the graphite and diamond are included in Fig. 3. The average size of diamond crystallites estimated from the FWHM is *ca.* 5 nm, and the formation of such nanosized diamond particles is also a characteristic of the shock-compression synthesis. The existence of diamond was confirmed by XRD, however, it could not be detected by Raman spectroscopy, probably because of its very small size. The mass ratio of diamond to graphite contained in the shock-compacted sample, which was estimated by calibration with the relative intensity of known composition, was *ca.* 70%. As already stated, diamond conversion of the carbon clusters exceeds 90% under even much lower pressures. A characteristic common feature of these starting materials is an abundance of active unsaturated bonds. The bonds would be easily fragmented even under mild conditions, which may be related to such a high diamond conversion.

TEM observation

Fig. 4 shows the HRTEM image of the shock-compacted sample. This reveals a large portion of graphitic domains and microdiffused fine crystalline particles showing a lattice image. The FETEM-ED patterns of the graphitic domains and crystalline particles showed a diffuse ring pattern and a spot pattern, respectively. The interplanar spacings determined from the spot pattern were 0.208 nm ⟨111⟩, 0.127 nm ⟨220⟩ and 0.0826 nm ⟨331⟩. The values are in accord with those of diamond within an experimental error of 2% using the silicon pattern. Therefore, the crystalline material was assigned to diamond. The graphitic domains were assigned to graphite from the similarity to the ED pattern of low crystalline graphite. These assignments were also supported by the Raman and XRD results described above. In addition to these materials, balloon-shaped particles as shown in Fig. 5 were occasionally seen. In this figure, the various balloon particles cluster together locally near the graphite domains. The outside of the particles is covered with a dense wall as a round closed shell in contrast to the inside which suggests a bright non-structured space. The shell structure is seen as laminated with graphitic thin layers oriented along the walls. The EELS spectrum showed both 1s→π* and 1s→σ* transitions at the carbon K-edge similar to those of graphite, which indicates the material is composed of graphitic sp^2 carbon. The size and thickness of the various balloon particles estimated from the TEM observation were *ca.* 40–300 nm and *ca.* 4–6 nm, respectively. This form of carbon material is probably new.

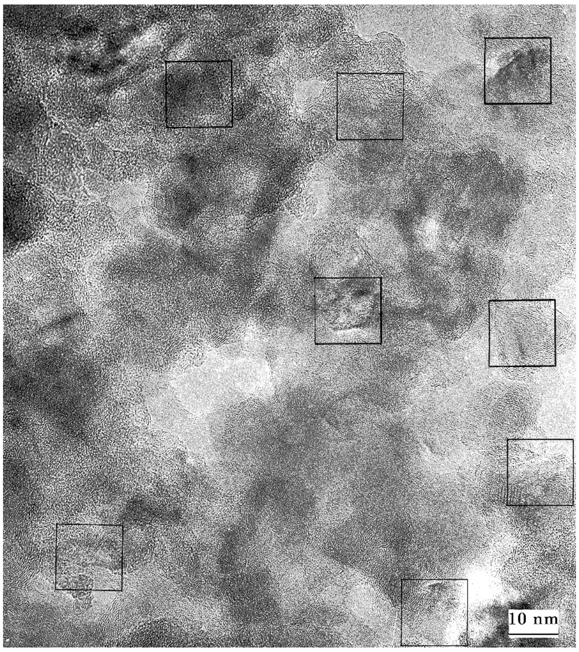

Fig. 4 High resolution TEM image of the shock-compacted sample. The areas enclosed within squares indicate microdiffused fine crystalline particles having a lattice image.

The shock pressure, P, applied to the sample and the particle velocity, U_{p}, estimated from the Hugoniot data by Marsh,[18] are 15 GPa and 5.2 km s^{-1} respectively. The internal energy increase, ΔE, and a temperature increase, ΔT, of the sample under shock-compression are derived from the well known Rankin–Hugoniot equations:[19]

$$\Delta E = U_{\mathrm{p}}^{2}/2 \qquad (1)$$

$$\Delta T = E/3R \qquad (2)$$

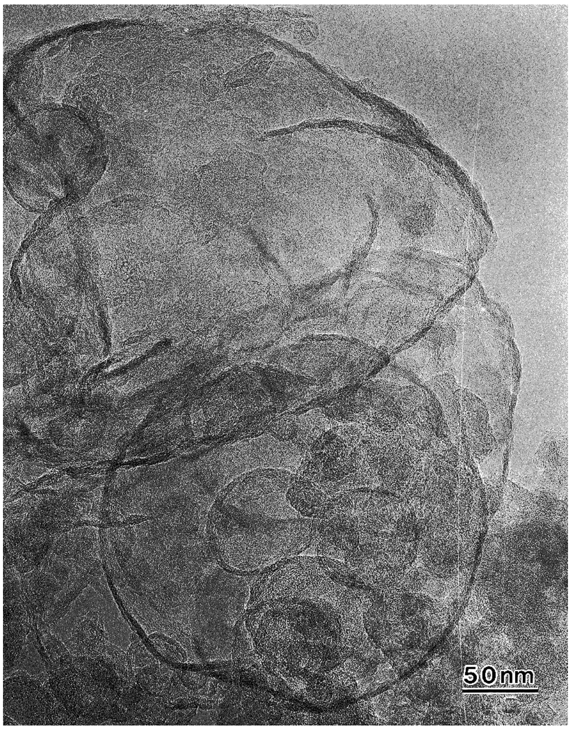

Fig. 5 High resolution TEM image of balloon-shaped particles contained in the shock-compacted sample.

where R is the gas constant. From these, $\Delta E = 13.5$ MJ kg^{-1} and $\Delta T = 6500$ K are obtained. This temperature is sufficiently high to make the sample fragment, therefore the composition of the shock-compacted sample would originate from carbonaceous fragments, that is, the carbonaceous fragments are presumably transformed into diamond as a high pressure phase, graphite as the thermodynamically the most stable phase, and the balloon-shaped graphitic carbon possibly as a high temperature phase. However, the previous crystalline carbon[16] was not observed in this work in spite of the same starting material. This is probably due to the difference in the shock conditions. The pressure and temperature in this work were much higher than those (several GPa, 600–800 K) in the previous study. The high pressure increased the yield of diamond, while the high temperature (6500 K) would completely decompose the previously observed crystalline material even if it were formed. Also, codeposition of known carbon clusters such as fullerenes, nanotubes and carbon onions is unknown. This exclusive tendency among carbon allotropes other than graphite and diamond (we do not know any examples of codeposition for the carbon clusters) suggests that the balloon-shaped material would be a kinetically controlled by-product but not a thermodynamically controlled intermediate leading to diamond.

Conclusions

Creation of a new type of carbon-based substance was attempted by shock-compression of dehydrochlorinated poly (vinylidene chloride). Codeposition of a small quantity of balloon-shaped graphitic-carbon material and a large quantity of graphite and of diamond was confirmed by TEM analysis. The size and thickness of the various balloon particles were 40–300 nm and 4–6 nm, respectively. The pressure and temperature applied to the sample by shock-compression were estimated to be 15 GPa and 6500 K, respectively. The balloon-shaped material was presumably deposited as a by-product from a carbon source fragmented under shock-compression and would not be related to the high yield of diamond.

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