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Preparation of carbon nitride C_2N by shock-wave compression of poly(aminomethineimine)

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Shock-wave compression of poly(aminomethineimine) under a pressure of 40 GPa produced no crystalline material but amorphous carbon nitrides having microscopically different morphologies, a quasi-spherically concentric closed-shell form, a random-layer-structure and a completely amorphous structure. These have the same composition, C_2N, and the same chemical structure consisting of sp^2 carbon and sp^2 nitrogen.

Carbon materials containing low atomic number group 13 and group 15 elements such as carbon nitride and carbon–boron nitride have recently attracted much attention for their potential for excellent heat resistance, superhardness, permanent abrasive resistance and wide bandgap semiconductivity. β-C_3N_4 and cubic C_3N_4 were predicted to have the highest hardness comparable or superior to diamond.[1,2] Synthetic approaches to β-C_3N_4 were made by various methods using high pulse energy, such as shock-wave compression,[3] pulsed laser ablation combined with radio frequency discharge,[4] radio frequency diode sputtering,[5] plasma arc discharge,[6] radio frequency sputtering,[7–9] laser ablation,[10] high dose nitrogen implantation,[11] high energy shock-plasma deposition,[12] and reactive pulsed laser deposition,[13–15] possibly considering the thermodynamically non-equilibrium property of this material.

These approaches produced amorphous carbon nitrides[8–15] and crystalline carbon nitrides.[4–7] The groups of Niu,[4] Yu,[5] Matsumoto[6] and Ze-Bo[7] assigned their crystalline carbon nitrides to β-C_3N_4, but their conclusions seem to be doubtful because their assignments were not made on the basis of all the evidence of β-C_3N_4 that the atomic ratio $C:N=3:4$, that the material is constructed with sp^3 carbon and sp^2 nitrogen, and that the crystalline structure is hexagonal. Recently, Chen *et al.* synthesized large Si–C–N crystals on Si⟨100⟩ substrates by microwave plasma assisted CVD.[16,17] They reported that the crystalline structure of this material is close to that of α-C_3N_4,[18] carbon atoms are tetrahedrally bonded with nitrogen and both C and Si are always bridged by nitrogen.

A breakthrough in the production of crystalline β-C_3N_4 or cubic C_3N_4 would be made by the best suited combination of pulse supply of high density energy and molecular design of the starting material. Shock-wave compression is able to load extremely high density energy to a sample in microseconds, as can be seen in the shock-synthesis of diamond. Wixom attempted to prepare β-C_3N_4 by shock-wave compression of several pyrolyzed C–H–N compounds, however, the product was not β-C_3N_4 but a mixture of amorphous graphitic material and well ordered diamond.[3] This result is possibly due to phase separation into thermodynamically more stable diamond during the long duration required for well ordered crystallization.

The most important points in preparing heterodiamonds such as cubic C_3N_4 and cubic B–C–N compounds, that are much more non-equilibrium materials than diamond, lie in quenching to avoid undesirable atomic rearrangements of the product and use of starting materials containing carbon–heteroatom skeleton bonds in which the heteroatoms are scarcely eliminated by high energy loading. Recently, we first prepared $BC_{2.5}N$ heterodiamond by shock-compression of graphitic $BC_{2.5}N$.[19] In this work, we attempted the synthesis of carbon nitride by applying the shock-compression technique to the C–H–N linear polymer, poly(aminomethineimine).

Experimental

Sample preparation

Poly(aminomethineimine), $-[C(NH_2)=N]_n-$, the starting material, was prepared by ring-opening polymerization of melamine with an excess of $ZnCl_2$ at 450 °C for 5 h in an autoclave, according to ref. 20. The obtained product was heated with conc. HCl in a water bath, filtered with a glass filter, washed with distilled water and vacuum-dried at 200 °C, to obtain a brown powder. The starting material thus obtained was mixed with small copper balls in a polymer : copper 2 : 98 mass ratio, placed into a steel capsule, and pressed into a disk. The bulk density of the disk was set at 70% of the theoretical value. The disk was shock-compressed using the shock-compression apparatus shown in Fig. 1. The apparatus was constructed with a detonator, a burster of a seat explosive (shock wave velocity = 6 km s^{-1}), an HMX explosive (shock wave

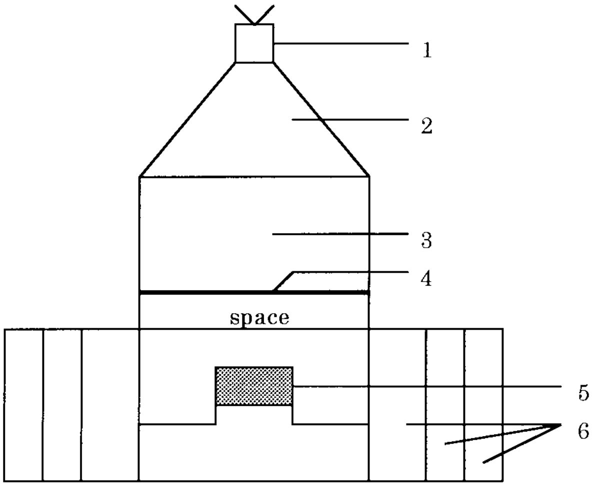

Fig. 1 Section of a planar shock wave compression apparatus: 1, detonator; 2, burster of a sheet explosive; 3, HMX explosive; 4, copper flyer; 5, brass-vessel including the sample disk; 6, steel momentum trap

velocity = 9 km s^{-1}), a copper flyer, a brass vessel including the sample disk and a steel momentum trap surrounding the sample vessel. The generated detonation wave accelerated the copper flyer, followed by impaction onto the sample. The incident shock pressure on the sample was estimated to be 40 GPa. The recovered sample was machined, immersed in aq. HNO_3 to remove the copper matrix, heated with conc. HCl to remove trace amounts of metallic contaminants, washed with distilled water, vacuum-dried at 200 °C and the black powder obtained. Recovery of the sample was *ca.* 43%.

In order to check the presence or absence of diamond-like materials in the above shock-compression product, the following treatment with a fusing agent was carried out: the shock-compression product was thoroughly mixed with an excess of NaOH and heated at 350 °C for 1 h. Appropriate amounts of distilled water were added to the residue, the mixture was centrifuged, and the precipitate was centrifugally washed with distilled water. Only a small amount of brown powder remained.

Measurements

The chemical compositions of the samples were determined using a Horiba CHN analyzer. XRD measurements were conducted with Ni-filtered Cu-Kα radiation generated at 50 kV and 200 mA using a Rigaku RINT-2500 X-ray powder diffractometer equipped with a position-sensitive proportional counter and graphite monochromator on the detector. The crystalline structure, elemental composition and chemical bonding nature in the microscopic regions of the samples were investigated using a Hitachi HF-2000 instrument for field-emission transmission electron microscopy (FETEM) equipped with an electron diffractometer, a parallel electron energy-loss (PEEL) spectrometer, and an energy-dispersive X-ray analyzer. These measurements were performed with an accelerating voltage of 200 keV. The IR spectra of the samples were measured in a KBr disk using a Perkin-Elmer FTIR-1640 spectrometer. The Raman spectra were measured at an excitation wavelength of 1064 nm generated with a 50–100 mW Nd : YAG laser using a Perkin-Elmer FT-Raman-2000 spectrometer.

Results

Chemical analysis

The elemental analysis of the shock-compression product gave the following atomic percentages: C, 59.9%; H, ≪0.1%; N, 31.1%. The atomic ratio is thus C : N = 2.25 : 1.0, and the chemical formula is formally C_2N. It is noted that significant amounts of nitrogen atoms of the starting material were lost by shock-compression. The small amount of incombustible residue was not investigated.

IR and Raman spectra

The IR spectrum of the starting material is shown in Fig. 2(a). The spectrum was similar to the reported spectrum of poly(aminomethineimine).[19] The IR bands were assigned as followed: bands at 1624 and 1511 cm^{-1} to C=N stretching; bands at 1350 and 1278 cm^{-1} to C—N stretching of the NH_2 group combined with aromatic carbons; two broad bands around 3358 and 3204 cm^{-1} to NH_2 stretching while a peak at 797 cm^{-1} was unassigned. The IR spectrum of the shock-compression product is shown in Fig. 2(b). The bands were assigned as follows: a broad band at 1600 cm^{-1} to C=N stretching mixed with C=C stretching of graphitic rings; the broad band around 1310 cm^{-1} to C=C stretching of disordered domains; the broad band at 3420 cm^{-1} to O—H stretching of H_2O but not NH_2 stretching. It is noted that the shock-compression product lost the NH_2 group in the side chain and some of the nitrogen atoms in the main chain of the starting material. Also, there is no C—H group and the C=N stretching bands shift to lower wavenumbers. These IR characteristics suggest graphite carbon nitride formation, since the vibrational modes of amorphous carbon nitrides are generally observed in the 1600 and 1300 cm^{-1} regions and an increased polarity by incorporation of nitrogen with carbon makes the IR forbidden modes of graphite IR-active.[13–15] The disappearance of the starting 1511 and 1278 cm^{-1} peaks is a consequence of carbonization by shock-compression.

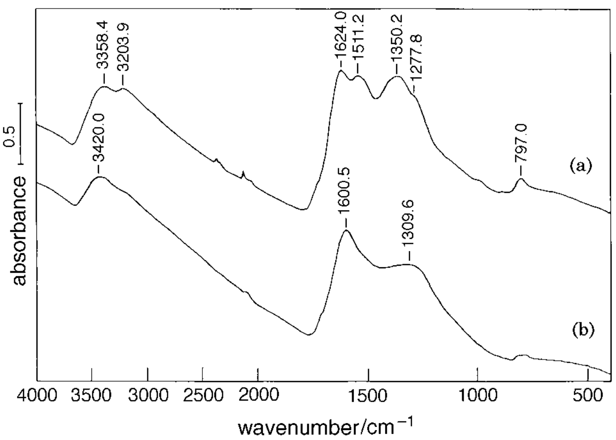

Fig. 2 IR spectra showing the chemical structure change before and after shock-wave compression of the polymeric compounds: (a) the starting compound, poly(aminomethineimine); (b) the shock-compression product

The Raman spectrum of the starting material showed two broad bands around 1600 and 1350 cm^{-1}, and that of the shock-compression product shows weak and very broad bands around the same positions. These broad bands were assigned to C=N stretching bands. However, the Raman spectrum after shock-compression did not show any bands of diamond (1332 cm^{-1}) or β-C_3N_4 (1212–1265 cm^{-1} estimated for β-C_3N_4[3]).

XRD diffraction

The XRD measurement of the starting material showed an amorphous pattern consisting of two broad peaks at $2\theta = 26.6°$ (strong peak, $d = 0.348$ nm) and 43.3° (weak, 0.209 nm). The shock-compression product also showed an amorphous XRD pattern consisting of two broad peaks at $2\theta = 26.4°$ (strong, 0.337 nm) having a broad shoulder around 21° and at $2\theta = 43.6°$ (weak, 0.207 nm) but showed no crystalline peak. The XRD patterns were scarcely changed before and after shock-wave compression.

TEM analysis

The TEM observation of the shock-compression product showed amorphous materials having three different morphologies but no crystalline material. One is a quasi-spherically concentric closed-shell particle (material 1) having a diffuse ring ED pattern, as shown in Fig. 3. The TEM image resembles those of carbon onions.[21,22] The fringe spacing estimated from Fig. 3 is *ca.* 0.40 nm. Another is a random-layer structure material (material 2) similar to glassy carbon, as shown in Fig. 4. The remaining material is completely amorphous (material 3) without any diffraction planes as shown in Fig. 5. All the materials 1–3 are elementally composed of carbon and nitrogen atoms, and both atoms show 1s→π^* transitions at the K-edges of the core-loss region in the PEEL spectra as shown in Fig. 6. This suggests that the materials are composed of trigonally bonding carbon and nitrogen atoms.

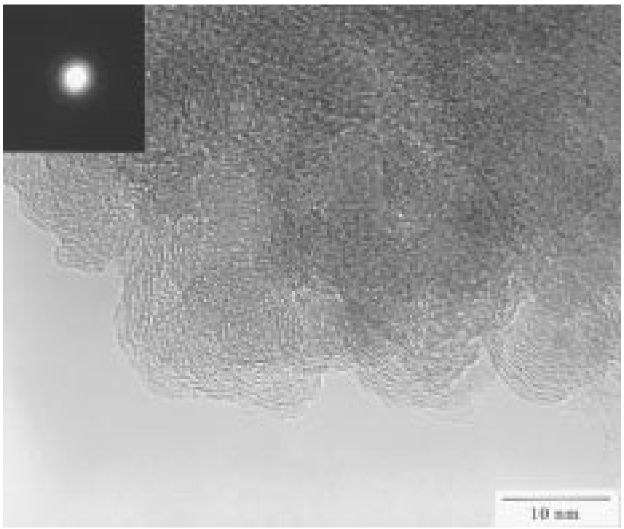

Fig. 3 FETEM image and ED pattern of the quasi-spherically concentric closed-shell particles included in the shock-compression product. The fringe spacing of the material is about 0.40 nm.

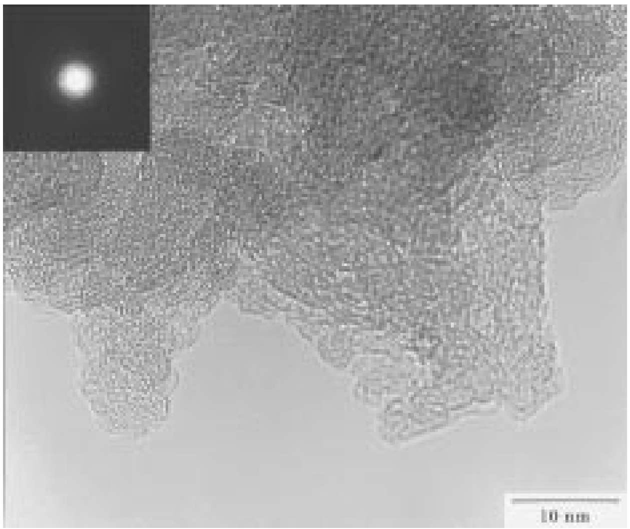

Fig. 4 FETEM image and ED pattern of a random-layer structure material included in the shock-compression product

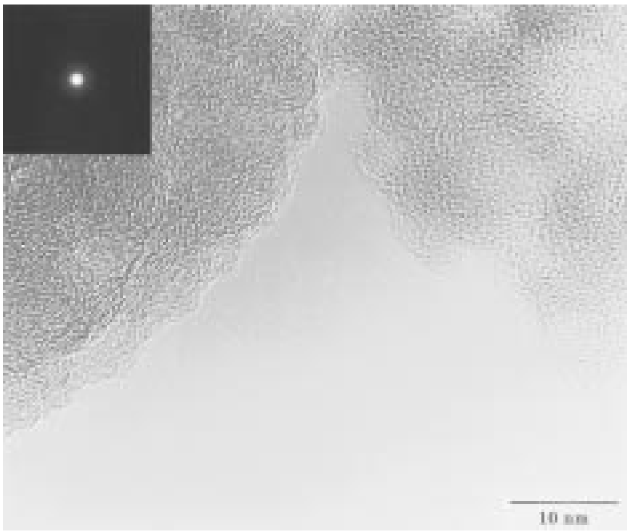

Fig. 5 FETEM image and ED pattern of a completely amorphous material included in the shock-compression product

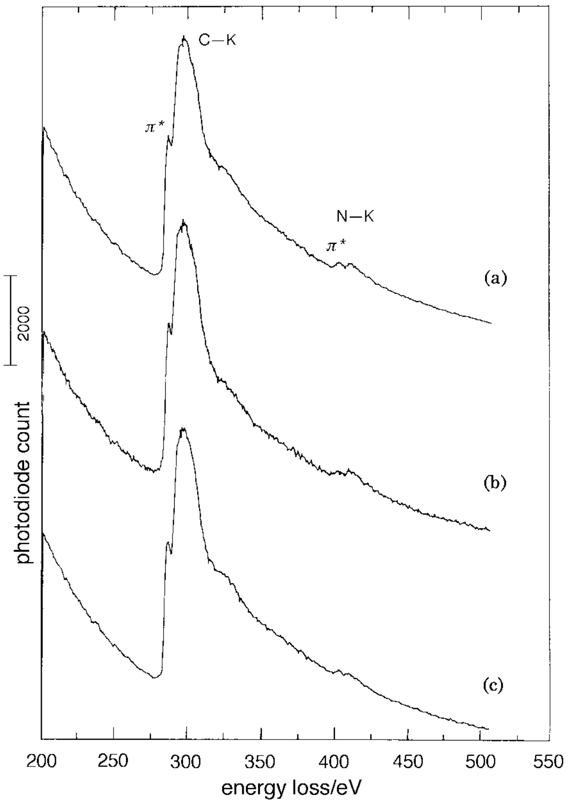

Fig. 6 PEEL spectra at the K-edges for the constituent atoms composing the particles observed in Fig. 3–5: (a) quasi-spherically concentric closed-shell particle; (b) random-layer structure material; (c) completely amorphous material. Note the presence of the π* feature for both carbon and nitrogen.

Discussion

Materials 1–3 were observed side-by-side. The chemical composition determined by the CHN combustion analyzer showed that the shock-compression product is composed of carbon, nitrogen and negligible amounts of hydrogen. From the results of chemical analysis, IR and PEEL spectroscopy, materials 1–3 were ascribed to carbon nitride. The three materials are probably the same with regard to the chemical composition and chemical structure, since the PEEL spectra are very similar. Fig. 7 shows a simplified structure model of carbon nitride, C_2N deduced from the structural characterizations described above. In this model, carbon atoms of graphite are

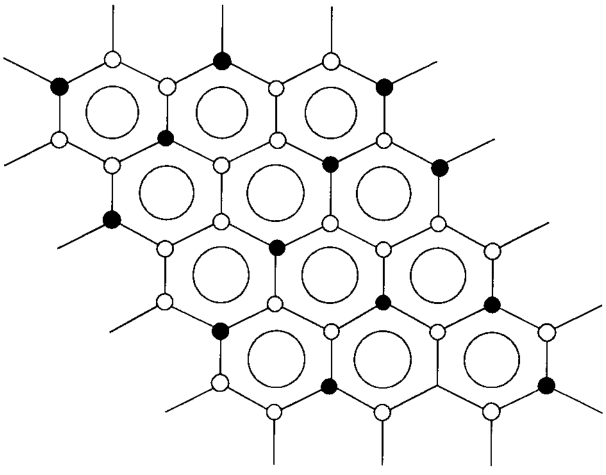

Fig. 7 Simplified structure model of the shock-produced carbon nitride, C_2N: (○), C; (●), N. In this model, carbon atoms of graphite are randomly substituted with nitrogen in a C:N=2:1 atomic ratio.

randomly substituted with nitrogen in a C : N = 2 : 1 atomic ratio, and such a layer is irregularly arranged.

Differences in the structural ordering are clearly found among these materials. The result suggests that the polymeric starting material is successively changed from completely amorphous carbon nitride to the onion-like carbon nitride in local regions. The occurrence of morphologically different phases is probably due to a temperature gradient in the cooling process after release of the shock-wave compression. The applied shock pressure was at a high enough level to lead to the phase transformation of graphite sp^2 carbon into diamond-like sp^3 carbon. However, no cubic materials were observed. The absence of diamond-like materials was further confirmed by micro XRD measurements of the residue after fusing with NaOH. As explained in the introductory section, the shock-compression of the pyrolyzed C–H–N compounds produced diamond but no β-C_3N_4 or cubic C_3N_4.[3] As to the present work, it is notable that the nitrogen content of *ca.* 30 mass% is present in the products, although they are amorphous. The absence of cubic material is probably due to the difficulty in the cubic transformation of the starting material. To achieve the synthesis of a cubic carbon nitride like cubic C_3N_4, a series of shock experiments using graphitic carbon nitrides instead of C–H–N compounds will be needed.

Conclusion

Shock-wave compression of poly(aminomethineimine) under a pressure of 40 GPa was attempted to prepare new carbon nitrides. The product was investigated in terms of the chemical composition, crystalline structure and chemical bonding, by means of chemical analysis, XRD, IR, Raman and analytical FETEM. Amorphous carbon nitrides having different morphologies were produced, but no crystalline material was observed. These are a quasi-spherically concentric closed-shell particle, a random-layer-structure material, and a completely amorphous material without any diffraction planes. These have the same elemental composition, C_2N, and the same chemical structure composed of sp^2 bonding carbon and sp^2 bonding nitrogen.

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