Modified Phases of Diamond Formed Under Shock Compression and Rapid Quenching

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Two modified forms of carbon were quenched by a rapid-cooling technique from graphite sheets shock-compressed to 65 gigapascals and 3700 K. One form, "ndiamond," which was obtained from the most rapidly cooled part, has a crystal structure close to that of cubic diamond. The other form, found in the relatively slow-cooled part, was comparable to an i-carbon prepared by an ion-beam technique. The n-diamond is interpreted as a metastable form, the same as hexagonal diamond, converted from graphite through a martensitic transition, for which either the region or the path may be different from that of hexagonal diamond. The second form was found to be produced through reconstruction.

ARBON EXHIBITS A WIDE VARIETY of forms that depend on the surrounding environment and processing techniques (1). Crystalline forms of pure carbon, such as diamond, lonsdaleite (hexagonal diamond), graphite, and carbynes have long been recognized. Diamond and hexagonal diamond have been synthesized by both static and dynamic high-pressure techniques. However, the carbon-phase diagram has not been explored in some high-pressure regions, nor have the mechanisms of transition among the forms been resolved for static compression (2) or for dynamic compression (3). Especially in the latter case, the question of whether shock-induced conversion is due to a martensitic (diffusionless) or a reconstructive (diffusive) transition is of great interest. The martensitic mechanism was proposed to explain rapid conversion (3), and reconstruction has been observed in many high-temperature experiments (2, 4, 5). Recently, the temperature dependence of the transition mechanism was described (6), and its sensitivity to the initial graphite materials was also reported (7). The shockinduced phase transition takes place in nanoseconds, and then it is subsequently affected by the cooling rate. The transition mechanism under shock compression, therefore, cannot be easily defined even among the well-known forms.

The above-mentioned studies were limited to transitions among the three known forms of carbon, graphite, hexagonal, and cubic diamonds. Hexagonal diamond has not been demonstrated to be a thermodynamically stable phase. Other unknown and metastable carbon forms might exist, and their formation would strongly depend on the transition mechanism. To see such behavior, it would be necessary to quench the initial phases after the transition. We

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 227, Japan. developed a rapid cooling technique to use in the shock compression of a graphite sheet. Preliminary observation of the recovered sample revealed a deviated structure, that is, n-diamond (8). We found evidence for this crystalline form, and the conversion process that n-diamond experienced was clarified. In addition, another crystalline form, "0.25-i-carbon," was found in the part of the sample held at high temperature for a longer time.

We used a commercial grade graphite foil composed of dense sheets with interstitials between the sheets as a starting material. Each constituent sheet was up to several micrometers wide and was superimposed, keeping the c-axis almost parallel. The graphite foil (less than 100 µm thick) was sandwiched by copper disks, which formed a heat sink, and set into a copper capsule. The sample assembly was subjected to shock loading perpendicular to the graphite sheets by the impact of a copper flyer in a shock gun. The impact velocity of the copper flyer was 2.5 km per second, which was comparable to a peak pressure of 65 GPa. We estimated the shock temperature to be 3700 K by assuming a mean density of 1.0 g/cm^3 for the graphite foil. A numerical analysis



Fig. 1. Calculated cooling rates at distances of 1, 5, and 17.5 μ m in the graphite foil and 5 and 30 μ m in the copper disk from the foil–copper disk interface.

based on the Fourier equation gave cooling rates of 10^{10} and 10^6 K per second in the foil at a distance of 1 μ m and 17.5 μ m from the interface of the copper disk, respectively (Fig. 1).

We characterized the recovered sample by using a transmission electron microscope (TEM). Before the detailed TEM work, we determined that the specimen fragments were not foreign contamination (9) by using an energy-dispersive x-ray spectrometer. Representative electron micrographs of the sample collected from the part closest to the interface between the foil and the copper disk are shown in Fig. 2, A and B. Granular crystals about 100 nm were found (Fig. 2A). Some of them were hexagonal-shaped and were intimately in contact with one another like mosaic tiles. Crystals larger than 1 µm were occasionally seen, and they were divided into polygonal-shaped domains (Fig. 2B). Electron diffraction patterns (EDPs) (Fig. 2C) from an aggregate of the granular crystals showed sharp-spotted

Table 1. Comparison of the observed d spacings of n-diamond and 0.25-i-carbon with those of cubic diamond and i-carbon (13). Intensities I are classified as strong (s), medium (m), or weak (w).

n	-Diamond		Cubic diamond JCPDS6-675			0.25-i-	i-Carbon (13)	
d _{obs} (nm)	hkl	· I	d (nm)	hkl	<i>I/I</i> ₁	carbon, $d_{\rm obs}$ (nm)	d (nm)	hkl
).206	111	s	0.206	111	100	0.337†		
0.178	200*	S						
).126	220	S	0.1261	220	25	0.304	0.303	
).107	311	s	0.10754	311	16	0.242	0.246	110
).104	222*	m				0.208	0.212	111
).0898	400	w	0.08916	400	8	0.170	0.171	200
).0818	331	w	0.08182	331	16	0.149	0.150	211
).0796	420*	m				0.126	0.127	220
).0726	422	m	0.07281	422		0.119		
).0683	511	m	0.06864	511				

*Forbidden reflection in Fd3m. †Corresponding to 002 of graphite.



Fig. 2. (**A**) Electron micrograph of n-diamond observed in a large host sheet. (**B**) Electron micrograph of a large grain divided into n-diamond domains. (**C**) EDP from an aggregate of n-diamond. Forbidden reflection rings indexed {200}, {222}, and {420} are observed. (**D**) A diffraction net showing {100} of n-diamond on which the {200} and {420} reflections appeared. (**E**) EDP showing the superimposition of {110} of n-diamond on graphite basal planes that are rotated (marked by a large arrow).

rings, and the EDP could not be identified as that of any carbon form in the literature. The observed d spacings (interplanar distance) (Table 1) are close to those of cubic diamond, but the "forbidden" reflection rings indexed as {200}, {222}, and {420} of cubic diamond (*Fd3m*) appeared with distinct intensities; thus we called the deviated structure n-diamond (8).

In order to confirm that the {200} and {420} reflections are not multiple reflections but intrinsic ones, it was our intention to obtain a {100} diffraction pattern as shown in Fig. 2D by tilting a single crystal domain located at the edge of a large grain. If the $\{200\}$ and $\{420\}$ reflections were due to multiple reflections, they should be absent on the pattern. But their presence as distinct components of the pattern (Fig. 2D) is evidence that the {200} and {420} reflections are attributable to n-diamond. The appearance of these reflections means the loss of the *d*-glide plane, but the basic structure is close to that of cubic diamond. In Fig. 2B a few domains showing sharp fringe contrasts provided the EDP which could be totally explained as reflections from two twin

individuals related to the spinel twin law. The spinel twin arises restrictively in cubic and close-to-cubic structure only. This result also supports our findings on the basic structure of n-diamond.

A large grain and sheet consisting of n-diamond domains produced an EDP in which several diffraction nets were rotated with respect to each other within about 10°, indicating the preferential orientation of polycrystallines. The EDP also showed that the {110} plane of n-diamond was oriented almost parallel to the host grain or sheet. n-Diamond had, in general, a fairly clear appearance but a few grains exhibited mottling. The EDP from such grains (Fig. 2E) suggested that the {110} plane of n-diamond was superposed on graphite basal planes that were rotated about 15°. In the EDP, the {111} reflections of n-diamond were almost coincident with the {100} reflections of graphite. The orientational relation between the product (that is, n-diamond) and the initial graphite material can be regarded as an indicator of a martensitic conversion.

It is well known that strong shock com-



Fig. 3. (A) A large host sheet consisting of n-diamond with 0.25-i-carbon located at the margin of the specimen. (B) Specimen of 0.25-i-carbon collected from the inner part of the sample. (C) EDP from 0.25-i-carbon.

pression induces heterogeneous deformation in brittle solids (10), and larger crystals deform into mosaic ones as demonstrated by flash x-ray diffraction studies under shock loading (11). If we apply these concepts to the generation of n-diamond, the present observations are consistent. Heterogeneous deformation occurred in the basal plane of the large graphite sheets, and the hexagonal mosaic tiles and their preferred orientation resulted. Simultaneously, a martensitic transition to n-diamond took place in each mosaic domain. n-Diamond can be interpreted as a metastable form, analogous to hexagonal diamond, formed from graphite through a solid-solid martensitic conversion. The conversion region or path in n-diamond is different from that of hexagonal diamond (2). The temperature and pressure for n-diamond formation are higher than those for hexagonal diamond (12).

Another crystalline form, less than 60 to 80 nm in size, was found at the margins of some large sheets (Fig. 3A). Because of the lower density of the margin, the resulting temperature was, in that area, higher than the mean value (Fig. 1). The shape of the form varied from a little rounded platelet to almost particle-like. In the specimen selectively collected from the inner part of the recovered sample (Fig. 3B), the rounded crystal was dominant and n-diamond could not be found. The EDP (Fig. 3C) could not be identified as any of the well-known crystalline carbon forms, but that was similar to an i-carbon (13) prepared by the ion-beam technique (Table 1). The d spacing of 0.25 nm has the strongest intensity, so we call this form "0.25-i-carbon."

The diffraction rings of the 0.25-i-carbon showed that each crystal was randomly oriented (Fig. 3C). The yield of 0.25-i-carbon increases in the parts where higher temperature was maintained for a longer time as a result of a slower cooling rate. The morphology, yield, and orientation lead to an interpretation that this form was grown from decomposed or molten graphite under higher temperature, implying a reconstructive transition. This is consistent with the fact that the original i-carbon form was prepared by the ion-beam technique (13).

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[*ibid.* **40**, **993** (1989)], and A. F. Goncharov *et al.* [*Sov. Phys. JETP* **69**, 380 (1989)] showed a few phases suggesting "proto" hexagonal diamond. Comparing the reported *d* spacings with those of n-diamond, n-diamond is different from any of these phases (8).

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Observations of Extreme Upwelling Filaments in the Southeast Atlantic Ocean

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Cold oceanic water upwells along the western coastline of most major continents. The thermal front that demarcates the farthest seaward extent of this upwelled water is sometimes characterized by extensive whisps or cross-frontal filaments. These may play an important role in the functioning of the upwelling ecosystem as a whole. Satellite observations on filaments of the Benguela upwelling system show filaments that exceed 1000 kilometers in length. Two mechanisms that may produce the exceptional length of these filaments are interaction with Agulhas rings and the effect of intense berg winds.

CEANIC UPWELLING REGIMES PLAY a principal role in the ecology of the eastern boundary areas of most ocean basins, in particular that of the Northeast Pacific (1), Southeast Pacific (2), and Southeast Atlantic oceans (3). It has been suggested that in many instances biological productivity of upwelling areas is concentrated at the fronts that separate cold upwelled water from the adjacent ocean surface water (4). Frontal behaviour may therefore be an important element in the potential primary productivity of upwelling areas as a whole. Moreover, by raising deeper water to the sea surface where it is warmed by insolation and atmosphere-to-ocean heat transfer, upwelling regimes modify the temperature and salinity of substantial volumes of water. The full areal extent of upwelling regimes, as delimited by their upwelling fronts, is therefore a factor in global water mass modification and thus by implication in climate. With the advent of satellite remote sensing it has become increasingly evident that upwelling fronts are, usually, not smooth but consist of a heterogeneous collection of mesoscale plumes, whisps, and filaments (5); these features significantly extend both the productive habitat associated

with the front (6) as well as the areal extent of cold surface water. The full geographic extent of these filaments in each individual upwelling regime has yet to be established. In this report, we describe unusually elon-



Fig. 1. (A) Thermal infrared image of the upwelling area of the Southeast Atlantic Ocean from the ME-TEOSAT II satellite for 5 July 1982. Colder water is indicated by lighter hues. An extreme, meandering upwelling filament is evident off Lüderitz. (B) Interpretive sketch of the same scene with lines of latitude and longitude. An approximate kilometer scale is given as reference.

gated filaments of the Benguela upwelling system in the Southeast Atlantic.

The upwelling regime of the Southeast Atlantic Ocean stretches from the Benguela-Angolan front at about 16°S to Cape Agulhas (3), the most southern tip of Africa. Upwelling occurs preferentially in certain specific upwelling cells (7), the location of which in many cases corresponds to narrow parts of the continental shelf (3). The central and most intense of these upwelling cells is the one at Lüderitz (27°S) (8). On average its surface water is colder than that in other upwelling cells, it extends farther offshore, and it exhibits active upwelling more frequently than any of the other identified cells (7). Upwelling filaments typically form on the fronts of all cells where the upwelling is well developed (9). This filamentous band, parallel to and seaward of the main, contiguous upwelled water, is usually between 100 and 500 km wide (10).

Upwelling filaments of this kind have been shown to have certain distinctive characteristics. They are quasi-geostrophic jets that entrain cold water at coastal upwelling sites and rapidly advect it far offshore (11). This flow pattern probably provides significant cross-shore transport of heat, nutrients, biota, as well as pollutants, and may be associated with adjacent mesoscale eddies (12). Measurement of the kinematic characteristics of such filament features in the California Current system (13) have shown that under certain conditions the flow configuration consists of a rapid offshore flow balanced by a slower, parallel return flow that converges at the front on the equatorward side of the filament. Filaments may extend to a depth of 100 m (14), last a number of weeks, and may carry a volume flux in excess of $10^6 \text{ m}^3/\text{s}$ (13).

The unusually long filaments were revealed in a study of a large collection of satellite thermal infrared images for the Southeast Atlantic Ocean covering more than 10 years (15) (Fig. 1). The filaments occasionally developed off the Lüderitz upwelling cell. Whereas most observed filaments extended about 300 km offshore (13), these extreme filaments off Lüderitz exceeded 1000 km in length.

An example of such an extreme upwelling filament is shown in Fig. 1. The filament had its origin in the surface upwelling front seaward of the continental shelf edge and extended more than 1300 km offshore. Sideways meanders with a wavelength of about 250 km and a wave amplitude of 100 km shaped the trajectory of the cold water (16). The surface expression of this extreme filament was persistent for about 10 days, from 5 to 14 July 1982. For this whole period it extended more than 1000 km offshore.

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