Formation of carbon macromolecules in diamond contacting with liquid carbon

A Yu Basharin, V S Dozhdkov and P R Levashov
Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13
Bldg 2, Moscow 125412, Russia
E-mail: abasharin@bk.ru

Abstract. In the present work, consideration is given to the non-b Brittle breaking of a diamond. The diamond in contact with droplets of liquid carbon was graphitized and the formed graphite stretched the diamond in the space between the droplets. Transmission electron microscopy was used to identify amorphous carbon in a region of the stretching. High resolution observations provided in-depth information about amorphous carbon inner structure. Mixture of branched and linear carbon macromolecules was observed. Molecular dynamics showed that sp bonds, responsible for the formation of macromolecules develops in a sp\textsuperscript{3} stretching diamond near its stability boundary. Transformation of bonds from sp\textsuperscript{3} to sp is by a sp\textsuperscript{2} formation. All this shows that in the process of thermal destruction diamond manifests itself not as a crystal, but as polymer passes from a dense mesh to linear form at tension.

1. Introduction
Diamond is one of the hardest materials on Earth. However, at non-hydrostatic compression \cite{1,2} and heating \cite{3}, part of the sp\textsuperscript{3} atoms passes into the sp\textsuperscript{2} state. Diamond is graphitized from the surface \cite{4} or inner defects only, which should allow the brief superheating of its volume in fast processes to be much higher than the graphitization temperature. Nevertheless, 1.55 times volume expansion during the graphitization eventually tears the diamond like ice raptures rocks \cite{5}. The stretching of the diamond leads to the formation of cracks. Mechanism of a crack development and phase transitions in a crack area is believed substantially depend on a diamond temperature.

Previously \cite{6}, we tested a new method for conductive heating of diamond by a liquid carbon with a temperature $T_{GM} = 4850$ K \cite{7}. This technique allowed us to melt graphite on a diamond and harden liquid carbon accompanying by unchanged diamond \cite{6,8}. A special role in this process was played by the extreme high thermal conductivity of diamond. It has the huge value of the order of 2.2 kW/(m K) \cite{9}. Unlike of our work \cite{6}, we increased the energy of the laser pulse to cause destruction of a diamond. In this paper, we study structural transformations in the region of a crack in a high-temperature diamond by transmission electron microscope (TEM). Also molecular dynamic (MD) results are present.

2. Experiment
2.1. Sample preparation and contact heating of diamond by liquid carbon
Flakes of highly oriented pyrolytic graphite (HOPG) with a diameter of cca 40 \(\mu\)m assembled into an islet were hand-pressed onto the \{111\} face of a crystal of natural diamond having a thickness...
of 1 mm and a side length of 3 mm. The sample thus prepared was placed into a gasostat with a quartz window in such a way that the face with the attached islet was vertical and the islet faced the window. Helium pressure $p_p = 25 \text{ MPa}$ was applied. Graphite is known to melt only above the pressure at the liquid–graphite–vapor triple point of carbon, $p_{GTP} = 10.7 \text{ MPa}$ [10], while at $p_p < p_{GTP}$ it sublimates transforming from a solid directly into a gas state. Our experience shows that liquid carbon vigorously vaporizes at pressures immediately close to $p_{GTP}$, so we selected higher value $p_p = 25 \text{ MPa}$. The surface of the islet was illuminated through the window by a single laser pulse of about 1 ms duration produced by a solid-state neodymium glass laser with a wavelength of 1.06 µm, energy of 5 J, and focal spot diameter of about 1 mm. Under the same experimental conditions [7], but on solid HOPG samples, liquid graphite existed for about 1 ms. The melting wave penetrated the diamond in 0.070 ms, and solid graphite was strongly heated upstream of the front.

It appeared that the transformation processes in diamond would run faster, if we do not overheat diamond until the complete melting of graphite. To reduce the thermal conductivity of graphite, we prepared flakes of graphite and assembled them into an islet. Melting of such a loose islet is equivalent to falling of a liquid droplet onto a cold substrate.

2.2. Preliminary examination of the sample surface
The surface of diamond cleaned of remelted graphite in an ultrasound chamber was examined through a scanning electron microscope (SEM) MIRA3 TESCAN in the low-vacuum mode. As shown in figure 1, the surface appears to be non-homogeneous.

The diamond sample is crushed in zone “A” as evidenced by the projecting octahedral cut crystals, while zone “B” of the sample is flat like for the original crystal. The image from an optical microscope AxioImager A01 Carl Zeiss with ×500 magnification demonstrates that the crushed diamond was white and diffusively scattered the light of the substage lamp. The interference color of the flat region was red.
Figure 2. TEM view of “B” zone of the section prepared by FIB: single arrow—\{111\} atomic plane of the diamond; XXX—the bend contours; double arrows—cavities.

2.3. Cross-section preparation by FIB
The cross-section was prepared by a focused ion beam (FIB) Ga+ with an energy of 30 kV in a scanning electron microscope (RAIM) Helios SEM–FIB (FEI, USA). A plate having a thickness–height–width of 1–0.7–11 µm was cut perpendicular to the surface of the diamond sample. The surface was coated with a layer of platinum to prevent etching of the section end at thinning. With a micromanipulator (Omniprobe, USA) the plate was extracted from the sample and welded to a standard copper half ring (Omniprobe, USA). Then the plate was finally thinned to a thickness less than 100 nm in RAIM by 5 kV Ga+ ions. It was examined through a high-resolution transmission electron microscope (HR TEM) of mark TITAN 80 300 TEM–STEM (scanning TEM) equipped with a Cs corrector sample at an accelerating voltage of 300 kV. Analysis of the samples included x-ray spectrum, microdiffraction and fast Fourier transformed (FFT) HR images.

2.4. TEM studies of the cross-section
Only fragments of cross-section relates to zone “B” we considered by TEM. Results are shown as low resolution (LR) image in figure 2, and as HR images in figures 3 and 4.

We remark here that in the depth of the diamond at a distance of 0.4–0.7 µm there was a flat channel filled with non-diamond carbon. Note a clear rectilinear orientation of the cavity along the \{111\} planes. The bend contours in figure 2 visualize considerable residual stresses. The channel is filled with amorphous carbon, see the halo in figure 3(b). The diamond along
the edges of the channel is graphitized, see the dot reflexes picture in figure 3(c). Considering image 3(d), we see that graphite has curved graphene planes, as in onions. Figure 3 clearly shows that amorphous carbon has cavities, and graphite is solid.

The HR TEM images of the typical fragments of amorphous phase are presented in figures 4. From a comparison of figures 4 and 5 it is seen that forms selected with rectangles in figures 4 are the polymeric macromolecules.

3. Model

We modeled the uniaxial stretching of a defect-free diamond cell. The NVE thermostat and the ReaxFF potential in the functional form presented in paper [12] were used. The potential parameters were taken from [13]. The initial cell is a rectangular parallelepiped with a diamond structure consisting of 20328 carbon atoms. The initial size is $\Delta X = 39.22$, $\Delta Y = 74.87$, and $\Delta Z = 39.22$ Å, respectively along the $X, Y, Z$-axes. The parallelepiped is stretched along the $Y$-axis. The initial average temperature is 2500 K, pressure is normal, the diamond density is $3.52 \text{ g/cm}^3$. The increase in the cell size $Y$ occurs at a constant linear velocity of 0.35 Å/ps corresponding to the deformation rate $\dot{V}/V_0$ of the diamond cell of the order of $4.67 \times 10^9$ 1/s. Here $V_0$ is the initial volume, $\dot{V}$ is the rate of its change with time. After each increase in size, the cell is relaxed for 0.05 ps until the next increase.

**Figure 3.** (a) HR TEM image in the rectangle of figure 2; (b, c) FFT images of the areas A and B correspondingly; (d) HR image of the curved graphite B.
Figure 4. HR TEM images 5×5 nm² of amorphous carbon fragments: (a, b, c) branched (comb-like, star-shaped and wire structures respectively); (d, e) linear (helical and folded conformation respectively); (f) pore.

The dynamics of the change in the mechanical stresses in the cell volume in figure 6 shows that the stress relaxation occurs at a tensile stress of cca. −90 GPa. Figure 7(c) shows that relaxation is accompanied by the appearance of voids. The question arises: do these voids appear in the diamond itself? The answer to this question was obtained by eliminating sp³ atoms from the analysis in figures 7(b) and 7(d). It turns out that even before the relaxation begins, sp² point defects appear in the diamond [figure 7(b)], and the appearance of a continuous region mainly from sp² and sp-atoms [figure 7(d)] leads to destruction. A more detailed study showed that the relative concentration of sp-atoms increases with respect to sp² atoms with the development of destruction. The destruction removes a huge strain in the diamond and defects disappear in the area not affected by the destruction, as can be seen from the comparison of figures 7(d) and 7(b).

The resulting substance is amorphous, which follows from the characteristic type of the pair correlation function in figure 8: the first peak is high and sharp enough, the first minimum goes to zero, the second peak is much smaller than the first and wide enough, when $r \to 10$ Å, $g(r) \to 1$.

Thus, voids do not appear in the diamond itself, but amorphous carbon with a complex coordination composition which is formed when the diamond is stretched.
Figure 5. Images of complex macromolecules from [11]. Branched macromolecules: (a) comb-shaped, (b) star-shaped, (c) tree-like. Linear macromolecules: (d) spiral, (e) lamella.

4. Discussion
In two zones “A” in figure 1, diamond particle protrudes above the flat surface of zone “B”. We suppose the formation of a significant amount of graphite in zones “A”. Increase in the specific volume of carbon during graphitization breaks the diamond into separate particles and pushes them beyond the original volume. The presence of a mixture of diamond and graphite particles in this zone explains the color and nature of the scattering of light which we observed by means of an optical microscope.

Inspection of the diamond surface in zone “B” in figures 2–4 shows that the surface layer is not destroyed, but there is a flat channel under the surface. Thickness $t$ of the diamond layer above the channel is responsible for red color of zone “B”. It appears when $2t/n = \lambda = 0.62–0.74 \mu m$, where $n = 2.4$ is the refraction index of diamond, and $\lambda$ is the wavelength of light. Inspection of curved bend contours in figure 2 shows that the channel was formed as a result of diamond stretching in the direction perpendicular to $\{111\}$. The cavities also indicate stretching.

We associate this picture with the fragmentation of the liquid carbon on the diamond surface into individual drops, as shown in figure 9. The heating of the diamond under the drops leads to its graphitization, which arises from structural defects. The situation shown in the figure reflects the early stage of the process, when formed graphite compresses diamond in zones “A”, and stretches it in zone “B” only, as on stress diagram, shown in the figure.
Figure 6. Dynamics of changes in mechanical stress along axes $i = X, Y, Z$. $P_X$ and $P_Z$ lines are merged.

Figure 7. Snapshots of the cell at time moments: (a, b) 29.5 ps; (c, d) 31.5 ps. In parts (a, c), all the atoms in the cell are shown; in (b, d), sp$^3$ atoms are not shown. Carbon atom type selected by color: red—sp$^2$; green—sp; blue—single.
Our interest is in temperature of the diamond under the conditions of experiment. It can be shown that the formation of characteristic curved crystals of graphite, see figure 3(d), requires breaking sp$^3$ bonds in a diamond. It is shown in [14] that for natural diamonds it originates at a temperature not less than 2300 K. Therefore, a close temperature of 2500 K is chosen for the MD simulation.

The data on the value of the strength of spallation at the break of a diamond depend on the speed of a stretching [15]. This work also notes that some part of the diamond transforms to disordered graphite-like phase at spallation. For MD simulation we took a sufficiently high rate of diamond stretching. This was done because the brittle failure of the diamond is a dynamic process and its speed reaches 8 km/s. We do not know the real speed of the non-brittle process of propagation of amorphous channels, but we assume that the sequence of phase transformations under tension sp$^3$-sp$^2$-sp, which we were interested at first, does not depend so much on the dynamics of the stretching.

After [11] the structures in figure 4 are polymeric macromolecules. They formed in the place of the stretched diamond indicate that tetrahedral single sp$^3$ linkage replaced by conjugated sp bonds of carbon atoms, which, according to [16], can be of the polyene −C≡C− or cumulene =C=C= type. Chains with kinks, according to the analysis in articles [17,18], are formed by the zipper mechanism when the basal plane of graphite is destroyed, as first described by Whittaker in [19]. Partial breaking of bonds could lead to the structures of branched macromolecules as in figures 4(a, c) and 5(a, c). The folded shape in figure 4(e) and in a more obvious form in figure 5(e) generally is characteristic for the construction of a crystal carbinde discovered by

![Figure 8. Pair correlation function of a region of a cell saturated with sp and sp$^2$ carbon atoms in figure 7(d).](image-url)
Figure 9. The qualitative diagram of mechanical stresses in diamond at the stage preceding the beginning of its destruction.

Russian scientists V V Korshak, V I Kasatochkin, A M Sladkov [20]. The spiral conformation in figures 4(d) and 5(d) is a typical form of isolated linear macromolecules. The mechanism of the star-shaped formation in figure 4(b) is not yet completely clear. The pores in figure 4(f) are further evidence that the amorphous structure under discussion arose when diamond was fractured in the stretching zone.

5. Conclusion
The HOPG-island was melted on the surface of natural diamond by a powerful laser pulse. The melt was broken up into individual drops owing to the island structure composed of individual flakes.

We studied the volume of diamond by TEM on a cross-section made by FIB method. Under the drops, the diamond was graphitized and formed graphite stretched the diamond between the drops. In the stretching zone a flat channel filled with amorphous carbon was found. Also carbon macromolecules were found by HR TEM.

With the help of MD modeling of diamond stretching, it was shown that at the breakage character of hybridization of carbon atoms change from sp$^3$ to sp$^2$ and sp. Relative concentration of sp-atoms increases with respect to sp$^2$ atoms with the development of destruction. We held that the zipper model of Whittaker is the most probable scheme for restructuring of the sp$^2$ to sp bonded carbon atoms. After MD modeling it became clear to us that the sp$^2$ and sp-rich carbon atoms are responsible for carbon macromolecules nucleation. One can also note that the sp-carbon is essential for liquid carbon too [21].

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