Study of a platelet-free infilling of a crack in natural diamond: evidence for a late growth event

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In the cores of coated diamonds, healed cracks may be detected electron-microscopically. At these, the parted crack surfaces have reunited coherently over a substantial fraction of the crack surface, which now contains dislocations and sometimes trapped non-diamond material as well. A healed crack has been discovered that is accompanied on either side by an extremely sharply-defined zone of absence of the electron-microscopically observable (100) platelet defects that populated the rest of the diamond core. (Such platelets are characteristic of nitrogen-impurity-containing natural diamonds that have undergone long storage at high pressure and temperature.) The maximum overall width of the platelet-free zone along the observable trajectory of the crack was about 0.5 μm. It narrowed as the crack was followed into the core. Experiments are described that led to interpretation of the platelet-free zone as consisting of a sheet of coherent diamond regrowth upon incompletely closed crack surfaces, filling the gap between them, and representing a late event in the diamond's growth history.

1. Introduction

Diamonds that have been brought up from depths below the Earth's surface are assumed to have crystallized within the field of diamond stability in the phase diagram of carbon allotropes. Certainly no evidence to the contrary has yet been demonstrated. At 1500 K the boundary between the graphite and diamond stability fields lies at a pressure of 4.8 GPa [1]. The sub-continental depth corresponding to this pressure is about 150 km. The slope of the diamond–graphite equilibrium line on the P–T phase diagram at 1500 K is 330 K/GPa, and this value applies with sufficient accuracy over the range 1000 to 2000 K. From studies of the P and T dependence of chemical equilibria of mineral inclusions found totally enclosed within diamonds estimates of the P and T conditions of diamond crystallization have been derived. Evidence drawn from macroscopic (i.e. diameters > 100 μm, say) syngenetic inclusions suggests that the majority of diamonds in which these inclusions are found crystallized at pressures from 4.5 to 7.5 GPa and at temperatures perhaps 200 to 400 K below the graphite–diamond equilibrium line [2,3]. Indeed, the mechanical robustness and chemical inertness of diamonds renders them most valuable sources of information on conditions at the great depths corresponding to these high pressures provided the evidence from their macroscopic and microscopic inclusions, and from microscopic lattice defects within the diamond matrix, can be read aright [4,5]. Establishing the thermal and mechanical history of natural diamonds forms an integral part of such enquiry.

As regards mechanical history, the evidence that has to be interpreted contains contributions from both plastic deformation and from fractures. Dislocation configurations in diamonds resulting from plastic deformation, with or without the subsequent development of annealing textures, can be studied by a variety of techniques, such as birefringence microscopy, X-ray topography, cathodoluminescence microscopy and transmis-
sion electron microscopy (TEM). Preferably, these techniques are applied in combination [6–9]. In the case of fractures, fewer investigations have been mounted. In fact, the prospect for scientifically meaningful outcome from such studies is not promising. This is because despite the common occurrence of cracks in diamonds, and frequent visible manifestation of non-diamond material in cracks, there is generally (at least in the case of cracks now, or possibly previously, open to the crystal surface) no means of telling at what stage in the diamond's history the non-diamond material infiltrated into the crack. For example, cracking and subsequent crack infiltration might have occurred during eruption to the Earth's surface, during rough transport on the surface, or even during ore crushing and processing.

The studies of a crack and its infilling that are reported here are of a novel nature. Analytical transmission electron microscopic techniques are employed. Their characteristics are exploited in such a way as to guarantee immunity from the above-described uncertainties regarding provenance of the crack-filling material observed. The experiments have disclosed an unexpected crystallization phenomenon, that of diamond regrowth on the parted fracture surfaces. This in turn raises new questions concerning the growth history of diamonds belonging to the large class known as "coated diamonds", of which the specimen studied was a representative.

To place in proper perspective the findings of the various TEM techniques deployed, the section describing them is preceded by some notes on defects in diamonds, including electron-microscopically observable lattice defects in natural diamonds (especially in coated diamonds) that are relevant in the present study, and that are diagnostically important regarding conditions of growth and subsequent storage.

2. Some microscopic defects in diamonds

Coated diamonds, which constitute a substantial fraction of the output from some major diamond sources, particularly Zaire, exhibit in their growth histories a dramatic switch in mode of crystallization. From normal, {111}-faceted, often virtually dislocation-free growth forming the "core" of the crystal, they change to a columnar, dislocation-rich growth in the "coat" that envelops the core [10,11]. Whereas the core is usually colourless, and often of gem quality, the coat is filled with a dense population of sub-micrometre, non-diamond bodies that destroy its transparency (but not its translucency). The transition from core to coat texture is usually abrupt, occurring within optical microscopic resolution distance in the growth direction [10]. The thickness of the enveloping coat may sometimes be only a small fraction of the whole crystal diameter; alternatively, the crystal may be virtually all coat and no core, from which a cubic habit overall may result [12]. The microanalytical techniques of electron probe X-ray spectroscopy, secondary ion mass spectroscopy, and Fourier transform infrared absorption spectroscopy have recently been applied to investigate the composition of the non-diamond material (some of which is non-crystalline or fluid) within diamond coat [13]. Richness in volatiles (H₂O and CO₂) and, inter alia, a high ratio of potassium to magnesium, chemically distinguish these inclusions significantly from the larger inclusions that over many years have been intensively studied in normal diamonds (to which the cores of coated diamonds are akin). For investigating individual crystalline micro-inclusions, the combination of TEM imaging, selected-area diffraction, and energy-dispersive X-ray spectroscopy has proved fruitful, and has led to the identification within diamond coat of sub-micrometre-sized crystallites of apatite [14], biotite [15] and mixed Mg, Fe, Ca carbonates possessing the dolomite crystal structure (Walmsley and Lang, publication in preparation). It appears then that diamond core and diamond coat grew in different chemical environments, on the evidence of these microanalytical studies.

The major known impurity incorporated in diamonds of all types is nitrogen. Several different states of aggregation of nitrogen within the diamond crystal lattice can be differentiated on the basis of their characteristic infrared absorption spectra, and in some cases nitrogen concentration
can be assessed by infrared absorption measurements [16-18]. In undoped synthetic diamonds grown by the usual methods the nitrogen is atomically dispersed, singly substituting for carbon atoms [19]. In all but very rare natural diamonds the nitrogen has aggregated into N-N pairs, the A defects (identified by the “A” infrared absorption spectrum), and into other small atomic clusters, of which the most important is the B defect (its presence identified also by infrared absorption, by the “B” spectrum) [5]. The only electron-microscopically detectable lattice defects commonly observed associated with nitrogen impurity in natural diamonds are the long-studied platelets on {100} [20]. (To platelets should now be added the (111)-faceted “voidites”, but the latter are found in a rarer class of nitrogen-containing natural diamonds [21].) Experiments at high T and P have shown that the initial stage of nitrogen aggregation is from the singly substitu- tional state into A defects [22]. At yet higher T and P, e.g. up to 2900 K at 9.5 GPa, a reduction in the A-defect population, accompanied by the appearance of B defects and platelets, takes place [5,23,24]. Though a good deal of uncertainty attaches to extrapolations from these findings to estimate the geological times needed for similar reactions to occur in Nature, it appears safe to conclude that, as far as normal, low-dislocation-density diamonds are concerned, specimens that contain B defects and platelets in addition to A defects have been held for longer periods at the same T, or for similar periods at higher T, or for longer at higher T, compared with specimens exhibiting “A-only” features in the nitrogen-impurity-dependent infrared absorption spectrum. The relevance of this distinction to studies of coated diamonds resides in the finding that whereas the cores may contain A defects and B defects (plus platelets) in varying proportions, the A-only spectrum is exhibited by coats [25]. Of special present relevance is the absence of platelets in coat growth. This is testified directly by TEM [26], and by absence of the characteristic infrared absorption produced by platelets (the B’ peak at = 1370 cm⁻¹) in more than 70 specimens of coat studied by Dr. Michael Seal (personal communication).

3. Experiments

Typical coated diamonds from Zaire have been studied. The sequence of experimental operations was as follows. Crystal sections exposed on the cut surfaces of coated octahedra sawn in half, or on central slices cut out of coated diamonds, were examined by cathodoluminescence topography. Selected sawn slices were mechanically polished, and from selected half-octahedra slices were sawn and polished, so as to provide specimens suitable for optical microscopic and X-ray topographic examinations. For TEM studies, fine-polishing of slices down to a foil thickness of about 50 μm was carried out, followed by ion-beam milling a chosen area of about 0.5 mm diameter until perforation occurred. Foil thicknesses exceeding 1 μm could be usefully studied with electron beam energies from 200 to 300 kV. The most informative foil orientation is (110), being perpendicular to two opposed pairs of octahedral facets; and this orientation was of special value in studying the core-to-coat transition on (111) facets. The observations of present concern were made in a region of core contained in a near (110)-orientation foil. They were encompassed within a thin area a few hundreds of micrometres wide surrounding a hole whose centre lay approximately on the local core-coat boundary. Crossing this thin area was a crack, one that was clearly not an artefact of thinning and handling operations. It was a “healed” crack, described below. The sequence of micrographs reproduced here, presented in the order of their recording, illustrates steps in the investigation.

The micrographs showed that the diamond core was filled with a population of platelets, just as is observed in the majority of nitrogen-containing natural diamonds. This population gives rise to the multitude of point-like, strain-contrast images that cover most of the fields in figs. 1a, 1b and 1c. At the relatively low magnification of these micrographs, the size and shape of individual platelets cannot be accurately determined: other TEM procedures, described below, provide this information. In the course of surveying the thinned area, with the electron beam incident nearly normal to the foil, there was discovered
among the population of platelet images an extended band of different contrast-producing objects, appearing as shown in fig. 1a. Three types of object are seen in the band. Dark objects are non-diamond substance; darkness in the print of the bright-field image arises from greater electron absorption than that by the diamond matrix, or from stronger Bragg scattering, or from both.

Fig. 1. Transmission electron micrographs of a healed crack in the core of a coated diamond. Width of field 5 μm. Local specimen thickness 0.74 μm. The specimen foil upper-surface normal is inclined 10° off [110] towards [001]. (a) View normal to specimen foil. Diffraction conditions: bright-field, g close to 220. (b) Foil rotated about 35° from orientation in (a) to give edge-on view of crack. Crack plane close to (151). Specimen direction [611] points towards observer. Scale mark 0.25 μm. Diffraction conditions: bright-field, g close to 022. (c) Dark-field image corresponding to bright-field image (b).
together. (The contribution from Bragg reflections can be found by tilting the specimen.) Light patches on the image correspond to cavities in the diamond matrix from which non-diamond material (possibly volatile) has been lost; at these localities electron absorption is diminished. An irregular cross-grid of dislocation images (some with anomalous image properties, discussed in section 4) covers the whole band, the individual dislocations tending to link up the non-diamond bodies still present, or the cavities. In areas between images of dislocations, cavities and inclusions, the diamond matrix appears continuous, coherently diffracting. This pattern of defects is characteristic of "healed" cracks in cores of coated diamonds. At healed cracks, the opposing crack surfaces, transiently parted, have re-closed, renewing lattice coherence over most of the crack surface. Non-diamond material may or may not be trapped between the closing surfaces.

Upon tilting the specimen to obtain an edge-on view of the crack, fig. 1b, a novel and unexpected image presented itself. Sharply-defined platelet-free zones, 0.23 μm wide at this point, accompany the sheet of defects on both sides. The transition from platelet-rich to platelet-free matrix takes place within an average projected platelet-to-platelet separation distance. (This distance sets the lower limit to transition sharpness that can be revealed by changes in platelet population density.) The enhanced contrast afforded by the dark-field image, fig. 1c, renders the sharp cut-off in platelet numbers even more striking.

Explanations for the platelet-free zone (hereafter abbreviated to PFZ) that have been considered fall into two categories. In the first it is assumed that the crack was able to close completely and that the PFZ lies in original diamond matrix whose platelet content has been modified by proximity to a free surface (the crack) and/or to the non-diamond substance trapped there. This model has two variants, both equally essentially involving diffusion processes. In one variant it is assumed that cracking took place before platelet formation in the core bulk, and that diffusion of point defects (including impurities) to (or from) the crack so modified the balance of platelet-producing reactants that platelet precipitation never occurred in the PFZ. In the other variant, platelet formation is assumed to have taken place before cracking, but in the PFZ the platelets have been completely re-absorbed in response to crack-engendered changes in defect concentrations. The second, and quite different, explanation holds that the crack was prevented from closing completely (presumably by some obstructing fragment(s) nearer its mouth), the original crack surfaces being now delineated by the PFZ boundaries. The PFZ then represents a film of fresh diamond growth upon the fracture surfaces, which growth displaced crack-filling fluid until the advancing growth fronts met, trapping some non-diamond material in the median sheet of micro-inclusions, cavities and dislocations that is now observed. Choice of which explanation to adopt was settled by subsequent observations.

First, the crystallographic orientation of the crack needed to be ascertained. Though cracks on the (111) cleavage planes dominate in coated diamonds, curving cracks, or cracks with appreciable segments not parallel to low-index planes, are fairly common. This crack belonged to the last category. Combining imaging and diffraction pattern observations showed that the diamond [611] axis lay in the crack plane. The large-angle convergent-beam [611] zone axis diffraction pattern was photographed superimposed on the edge-on image of the crack. The crack trace lay nearly parallel to one particular pair of Bragg-reflection deficiency lines crossing the image. Matching with the computer-simulated diffraction pattern identified these lines as due to Bragg reflections with diffraction vectors \( g = \pm 151 \). Thus the rational indices \( (151) \) were adopted to describe sufficiently closely the crack-plane orientation, and are so employed in the stereographic projection, fig. 2.

If the boundaries of the PFZ had been determined by diffusive processes within a continuous matrix, then some change in size, shape or diffraction-contrast properties of platelets close to the boundary might be observable under high resolution, even though no change other than a perfect step function drop in platelet population density (from \( \approx 1500 \text{ μm}^{-3} \) to zero in the field of fig. 1) can be seen in micrographs taken at
Fig. 2. Stereographic projection on the upper surface of the specimen, as viewed in fig. 1a. Solid and open circles show poles on the upper and lower hemispheres, respectively. The crack plane, which lies very close to (151) in the field of fig. 1, is indicated by the great circle.

moderate magnification. Accordingly, high-resolution studies of platelets at the boundary were undertaken, applying weak-beam dark-field imaging techniques with which platelet dimensions can be measured to within 1 nm [27]. No abnormality in platelets close to the PFZ boundary compared with those remote from it was detected. (Like platelets of similar sizes previously studied, the platelets in this specimen tended to be of “race-track” shape, elongated randomly in one or other of the two (110) directions in the cube plane of the platelet; the mean major and minor diameters were 20 and 10 nm in the region sampled in fig. 1.)

From the point where the crack met the ion-beam-milled hole in the specimen foil to where it ran into diamond too thick for micrography with 300 kV energy electrons, a distance of about 250 μm, neither crack outcrop direction nor crack dip relative to the foil surface altered by more than a degree or two. The presence of the hole, which straddled the junction of the core–coat boundaries parallel to (111) and (111), made it impossible to determine from which boundary the crack entered the core. In consequence, the length of crack in the core that had been lost in the hole was undetermined, but it would have had a value between 70 and 225 μm. The whole observable crack length was micrographed, taking both edge-on and oblique views, requiring about 100 micrographs. On tracing the crack inwards into the core, the PFZ was observed to get narrower at an apparently uniform rate. Fig. 3 is an edge-on view where the specimen thickness has increased to about 2.5 μm, taken 170 μm further into the core from the field of fig. 1. Contrast has deteriorated because of the large specimen thickness, but it can be seen that the overall width of the PFZ has diminished to about 0.25 μm, which compares with nearly double that width in the field of fig. 1.

Fig. 3. Micrograph taken under diffraction conditions similar to fig. 1b, but at a point 170 μm further into the core. Magnification same as fig. 1. Local specimen thickness about 2.5 μm.
In diamonds it is usual to find marked zonal variations in properties dependent upon concentration and state of aggregation of nitrogen impurity [7]. In TEM studies of platelets it is observed that strong variations in number density and/or size of platelets can occur over distances in the growth direction as short as an interplatelet distance [8,20]. With substantial foil thicknesses, abrupt changes in platelet population density only become clearly noticeable when the electron beam is transmitted strictly parallel to the growth facet perpendicular to which the variation occurs. In the present specimen only one major jump in platelet density within core matrix was encountered along the observable trajectory of the crack. To view it distinctly, the specimen was oriented for the [110] zone axis diffraction condition, so that the local growth facets, parallel to (111), are viewed edge-on. On the resulting high-contrast micrograph, fig. 4, several fine-scale variations in platelet density in addition to the major jump are seen to reveal growth horizons. As is clearly evident, there is a bodily displacement of the whole stratigraphic record of core matrix growth, and hence of matrix itself, between one side of the crack and the other. This image provides conclusive evidence favouring “the crack-filling diamond regrowth” explanation of the PFZ.

4. Discussion

In early stages of the investigation, before the observations illustrated in fig. 4 were recorded, serious consideration was given to the “matrix modification” explanation of the PFZ. Cases of precipitation-free zones straddling grain boundaries in metals served as models [28]. (The tapering of the PFZ did introduce complications, requiring a particular law for the velocity of propagation of the crack inwards during the period when the temperature was high enough for the diffusive reactions to take place.) On the assumption that the crack had closed completely after the fracturing event, any resulting misorientation between matrix on either side of the crack would have to be of twist-boundary type only, without any tilt-boundary component. An investigation of the actual misorientation present was performed. The electron diffraction patterns are not sensitive to rotations about the electron beam axis because of the small Bragg angles, but with long camera lengths such as the 700 mm employed, sensitivity to misorientations about an axis perpendicular to the electron beam is high. The Kikuchi-line patterns corresponding to the images in figs. 1b and 1c, i.e. incident electron beam parallel to (111), revealed a misorientation between matrix on ei-
ther side of the PFZ amounting to $1.1 \times 10^{-3}$ rad ($\approx 4$ arc min) with rotation axis [011]. Since this axis is not perpendicular to the crack plane (151), but makes only 34° with it, significant tilt boundary character is present; and the tilt component about a rotation axis lying in the crack plane and perpendicular to [611] is $(1.1 \times 10^{-3}) \cos 34^\circ$, i.e. $0.9 \times 10^{-3}$ rad. If it is accepted that the PFZ boundaries delineate the original crack surfaces, then the tilt component having rotation axis parallel to [611] is given by the PFZ taper angle, which is $= 1.2 \times 10^{-3}$ rad. The next investigation was to check whether the dislocation density observed in the PFZ median plane was consistent with the misorientation measured.

Examination of images in the series to which fig. 1a belongs indicated that it is possible to take a path along the strip of defect-containing sheet captured between top and bottom surfaces of the foil that, by avoidance of inclusions and cavities, and with but occasional interruptions, can keep within continuous diamond except for crossings of dislocation images. A count of the number of dislocations running between top and bottom surfaces crossed per unit distance parallel to foil and crack, combined with knowledge of their Burgers vectors, would show the tilt component about [611]. Little success attended Burgers vector determination efforts, partly due to inaccessibility of some of the Bragg reflections needed, but mainly due to anomalous contrast characterizations of the dislocations. Counts along segments of the crack ranging in length from 5 to 20 $\mu$m gave mean dislocation crossing frequencies between 7 and $5 \mu$m$^{-1}$. Taking $6 \mu$m$^{-1}$ as mean, and assuming that the dislocations all had Burgers vectors parallel to [110] or [011], which among all $\langle 110 \rangle$ orientations make the smallest angle, 35.26°, with [151], then the rotation component about [611] would be $1.2 \times 10^{-3}$ radians. This agreement with the observed PFZ taper angle is satisfactory, except for the assumption necessary regarding Burgers vectors. The question of Burgers vector type is one of several aspects of the diamond regrowth phenomenon on which the structure of the diamond substrate surface has an important bearing. First, the structural roughness of the (151) surface provides unlimited sites for accretion of carbon atoms, a growth-promoting feature in contrast to conditions that apply more usually, on [111] facets. Secondly, the absence of [111] surfaces may well have helped to keep the PFZ free from incorporation of non-diamond material, which was pushed ahead of the growing diamond films until becoming trapped between the opposing growth fronts. All micro-inclusion crystal species referred to in section 2 as occurring in bulk diamond coat have also been detected among the micro-inclusions lying in the median plane of the PFZ (an observation strongly suggesting that the crack-invading medium was of similar composition to that into which the diamond coat crystallized). Probably the commonest of these species is biotite. In bulk diamond coat, about half the biotite crystallites examined lie in special orientation with respect to the diamond matrix, biotite (001) parallel to diamond (111) [15]. This contact evidently forms a reduced-energy interface. Now whereas the structural roughness of the diamond surfaces exposed in the PFZ presumably favoured wetting by the medium that invaded the opened crack, it did not offer a surface favouring attachment of biotite microcrystals. Lastly, because of the structural roughness of the meeting growth fronts, it is plausible, even probable, that some of the dislocations generated in the closure of the fronts had Burgers vectors greater than the minimum lattice translation. Fig. 5 crudely models the situation. Continued random accretion on rough surfaces will give rise to undulating growth fronts, which will come together at a series of points, such as X and Y on the sketch, uniting there to form expanding areas of lattice coherence. In fig. 5 the growth front protruberances are drawn as terraced, just for convenience; the terrace step height is arbitrary.

![Fig. 5. Generation of a double-strength dislocation by the growing together of two mutually tilted, undulating growth surfaces. Islands of coherent union, first established at X and Y, expand laterally as arrowed to enclose the dislocation. (Mutual tilt greatly exaggerated.)](image-url)
but for purposes of illustration could be taken as the minimum perfect Burgers vector. Quite mild undulations relative to the mean growth surface plane of each growth front will lead to approximate simultaneous contacting of higher opposed protruberances where the crack is wider and lower protruberances where the crack is narrower. Then, as indicated by arrows in fig. 5, united growth closes in upon trapped fluid from both sides of this section. In the situation sketched a dislocation with double-strength Burgers vector is generated. It might retain a filament of non-diamond substance trapped along its core. One or both of these circumstances could account for the anomalous visibility behaviour in TEM images. If only a few dislocations had the non-minimum Burgers vector \( \frac{1}{2}[111] + \frac{1}{4}[110] = \frac{1}{2}[121] \), for example, the tilt components measured could be accounted for more adequately.

At present no detailed models are available to explain the prevalence of cracking in coats of coated diamonds, and of cracks propagating into their cores. However, the compressibility and thermal expansivity of diamond will certainly be less than those of any non-diamond included material. Thus rise in temperature, or a reduction of ambient pressure below that at which non-diamond material was enveloped by growing diamond, will produce fracture-promoting stresses in diamond coat and in the core underlying it. The one known substantial pressure drop to which diamonds have been subjected is that accompanying their rise to the Earth’s surface. If before or during ascent the diamond-carrying material was heated by performance of mechanical work upon it, fracture-promoting stresses would be enhanced. However, the absence of B-defects and platelets from diamond coat suggests that if subsequent to coat growth these diamonds have been stored under \( P \) and \( T \) conditions not far off the average continental shield geotherm, and under diamond-stable conditions as well, then such storage must have been close to the lowest temperatures satisfying both conditions, i.e. in the region of the intersection of the diamond–graphite equilibrium line by the geotherm (slope say 100 K/GPa at the intersection point, which probably lies within about ±100 K of 1300 K). In such circumstances any major drop in \( P \) or rise in \( T \), such as could cause cracking, would take the crystal out of the field of diamond stability. Although this argument does no more than point to the possibility that the crack-filling diamond growth discovered in the present investigation occurred under diamond-metastable conditions, it does suggest that study of such growth, and efforts to find out more about the chemical nature of the crack-filling material that fed the diamond growth, might yield information not devoid of possible practical utility.

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