Birefringence, X-ray Topography and Electron Microscope Examination of the Plastic Deformation of Diamond

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ABSTRACT

The defect structures of types I, II A and II B diamonds were examined by the techniques of birefringence, x-ray projection and section topography and electron microscopy. It is suggested that the higher critical resolved shear stresses required to plastically deform type I diamonds compared with type II diamonds are due to the differences in the initial defect distribution in the two types of diamond. Type I diamonds have an extremely low dislocation density and a high density of coherent nitrogen precipitates in the cube planes, whereas type II diamonds have a high dislocation density (in excess of 10^6 lines per cm^2) with no nitrogen platelets present. There was no evidence for the relief of internal strains by heating the diamonds to 1800°c, although strains at surface scratches appeared to have been decreased by the heat treatment.

§ 1. INTRODUCTION

Work on the plastic properties of single crystals with the diamond-type structure at elevated temperatures has shown that the initial defect structure of the specimens can be important in determining yield phenomena and subsequent deformation characteristics (see, for instance, Bell and Bonfield 1964, for tensile properties of germanium). Recently Evans and Wild (1965) reported experiments in which diamond plates were plastically bent by three-point loading at 1800°C. Type I diamonds (which contain precipitated nitrogen platelets in the cube planes) required a higher resolved shear stress to initiate plastic deformation than did type II specimens (which do not contain nitrogen precipitates). Examination by electron microscopy showed that the nitrogen platelets in the type I specimens hindered the movement of dislocations and thus contributed to the higher critical resolved shear stresses required for the deformation of the type I specimens. Because this type of examination involves the destruction of the specimen it was not possible to obtain information about the initial dislocation distribution in the specimens before they were plastically deformed. This is rather serious because the initial density of
dislocations has been shown to have a strong effect on the yield stress for another material of the diamond-type structure, namely germanium. For this reason diamond plates were examined by x-ray topography and by recording the birefringence patterns before deformation.

§ 2. EXPERIMENTAL METHOD

Eight diamond plates with dimensions of about $5 \times 3 \times 0.5 \text{mm}$ were used in the experiments. The large faces were approximately $\{100\}$. The plates were classified by measuring the ultra-violet absorption between 2000 and 3500 Å and also by measuring their electrical conductivity. Four of the plates were type $\Pi B$, two were type $\Pi A$ and two were type I diamonds. The type I specimens were obtained by cutting a larger plate along a $\{110\}$ direction into two equal parts. Figure 1 shows a plate and its orientation relative to three tungsten wedges with which plastic bending could be produced at $1800°C$. The orientation convention shown in the figure will be used throughout the paper to index the various observations. Birefringence patterns were photographed for all the specimens so as to record the distribution of initial strains in the plates. X-ray projection topographs (Lang 1959) of the specimens were then recorded. Two topographs of each specimen were taken, one with the $(022)$ reflection operating and the other with the $(022)$ reflection. Dislocations in the diamond structure have a Burgers vector of the type $\frac{1}{2}(110)$. Thus the use of these two reflections ensured that all dislocations were detected since no dislocation could satisfy the condition $g \cdot b = 0$ and be invisible, or nearly so, in both reflections. The four type $\Pi B$ and the two type $\Pi A$ diamonds contained a high density of lattice imperfections and in the case of the type $\Pi B$ specimens there were strong indications of a mosaic-block

Orientation of diamond plate relative to three tungsten wedges showing the four possible slip systems.
type of structure. The dislocation density was too high for clear resolution of individual dislocations in the type II specimens; the density was probably everywhere in excess of $10^7$ lines per cm$^2$. In such crystals the addition of a large number of dislocations as a result of plastic deformation would be readily measurable by x-ray topography. However, the initial stages of plastic deformation would have been difficult to follow in the presence of the high density of dislocations already present. For this reason no further experiments were done with these specimens. In both of the type I specimens, on the other hand, not more than three or four dislocations were present initially. Previous examinations by electron microscopy (Evans and Phaal 1962, James and Evans 1965) also indicated an extremely low dislocation density in this type of diamond. Attempts were made to deform plastically the two type I diamonds at $1800^\circ$C by three-point loading. Previous experiments (Evans and Wild 1965) had shown that very high resolved shear stresses (above about $10^{19}$ dynes cm$^{-2}$) were required to produce detectable plastic deformation with this type of diamond. Stresses of this magnitude are close to those necessary to produce brittle fracture in diamond (Bowden and Tabor 1964). Three-point loading experiments were done on the two plates at appropriately high stresses. After the load had been maintained for several minutes, the plates cleaved parallel to and near the centre wedge. The pieces were examined with an optical microscope and the birefringence patterns photographed. X-ray projection and section topographs (Lang 1957) were taken with the (022) and (022) reflections being used. Finally the pieces were thinned sufficiently by oxidation for examination by transmission electron microscopy. The thinning procedure has already been described (Evans and Phaal 1962).

§ 3. Results

3.1. Examination before Plastic Deformation

3.1.1. First type I plate

The birefringence pattern of the first type I plate is shown in fig. 2. The main feature is a light band representing a strained region in the form of a long side and two short sides of a rectangle. The directions of these sides are [011] and [011], respectively. The x-ray topographs are shown in figs. 3 (a) and 3 (b). Figure 3 (a) was produced with the (022) reflection operating and fig. 3 (b) with the (022) reflection. The band of strain recorded in the birefringence pattern is also detected by x-ray topography. When the (022) was used the short sides of the band of strain were visible and the long side invisible. When the (022) reflection was used the reverse situation occurred. It is considered that most of the band of strain arises at the intersection of growth layers parallel to the {111} planes with the surfaces of the specimen. Lattice displacements due to variation in unit cell dimensions in these layers are constrained to lie in the plane normal to the line of intersection of the layer with the specimen surface.
From this restriction arises their observed visibility behaviour. In both figs. 3(a) and 3(b) the images of surface scratches appear. These are the long curved lines without a definite crystallographic orientation. It is clear that the plate contained only three or four dislocations and so dislocations introduced by plastic deformation would be readily detectable. A section topograph was also taken with the (022) reflection operating and showed a high crystallographic perfection of the plate, since clearly defined and undistorted Pendellösung fringes were present. The fringes exhibited a more perfect pattern than has previously been observed in diamond and compares well with that given by essentially perfect silicon (Lang 1964).

Fig. 2

Birefringence pattern of the first type I diamond plate before plastic bending.

3.1.2. Second type I plate

The birefringence pattern for this plate shows that a prominent feature was again a band of strain in the shape of two short sides and one long side of a rectangle and is similar to fig. 1. When the birefringence patterns for the two type I plates are compared it is clear that in the original plate from which the two plates were cut, the band of strain was in the shape of the sides of a square. A similar distribution of strain was reported by Pfaal (1965) and attributed to the effect of plastic deformation by indentation at the centre of the square. It appears that such a distribution of strain can be incorporated into a diamond during growth and subsequent history without the necessity for postulating that it is produced by plastic deformation in the laboratory. Examination of birefringence patterns,
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Fig. 3

X-ray projection topographs of first type I diamond plate; Cu Kα radiation;
(a) (022) reflection, (b) (022) reflection.
ultra-violet micrographs, x-ray topographs (Takagi and Lang 1964, Lawn et al. 1965) and etched surfaces (Seal 1965) commonly show square ‘picture frames’ in plates which have been cut parallel to the cube planes of diamond. X-ray projection topographs using in turn the (022) and (022) reflections detected the strained region with the same conditions for invisibility as for the first type I diamond.

3.2. Plastic Deformation of the Plates

The first type I diamond was heated to 1800°C in a furnace and protected from oxidation by a flow of purified argon gas. The plate was subjected to three-point loading with the orientation shown in fig. 1 between the plate and the tungsten knife-edges. A resolved shear stress of $12.5 \times 10^8$ dynes cm$^{-2}$ in the $\langle 110 \rangle$ slip directions of the active $\{111\}$ planes was imposed. After this stress had been imposed for 3 min, the diamond cleaved immediately below the centre wedge. Examination with an optical microscope showed that plastic deformation had occurred before cleavage, since slip lines were observed on either side of the cleaved region. There were two sets of slip lines on the large (100) surfaces in a direction approximately parallel to the centre wedge (and to the cleavage direction). The two sets of slip lines made an angle of 8° with one another. Examination of the plate by the back-reflection x-ray technique showed that the normal to the large surface was about 5° from the [100] direction. This could account for the two sets of slip lines, since the intersections of the two active slip planes ((111) and (111)) with the surface would make an angle of about 8° with one another under these circumstances. It was confirmed that these were in fact the active slip planes by measuring the directions of two sets of slip planes on the side surfaces of the specimen.

The second diamond was heated to 1800°C and a resolved shear stress of $11.7 \times 10^8$ dynes cm$^{-2}$ was imposed. The plate cleaved after the stress had been imposed for 5 min. It was found that the specimen had cleaved into one-half of the original plate and several smaller pieces. The presence of slip lines on the surfaces of the pieces again showed that plastic deformation had occurred prior to cleavage.

The two pieces from the first diamond were placed together and the birefringence pattern photographed (fig. 4). The band of strain was still present with no noticeable change, but intense strain had been introduced in the regions of plastic deformation on either side of the cleavage. Localized strains had also been introduced in the regions where the plate had rested on the two outer wedges. The birefringence patterns showed no evidence for diminution of the strains which were initially present from any annealing effects at 1800°C.

X-ray projection topographs with the (022) reflection operating were taken of the two pieces; fig. 5 shows the two topographs placed together. The x-ray topographs show no obvious change in the distribution of internal imperfections in regions remote from the deformed region, but they do
Birefringence pattern of two halves of first type I diamond plate after bending and cleavage.

Fig. 5

X-ray projection topographs of two halves of first type I diamond after bending and cleavage; Cu K$_a$ radiation; (022) reflection. Compare with fig. 3 (b).
show evidence for the relief of strain along surface scratches. Images of fresh dislocations introduced during plastic deformation extend to about half a millimetre away from the fracture surface. They are also seen locally where the outer knife edges touched the plate.

X-ray section topographs were taken to resolve the defects in more detail. Figure 6 shows the geometrical relationship between the x-ray beams and the specimen in the formation of the section topographs and indicates how the latter may be related to the projection topographs and birefringence patterns, and also to the geometry of the bending experiment.

![Fig. 6](image)

X-ray geometry of the section topographs showing relation to bending geometry. Explained in text.

A schematic plan view of the specimen, viewed parallel to the x-ray goniometer axis and looking down on the cleaved specimen surface, is shown in fig. 6(a). A side elevation of the specimen is sketched in fig. 6(b); this indicates schematically the jagged fracture surface and also shows where the knife edges were placed with respect to the specimen during bending. In fig. 6(a) the incident x-ray beam XO, which was, in cross section, a ribbon parallel to the goniometer axis, entered the specimen along path OA. The x-ray beam, which was about 15 microns in thickness, covered the height of the specimen. The beam was reflected by Bragg planes such as OO', the Bragg angle for diffraction from \{220\} planes being 38°. Diffraeted rays left the crystal between A and B and fell normally upon the photographic plate, forming an image between P and P'. This image showed predominantly the extra diffracted intensity produced by imperfections cut by the beam OA. The top part of the section pattern which included the region of fracture is shown schematically in fig. 6(c). The width of the section was 1.23 times the crystal thickness OO'. The vertical scale of the section topograph was almost the same as for the specimen itself. It follows that traces of the active slip-planes ((111) and (111)) should make 30° with the horizontal on the section topographs. Figures 7(a) and 7(b) show two of the section topographs. On these the intense blackening arises from the enhanced x-ray reflecting power in
regions where strong strain gradients existed. These distorted regions are associated with cracks close to the fracture surface and with concentrations of glide dislocations. The area of the topograph images which have been reproduced can each be divided roughly into three regions. From the top of the image to a depth of about 250 microns the presence of cracks and of intense deformation was sufficient to cause variations in image intensity through 'orientation contrast', even in this reflection for which the Bragg plane was normal to the axis of bending. The incident beam width was only about 1 min of arc, so a component of misorientation, to be effective in changing the glancing angle made by the incident beam with the Bragg planes, needed to be only about 30 sec of arc to provide contrast due to misorientation. In the next-lower region, down to about 500 microns from the top of the image, a remarkable feature is lines of blackening whose traces on these and other section topographs indicate concentrations of distortion in layers parallel to the (011) plane. They have an appearance similar to traces of slip-planes. On the other hand, the expected manifestation of lines of blackening on the topographs in directions corresponding to traces of the expected slip-planes ((111) and (111)) only occurs in a few parts of the images. Below about 500 microns from the top of the image, fresh dislocations can be resolved individually. For example, an isolated group of dislocations may be seen in the lower part of fig. 7(a). The configurations of individual dislocations have not been fully mapped and it is not known whether their sources were internal or at the surface. These dislocations do not appear to be confined to the slip-planes (111) and (111). In the region of low dislocation density and just below it in fig. 7(b) the Pendellösung fringes were distorted by the long-range stresses present. The order of Pendellösung interference was increased, as predicted by theory (Kato 1963, 1964) and observed experimentally (Hart 1965, Kato and Ando 1966). The fringes splay outwards as shown schematically in fig. 6(c). In fig. 7(b) some of the vertical bands are intersections of growth layers with the section OA (fig. 6(a)) cut by the incident x-ray beam. In this and other topographs interactions between growth layers and glide dislocations are observed.

After completion of the examination of the type I pieces by birefringence and x-ray topography, they were cut in such a way that after thinning by oxidation, fragments suitable for transmission electron microscopy were obtained. Some of the fragments were from regions which had not been deformed plastically and others from the regions near the centre wedge where substantial plastic deformation had occurred, as shown by the slip lines, birefringence patterns and x-ray topographs. Examination of regions where no plastic deformation had occurred showed that the nitrogen platelets were between 200 and 300 Å in diameter with a concentration of about $1.5 \times 10^{15}$ platelets cm$^{-8}$, assuming a fragment thickness of 1000 Å. The platelets appeared to be uniformly distributed and there were no dislocations present in the fragments examined. Fragments were produced from the plastically deformed regions such that the fragment
surfaces were parallel to the original (100) plate surface, (fig. 8). The nitrogen platelets can be seen in the cube planes and also a high density of dislocations which were produced by the plastic bending. It is clear that the dislocations tend to lie along the [011] direction for them to accommodate the plastic bending which has occurred about the [011] axis. A contributory factor also is that a (110) direction is a favoured low-energy direction for a dislocation in the diamond-type structures (Shockley 1953). The dislocations appear to be held by the nitrogen platelets and it is probable that movement of these dislocations during bending was hindered by the platelets.

Fig. 7

Section topographs of plastically deformed diamond in a vicinity of the fracture surface; Cu Kα radiation; (022) reflection. The geometry is explained in fig. 6. The field height is ~1 mm.
§ 4. Discussion

Examination by x-ray topography has shown that the type II A and type II B diamond specimens contained such a high dislocation density that individual dislocations could not be resolved. The type I specimens however contained very few dislocations. Thus to explain the higher resolved shear stresses required to produce plastic deformation in type I specimens than in type II specimens (Evans and Wild 1965) there are two differences in the defect structure between the two types to be considered: (1) the initial dislocation density in type I specimens is far less than in type II specimens; (2) type I diamonds contain a distribution of coherent platelets in the cube planes which is absent from type II specimens. That the nitrogen platelets have an effect in inhibiting dislocation movement is shown by the locking of the dislocations by platelets observed.

Fig. 8

Electron micrograph of thinned fragment from plastically bent region of the first type I diamond.
in type I diamonds by electron microscopy. Work on the plastic properties of germanium specimens containing differing initial dislocation densities by Bell and Bonfield (1964) showed that at sufficiently low densities \((5 \times 10^4 \text{cm}^{-2})\) the specimens cleaved even at high temperatures without yielding. Also crystals with higher dislocation densities which did yield showed a marked dependence in plastic properties upon the dislocation density. It thus appears that the high critical resolved shear stress for type I diamonds as compared with type II diamonds is due to a combination of an initial low dislocation density for the initiation of plastic deformation and the hindrance to movement of the mobile dislocations by the nitrogen platelets. Further work is required to separate the relative importance of the effects of the two parameters on the plastic properties of type I diamonds.

In the experiments there was no evidence for the diminution of internal strain by annealing processes at 1800°C, nor was there evidence for polygonization taking place in the plastically-bent regions at 1800°C. There may be some dislocation nucleation at graphitized sites on the surface of diamond (Evans and James 1964) but if present, this is too localized for detection by x-ray topography. The only apparent change in the structure of the diamond plates due to the heating effect at 1800°C was that cracks on the surface appeared to have been partially healed by the heat treatment. Perhaps the highly strained regions at the tips of the cracks were relieved by the nucleation and movement of dislocations at the elevated temperature.

Elasticity theory predicts that in bending experiments the specimen should contain a neutral plane where the applied stress is zero. This would imply that in plastic deformation experiments by bending there should be a dislocation-free zone near this neutral plane, and that dislocation nucleation and movement should be confined to the crystal on either side of this zone. In fact, as seen in the section topographs of figs. 7(a) and 7(b) there was no dislocation-free zone near the neutral plane. An explanation of the observation can be found in the work of Miles (1964) who examined by a photoelastic technique the elastic and plastic bending by three-point loading of magnesium oxide plates. He found that during elastic bending the neutral plane was midway between the top and bottom surfaces. Plastic deformation started in the region of the centre wedge and the deformed region propagated downwards until it depressed the neutral axis towards the bottom surface. As the load was increased plastic deformation occurred at the bottom surface and a deformed region moved upwards to restore the neutral axis to its original position. If this process occurs in diamond it would explain the high density of dislocations near the neutral plane in the section topographs. There is evidence that this process does occur in diamond, since several cases have been found where slip lines have been present near the top centre wedge and absent from the bottom surface at the initial stage of deformation. This would suggest that plastic deformation starts at the top compressive surface of diamond and propagates downwards as in magnesium oxide.
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