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The microstructure of natural polycrystal diamond, carbonado and ballas

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Natural polycrystal diamonds, carbonado and ballas, were observed with an ultra-high voltage transmission electron microscope and the characteristic microstructures were discussed. Carbonado had randomly oriented dislocations with Burger's vectors, $a/2\,\langle 1\,1\,0\rangle$. From diffraction patterns an inclusion in carbonado was thought to correspond to a mineral such as a serpentine. On the other hand, ballas had polygonized dislocations and dislocation loops and the inclusion in it was uncertain. The microstructural differences between the two diamonds were discussed from the view point of the conditions of diamond formation.

1. Introduction

Polycrystal diamonds have a fracture toughness superior to single crystal diamonds, because grain boundaries hinder further cleavage crack propagation. Therefore, these are very desirable materials for such applications as drilling bits, cutting bits and grinding powders. Many workers have tried to sinter diamonds. Hall [1], Stromberg and Stephens [2], and Suzuki *et al.* [3] have sintered diamonds without additives at high temperatures and high pressures. They have suggested that the bonding strength between diamond grains are mainly due to reconverted graphite. Also, Katzman and Libby [4], Wentorf and Rocco [5, 6], and Notsu *et al.* [7] have sintered diamonds in the presence of cobalt. They have shown that direct bonding between diamond grains are difficult without the metal. Recently Akaishi *et al.* [8] suggested that in the sintering of a diamond–cobalt system the presence of a sufficient amount of graphite needed to transfer the cobalt between the diamond grains is very important for the sintering process.

On the other hand, it is well known that polycrystal diamonds [9], known as carbonado and ballas, occur naturally. The ability to observe natural polycrystal diamonds and to clarify these characteristic microstructures would give important information on the growth conditions for natural diamonds. Also it would give useful information for the sintering of not only diamonds but also other covalently bonded materials such as carbides and nitrides which are difficult to sinter to a high density.

In this study we observed in detail natural polycrystal diamonds, carbonado and ballas, with an ultra-high voltage transmission electron microscope and we will discuss here the characteristic microstructures and growth conditions for them.

2. Experimental procedure

Polycrystal diamonds, carbonado and ballas, with a milky white colouration, were cut into thin plates using a laser. The resultant plates were ground using a fine grained diamond powder to less than about 300 μm in thickness. The sheets obtained were thinned by argon ion bombardment from both sides at a rate of about 0.3 μm h^{-1}. In order to prevent the foils from becoming charged, a carbon coating was applied to one side of the foil. The resultant thin foils were observed with a transmission electron microscope (Hitachi H-1250) operating at 1000 kV.

3. Experimental results

3.1. Carbonado

Carbonado is Portuguese for "carbonated", since it was first found in Brazil. It is defined as a porous, randomly polycrystallized diamond aggre-

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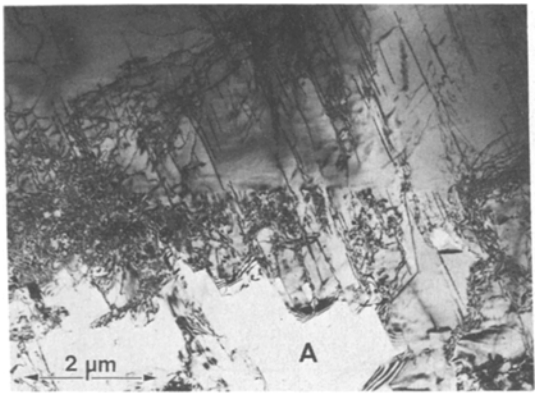


Figure 1 A typical transmission electron micrograph of carbonado.

gate. Its occurrence has been reported [9] in Brazil, South Africa, Central Africa and Siberia.

Fig. 1 shows a typical transmission electron micrograph of carbonado. Clearly from the micrographs, we can see many dislocations in the grain. In the white part marked A in Fig. 1, it would appear that no dislocations are present. But as shown later, dislocations are present but require conditions of high contrast in order to be observed. Fig. 2a is taken under (1 1 0) diffraction conditions. There are many dislocations in the grain marked A. On the other hand, dislocations are not visible in the grain marked B. Tilting observations also show that there are many dislocations in the regions marked B as shown in Fig. 2b, that is, many dislocations exist in the grains of carbonado. However, polygonized dislocations were not observed. The density of the dislocations is about 10^{12} cm^{-2}, assuming a foil thickness of 300 nm. The sizes of the grains range from below one micrometre to several micrometres in diameter. No appreciable precipitations are observed both in the grains and along grain boundaries. The grain boundary shapes are irregular. This is different from that of oxides in general, which are obtained from sintering.

Fig. 3 indicates a bright-field image of a foil viewed from (1 1 2) surface as shown in the diffraction pattern. By observing the images of dislocations from a selected diffraction spot using the central dark-field method [10], it can be presumed that the similar images produced from different spots obey the conditions, $\mathbf{g}_1 \cdot \mathbf{b} = \mathbf{g}_2 \cdot \mathbf{b}$, where **b** is the Burger's vector and $\mathbf{g}_1$ and $\mathbf{g}_2$ are the particular diffraction vectors which give identical images. The numbers on the diffraction pattern, 1, 2, 4, 5, 6, 7, 8, and 9 of Fig. 3 correspond to $[11\bar{1}]$, $[3\bar{1}\bar{1}]$, $[\bar{1}\bar{3}1]$, $[\bar{1}\bar{1}1]$, $[40\bar{2}]$, $[22\bar{2}]$, $[\bar{1}3\bar{1}]$ and $[\bar{3}11]$, respectively. The illustrations for this approach are shown in Fig. 4a to h. Similar image pairs of dislocations took place with a central dark field on 1 and 5, 2 and 4, 6 and 7, and 8 and 9. As a result, the Burger's vectors, $a/2[101]$, $a/2$ $[011]$, $a/2[110]$, $a[001]$ and $a/2[101]$ are considered to be present in the grain. This agrees with the reported data [11] that the glide plane in diamond $\{111\}$ and the perfect dislocations have Burger's vectors, $a/2\langle 110\rangle$. However, dislocations with Burger's vectors of $a\langle 100\rangle$ would not exist, since they are energetically higher than those with Burger's vectors, $a/2\langle 110\rangle$.

The diamond grains mentioned so far have many dislocations in them. However, locally there are grains with low dislocation density. In this case, the diamond grains have crystal habits and they are surrounded by other inclusions as shown in Fig. 5a. Since the plastic flow of the inclusions relaxes the stress applied to them, they have low dislocation density. The electron diffraction

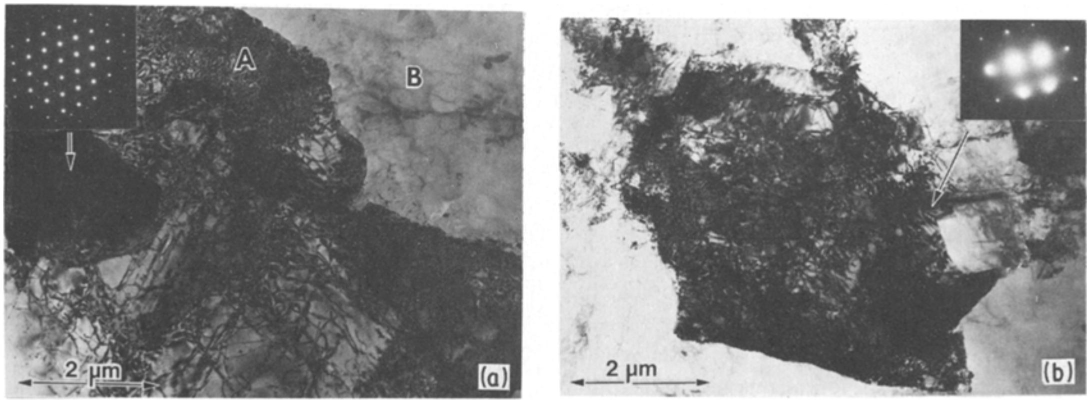
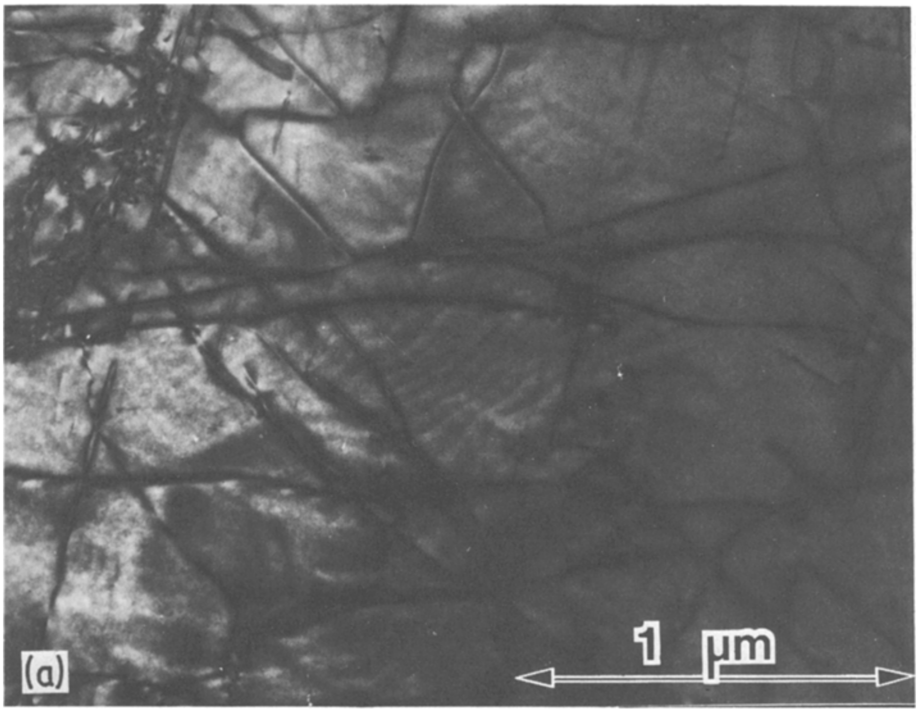


Figure 2 (a) Transmission electron micrographs of carbonado under (1 1 0) diffraction condition and (b) (1 0 0) diffraction condition of the grain marked B in (a).



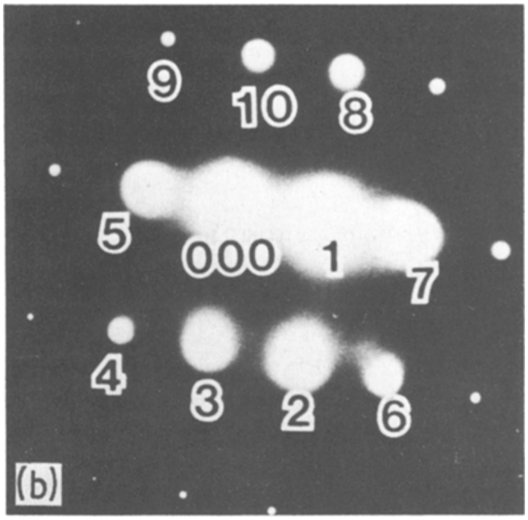


Figure 3 (a) Bright-field image and (b) its diffraction pattern.

pattern of an inclusion indicates that they correspond to a mineral such as a surpentine as shown in the diffraction pattern in Fig. 5b. As shown in Fig. 6, there are textures in which diamond grains can not be clearly identified. The diffraction pattern of dark grains in Fig. 6 indicates the presence of diamond, but on the other hand, the region of slight contrast indicates graphite.

3.2. Ballas

Ballas is defined as a polycrystalline diamond of oriented globular growth in which the crystallites have radial [110] directions. It is said to be a synonym for a round bort or a spherical bort. Its occurrence has been reported [9] in Brazil, the Premier mine in South Africa, and the Urals, Russia.

Fig. 7 shows a typical transmission electron micrograph of ballas. As can be seen from Fig. 7, the dislocations in ballas lie in a gathered state which is in contrast to the random array of dislocations in carbonado. Usually dislocations tend to line up to form low angle grain boundaries as shown in Fig. 8a and b, that is, the dislocations rearrange themselves into low-angle grain boundaries by dislocation glide and climb (a process known as polygonization). This is a very important structural feature in ballas. The dislocation density in ballas is about 10^9 cm^{-2} which is lower than carbonado.

Another important structural feature is the presence of dislocation loops as shown in Fig. 9. The dislocation loops are lying along a [100] direction. They are in the vicinity of dislocations and they never become isolated from the dislocations. According to the central dark-field method, the dislocation loops also have Burger's

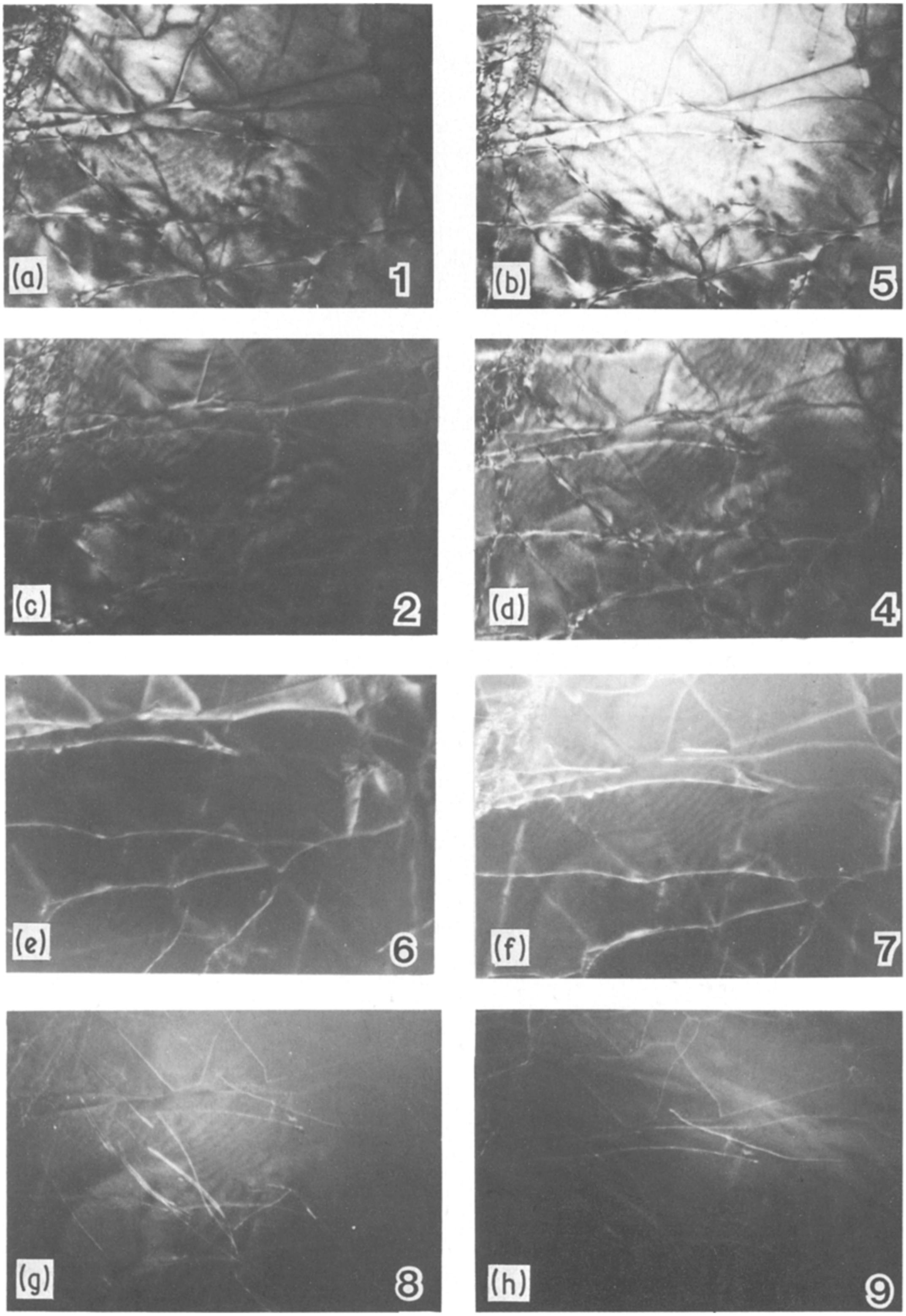
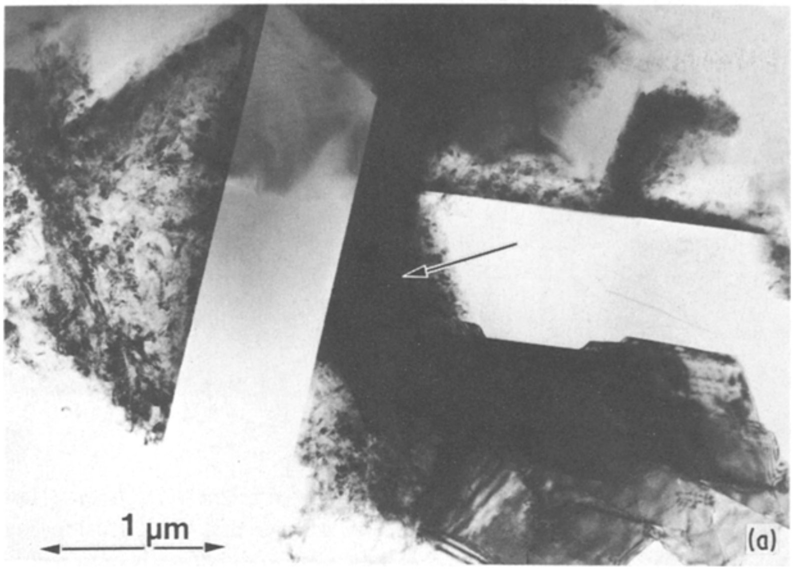


Figure 4 Similar dark-field image pairs produced from diffraction spots.



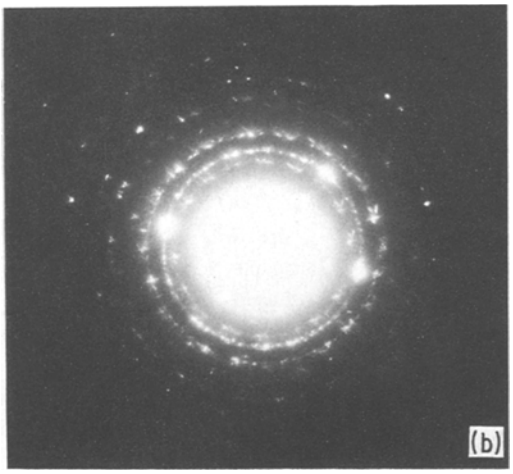


Figure 5 (a) Diamond grains with crystal habits and (b) the diffraction pattern of the inclusion.

vectors, $a/2\langle 1\,1\,0\rangle$. The mechanism of dislocation loop formation will be discussed later.

Fig. 10 shows a typical transmission electron micrograph of a grain edge of ballas. We can clearly see the zigzag and stair-like grain boundary. This indicates that vigorous plastic deformation took place under high stress at a high temperature. Generally grain boundaries between grains are angular in shape. The grain size range in ballas is from below one micrometre to several tens of micrometres in diameter. In grains of a size less than one micrometre diameter, structural defects such as dislocations and dislocation loops are not clear because of irregular, extinction contours as shown in Fig. 11.

The texture as shown in Fig. 12 is observed in ballas. Its selected area diffraction indicates that the areas of dark contrast are that for diamond

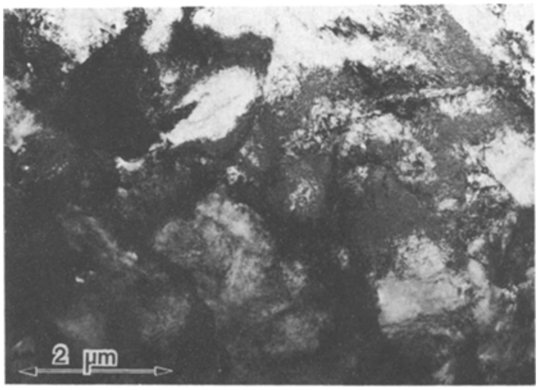


Figure 6 A characteristic microstructure in carbonado.

Figure 7 Typical transmission electron micrograph of ballas.

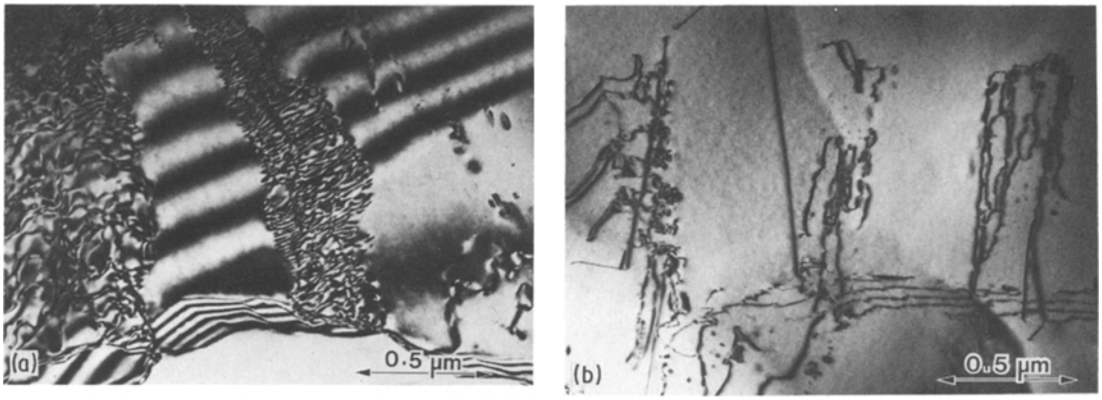


Figure 8 Polygonized dislocation in ballas.

and the white is that for graphite. An inclusion as shown in Fig. 13 is observed at three grain junctions of diamond grains, but it is not identified from the diffraction pattern. The main reason for this is that not good enough foil is available for observation purposes because of the selected thinning by the ion bombardment. Stacking faults and microtwin in synthetic diamond have been reported by Woods [12], but they were not observed in carbonado or ballas in the present study.

4. Discussion

Dislocations are thermodynamically unstable. Therefore, if we heat crystals with a high dislocation density at a very high temperature, the dislocations would diffuse out from the crystals. However, this is based upon a thermodynamical view. Actually, they tend to line up to form low angle grain boundaries, so called polygonization, at high temperature. The process is controlled by dislocation climb, that is, diffusion of carbon ions. Unfortunately we have no data for the carbon diffusion coefficient of diamond, but we can reasonably assume that the diffusion coefficient of carbon ions in diamond is extremely low, since generally covalently bonded materials such as Si_3N_4 [13] and SiC [14] have low diffusion coefficients for ions. If we assume that it is similar to that of carbon ions in graphite, the value is several orders of magnitude lower than for oxides [15]. As it is reported that polygonization of dislocations in MgO at 2000° C takes place within a few minutes [16], the time for diamonds is presumably a few hundred hours at the same temperature. As mentioned before, we could see polygonized dislocations in ballas but not in carbonado. This indicates that the polycrystalline formation process in both diamonds is different.

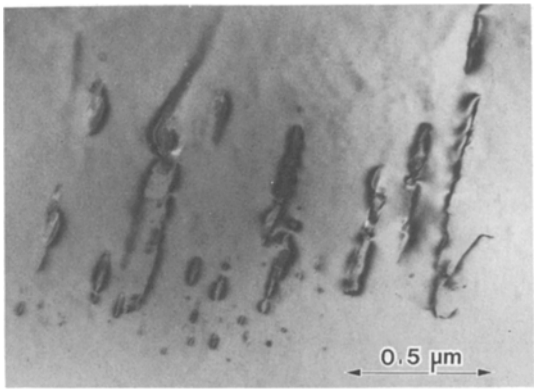


Figure 9 Dislocation loops in ballas.

As shown in Figs. 1 and 2, dislocations in carbonado are not polygonized. Also we can not see any dislocation loops which are a characteristic feature of single crystal diamonds [17, 18]. On the other hand, as shown in Figs. 8 and 9, ballas has polygonized dislocations and dislocation loops in it. This would reflect the difference of formation conditions in both diamonds.

When a thin foil of ceramics is picked with a sharp needle at room temperature, microcracks are easily introduced into the foil. In this case, dislocations are always observed in the vicinity of the cracks. Fig. 14 shows dislocations around a microcrack in a MgO single crystal. Many dislocations along the crack can be seen. Hence, we tried to introduce microcracks into the foil of a single crystal diamond in the same way. However, dislocations could not be introduced near the microcracks as shown in Fig. 15. This indicates that the diamond does not plastically deform at room temperature. Evans and Wild [19] reported

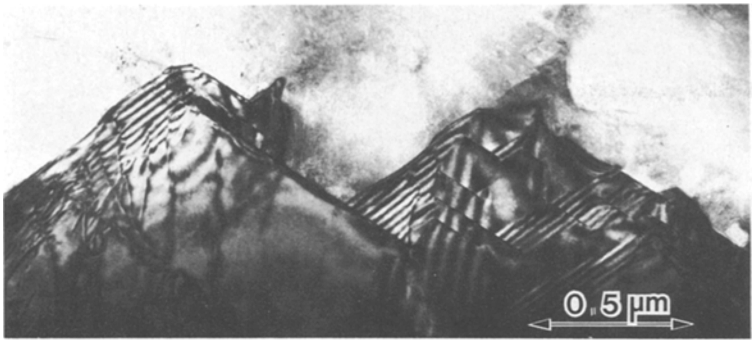


Figure 10 A typical transmission electron micrograph of a grain edge in ballas.

from a three-point bending test of single crystal diamond that the plastic deformation of diamond took place at about 1800° C. The experimental data suggest that high temperature and high pressure are absolutely necessary to introduce dislocations into diamonds. As mentioned before, the many dislocations without polygonization in carbonado suggest that the duration time under high temperature and high pressure conditions is not very long, because the polygonization of dislocations is preferable for long heating time. On the other hand, as shown in Figs. 8 and 9, ballas has polygonized dislocations and dislocation loops in it. This would indicate in ballas whether the duration time under the conditions of high temperature and high pressure is fairly long or that the temperature of formation of ballas is higher than that of carbonado, since polygonization is faster at higher temperatures and dislocation loops are formed by dislocation motion which is easier at high temperatures [20, 21]. Therefore, we tentatively speculate that carbonado is converted into ballas if carbonado is maintained for a long time under high temperature and high pressure conditions, or, if it is kept at a much higher temperature at which diamonds are not transformed to graphite. Graphite would be generated in both diamonds during their cooling stages. The grain boundary between the two grains as shown in Figs. 1 and 2 have no appreciable impurity precipitations. Also no heavy metals detected with a scanning transmission electron microscope which operated in the energy dispersive X-ray microanalytical modes. As the boundary segregation of light atoms such as boron, carbon, oxygen, nitrogen and magnesium is uncertain, we can not discuss direct bonding between diamond grains at present. However, if we judge from both the transmission electron microscopic images and the excellent mechanical properties of carbonado and ballas that there are no detectable impurities at the grain boundaries, we can speculate reasonably that direct bonding between diamond grains is possible under optimum conditions of temperature and pressure or that polycrystal diamonds are mechanically strong enough if the segregated layer between the grains is extremely thin. Further work on light atom segregations at grain boundaries is being carried out.

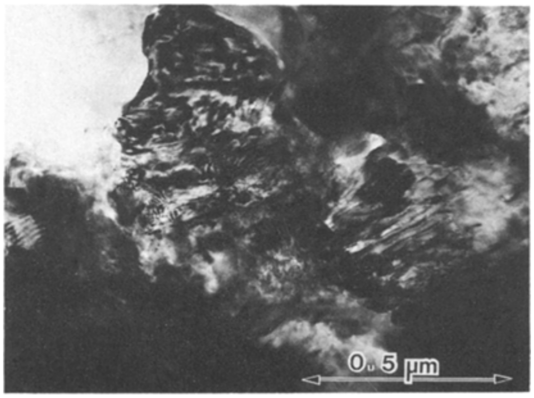


Figure 11 Subgrain diamonds in ballas.

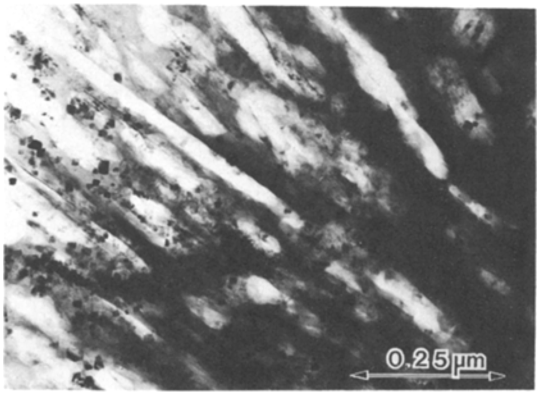


Figure 12 A transmission electron micrograph of ballas with texture.

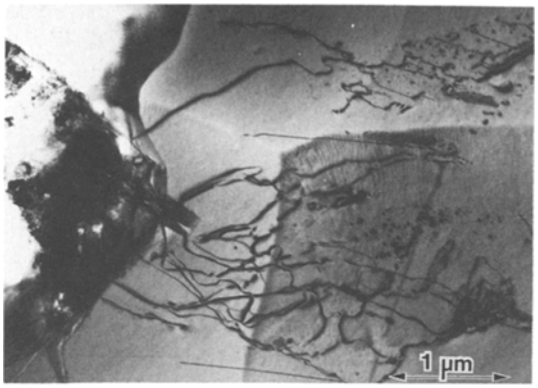


Figure 13 An inclusion surrounded with diamond grains.

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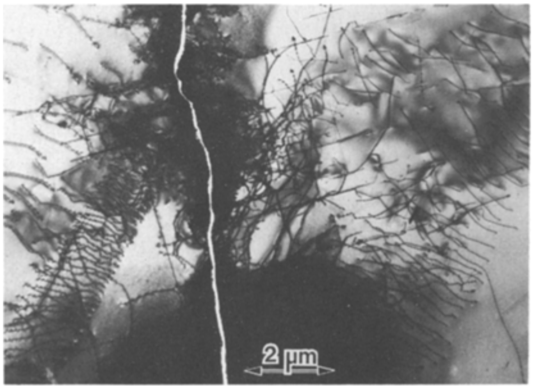

Figure 14 Dislocations around a microcrack in 2000 ppm iron doped MgO single crystal.

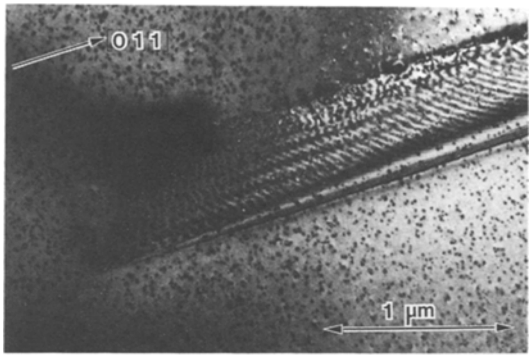

Figure 15 A microcrack in single crystal diamond.

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