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Deformation processes during high-pressure sintering of the diamond powders produced by catalytic synthesis

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Deformation structures formed in diamond grains during polycrystalline sample sintering at 7.7 GPa were studied using TEM. A number of deformation features were observed in diamond during sintering in the temperature range 700–2500 °C. Based on these data a sequence for the structure formation processes in diamond grains under *P–T* treatment was ascertained.

1. Introduction

Today, the feasibility of plastic deformation in diamond seems undoubtful. Such processes are confirmed by the X-ray diffraction and electron microscopic data for the single- and polycrystalline diamond samples under different thermomechanical treatment [1–4]. However, plastic flow mechanisms and diamond microstructure development have been little studied to date. However, such a study is of practical value, because the structure state formation in diamond polycrystalline materials produced under high pressures and temperatures is largely controlled by plastic deformation. One should note that plastic flow during diamond powder sintering under pressure–temperature (*P–T*) treatment differs from deformation under the customary mechanical testing. Two basic features of *P–T* treatment effecting grain deformation and polycrystalline diamond structure formation on the whole may be noted: (1) deformation starts in a highly porous sample where subsequent decrease in porosity up to the fully dense state is observed. It is accompanied by intergrain contacts extension and hence, changes in both the bulk stressed state and local stresses in grains; (2) in the first stage of treatment the powder is cold compacted with the pressure increase at room temperature and then heated up to the desired temperature. Thus, at any final sintering temperature there is a low-temperature effect (pretreatment stage). Hence, the final structure state formed in a polycrystalline sample is determined by a combination of the processes taking place under cold compaction, during the temperature rise and during isothermal treatment at a given pressure and temperature. Stage-to-stage transition correlates with new mechanisms involved in the diamond structure transformations.

The present paper is concerned with the results of studies on intragrain structure evolution in diamond polycrystalline samples as the sintering temperature is increased from 700° to 2500 °C under high pressure. Based on these data plastic deformation in diamond grains is considered.

2. Experimental procedure

Diamond powders of 5/7 and 28/40 μm grain size produced by catalytic synthesis were used for sample preparation. Polycrystalline samples were sintered in a high-pressure chamber of “toroid” type at 7.7 GPa in the temperature range 700–2500 °C with 100 °C intervals. Isothermal exposure at each given temperature was for 30 and 60 s. The duration of the temperature increase from room temperature up to the desired temperature was ~ 10–12 s (pretreatment time).

Using diamond saws, 200 μm thick plates were cut from the sintered samples and subsequently ground with diamond paste (successively using powders of 40/28, 14/10 and 7/5 grain size) to obtain 50–80 μm thickness. Thin foils for transmission electron microscopy (TEM) were prepared by the ion-milling technique. Samples for the study of starting powders were produced from compacts with the epoxy resin binder.

The microstructure was studied using electron microscopes HU-200F and JEM-100CX. Sample density was determined by hydrostatic weighing.

3. Results and discussion

A study on the structure of the starting powders showed most diamond particles to be single crystals possessing no defects. Only in grains of 40/28 μm fraction were sporadic dislocations or their groups, as well as single twins, observed. Grain aggregates with high-angle boundaries are rare. On the whole, dislocation density in the particles did not exceed 10^{12} m^{-2}. In coarse grains, single inclusions up to 1 μm containing nickel and iron were observed.

In the samples sintered at different temperatures the density of defects was significantly higher than in the starting particles (Fig. 1a–c). Changes in grain defect

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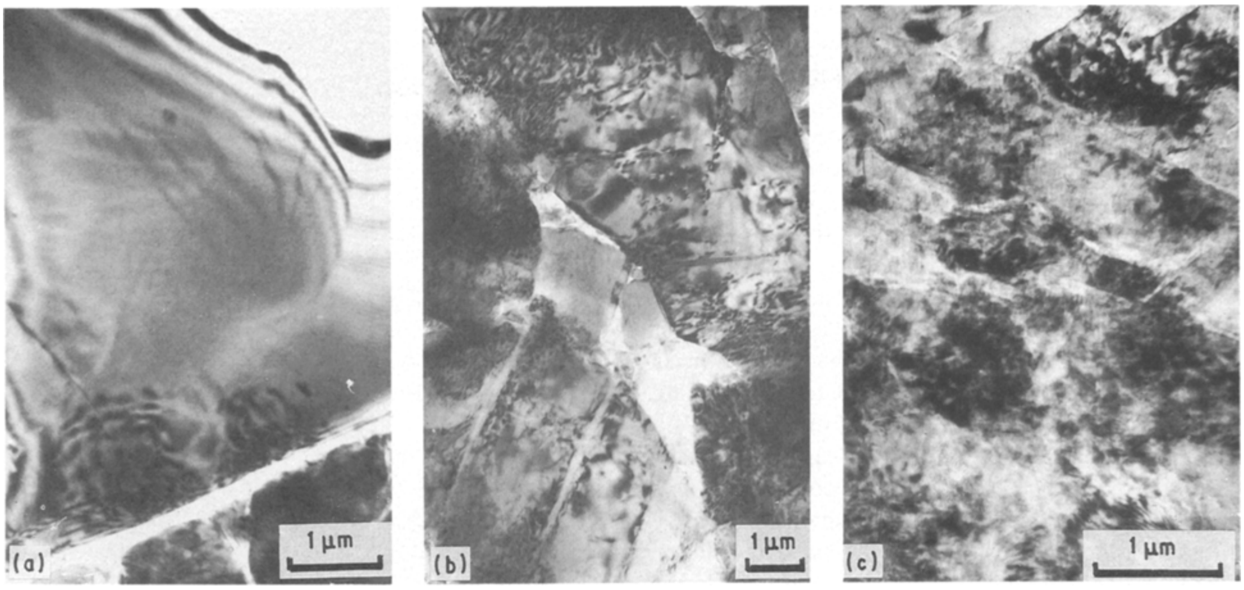

Figure 1 Transmission electron micrographs showing the defect density in diamond grains at different stages of P–T treatment. (a) 700 °C, (b) 1300 °C, (c) 2100 °C.

density and in their distribution with increasing sintering temperature allowed three temperature ranges of sintering, characterized by the different processes of structure formation, to be identified. The structure formation in the grains for each temperature range is now discussed in more detail.

3.1. Temperature range 700–1400°C

In this temperature range under the pressure mentioned, samples with a porosity of at least 10% were produced. Owing to brittle fracture of the diamond starting particles during cold compaction, fine-grained fraction of particles ($d < 1$ μm) appeared. Such particle aggregates are usually localized in coarse-grain joints (Fig. 2a). Interparticle bonding after P–T treatment is due only to mechanical contacts in this temperature range. The basic components of the subgrain structure are dislocation groups and microtwins initiating from the grain surface (mainly from the particle contact zone) (Fig. 2b, c). Defect type and arrangement indicate three basic mechanisms responsible for low-temperature plastic flow in diamond. The first is local plastic deformation in regions of particle contact interaction. According to the concepts of similar processes (termed elsewhere the "mechanical implantation of material" [5, 6]), local plasticity is connected with the motion of point defects and their clusters in the zones of great stress gradient. Unfortunately, such processes in diamond have been

Figure 2 Details of substructure formed in the temperature range 700–1400 °C. (a) Submicrometre fraction of particles, (b) half-loops of perfect dislocations (dark-field image), (c) microtwins emitted from the particle surface.

poorly studied owing to methodical difficulties. In the grain contact zone, a very high defect density is usually observed which cannot be identified even when studied by the weak-beam TEM technique.

The second and third plastic flow mechanisms realized in the 700–1400 °C temperature interval are connected with dislocation plasticity, i.e. the second is the sliding of perfect dislocations, the third is the sliding of Shockley partial dislocations (SPD) (Fig. 2b, c). SPD generation related to deformation stacking faults (SF) as a rule is an ordered one, and results in microtwin (MT) formation. Hence, the third deformation mechanism may be considered to be twinning. Microtwinning is the basic mode of diamond plastic deformation in the temperature interval under consideration, providing shifts at distances comparable with the grain sizes. Generation of perfect dislocations is more sporadic. Such dislocations are nucleated similar to SPD in contact zones as half-loops but they do not advance far from the grain surface. Generation of different defect types in the grain interaction contact zone may be interpreted as the feasibility to activate simultaneously some systems of light basal sliding, i.e. systems with shifts $\langle 1\,1\,2 \rangle$ (with SPD participation) and those with shifts $\langle 1\,1\,0 \rangle$ (with perfect dislocation participation). Preferential formation and distribution of SPD may be related to a kinetic factor, namely, in the relationship between dislocation sliding velocity, v, and shear stress, τ, $v = M(\tau/\tau_0)^m$, m is greater for SPD compared with that of perfect dislocation [7]. With increase in stress, a difference is especially appreciable. Light basal sliding with SPD participation only in one system of parallel planes (1 1 1), results in microlamellar structure formation (Fig. 3a). In coarse grains a system of intersecting MT is usually formed (Fig. 3b). Intersecting groups of the flat thin defects readily retard light sliding in the early stages of plastic deformation under low defect density. This results in a new mechanism of plastic flow with a higher activation energy. TEM observations enable one to identify at least three types of process originating in the first temperature range after light sliding, i.e. SPD cross-slip, SPD movement through MT boundaries (in the case of non-parallel arrangement of SPD sliding planes and MT location planes), and prismatic sliding of perfect dislocations. However, at higher temperatures the above processes are more intensive.

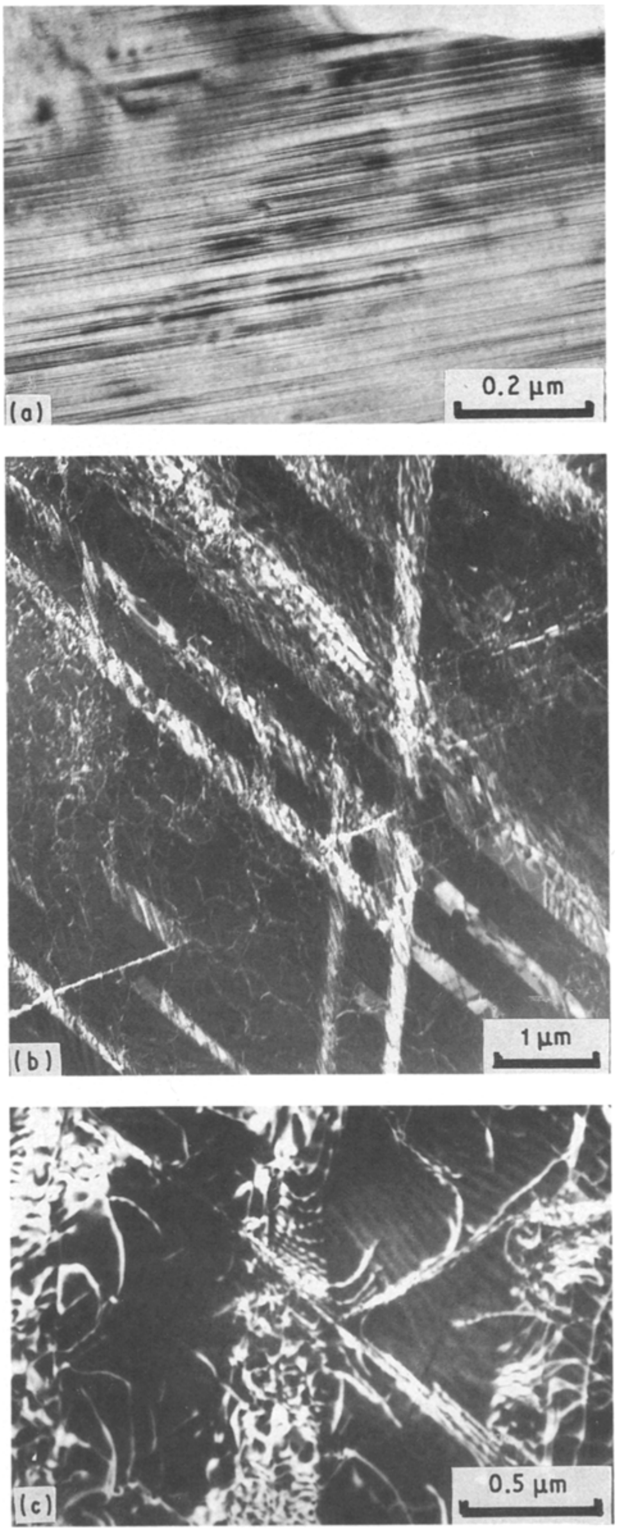

Figure 3 Microtwins in diamond grains. (a) The lamellar substructure, (b) intersecting microtwins, (c) dislocations on MT boundaries (dark-field images).

3.2. Temperature range 1400–1900°C

Judging from the defect character and density in this temperature interval, the processes initiated at lower temperatures are intensified. The structure features show that SPD cross-slip and MT intersection are more intense. Such processes lead to the accumulation of dislocations on twin boundaries and the formation of a stair-rod dislocation forest. (Fig. 3b, c). Perfect dislocation sliding (also involving that along prismatic planes) is predominant in this temperature interval (Fig. 4). With increase in grain defect density, due to volume filling with perfect dislocations (up to density $10^{15}\,\mathrm{m}^{-2}$ and higher), deformation via microtwinning ceases. This is probably also facilitated by a local stress drop due to the formation of continuous contacts between grains. A decrease in SPD sliding contribution and an increase in the role of perfect dislocations in diamond plastic flow in the second temperature interval may be interpreted as follows. SPD sliding is kinetically more preferential in defect-free crystals under high local stresses, and perfect dislocation mobility as a thermally activated process increases with increasing temperature. Plastic deformation in this temperature range is characterized by

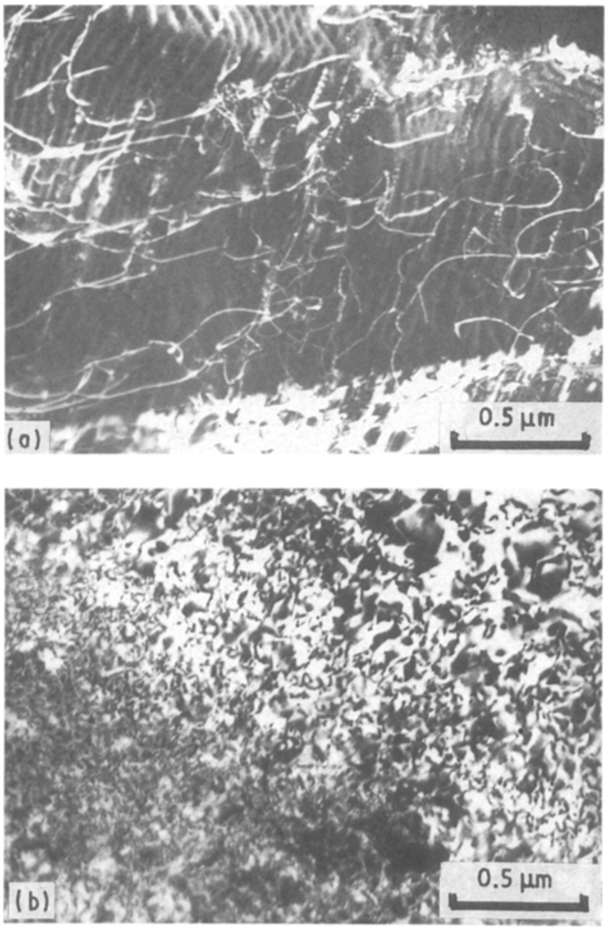

Figure 4 Diamond grains with different perfect dislocation densities.

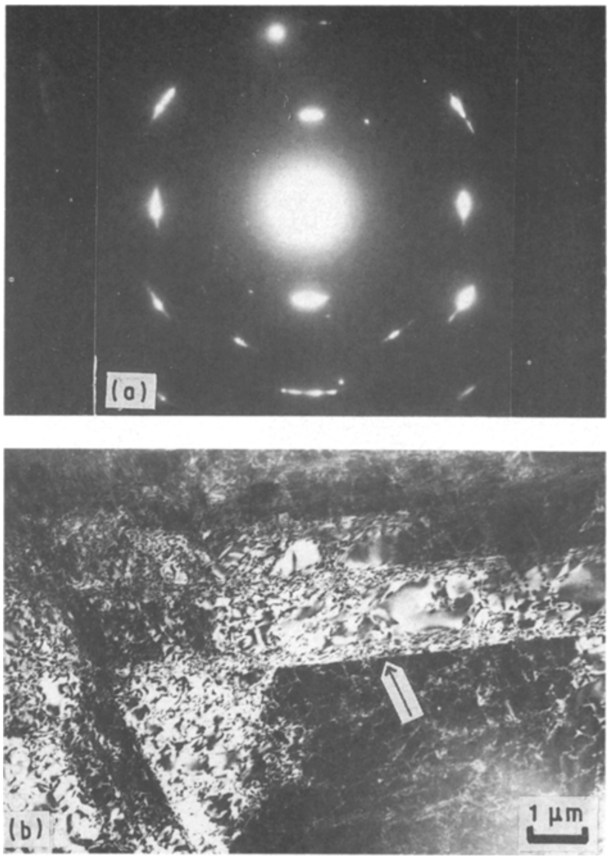

Figure 5 Fragmentation of grains. (a) SAD pattern from deformed region, (b) TEM image of deformed regions with disoriented boundaries (indicated by arrows).

grain fragmentation with fracture, i.e. by the formation of disoriented regions in them. This process is due to inhomogeneous defect aggregate formation. Fragmentation is readily identified on the geometry of selected-area diffraction (SAD) patterns characterized by azimuthal broadening of diffraction spots (Fig. 5a). TEM images of such grains do not show sharp boundaries formed between fragments, i.e. disorientation is smooth (Fig. 4b).

3.3. Temperature range 1900–2500 °C

Plastic deformation in this temperature range is observed in the practically fully dense sample. In this case local stresses and stress gradients in grains are much lower than in those of the samples prepared in the ranges mentioned above. Moreover, deformation at this stage takes place in the grains with a high defect density formed during pretreatment. Hence, high-temperature mechanisms of stress relaxation must be connected with the dynamic rearrangement of defect structures (dynamic recovery) rather than with new defect generation. In fact, in the grains of the samples sintered at $T > 1800\,^{\circ}\mathrm{C}$ some decrease in general defect density is observed with subgrain boundary formation, while subboundaries between disordered fragments arise mainly on thin microtwins (Fig. 5b). Such disorientation boundaries were also observed in cubic BN grains after P–T treatment [8]. Their formation mechanism is as follows. MTs formed in practically all grains at the starting stage of deformation initially contain in their twin boundaries only pile-ups of twinning partials. As deformation proceeds, numerous lattice dislocations accumulate on the twin boundaries, resulting in disorientation of matrix regions on both sides of the MT. Hence, in a grain with MTs, a system of flat boundaries is formed to separate grains, into fragments ranging in size from some micrometres to some parts of micrometres.

In polycrystalline diamond samples sintered at $T > 2000\,^{\circ}\mathrm{C}$, local regions are observed which consist of fragments < 0.1 μm in size, with high angle disorientation. The mechanism of such fragmentation is not yet clear; one should note that such substructure formation in metals with a high deformation degree correlates with intensive fragment disorientation, i.e. the realization of a "rotation plasticity" mechanism [9].

In diamond grains after high-temperature deformation, ordered dislocation aggregates in the form of thin dislocation walls, nets or subgrains of cellular type, are very rarely observed. This indicates that dislocation climbing is retarded due to the diffusion rate. Practically a complete absence of diamond grain recrystallization coarsening, even at 2400–2500 °C, also indicates retardation of diffusional processes. Evidently a limiting factor is the low mobility of point defects although the concentration of these defects must be high after deformation.

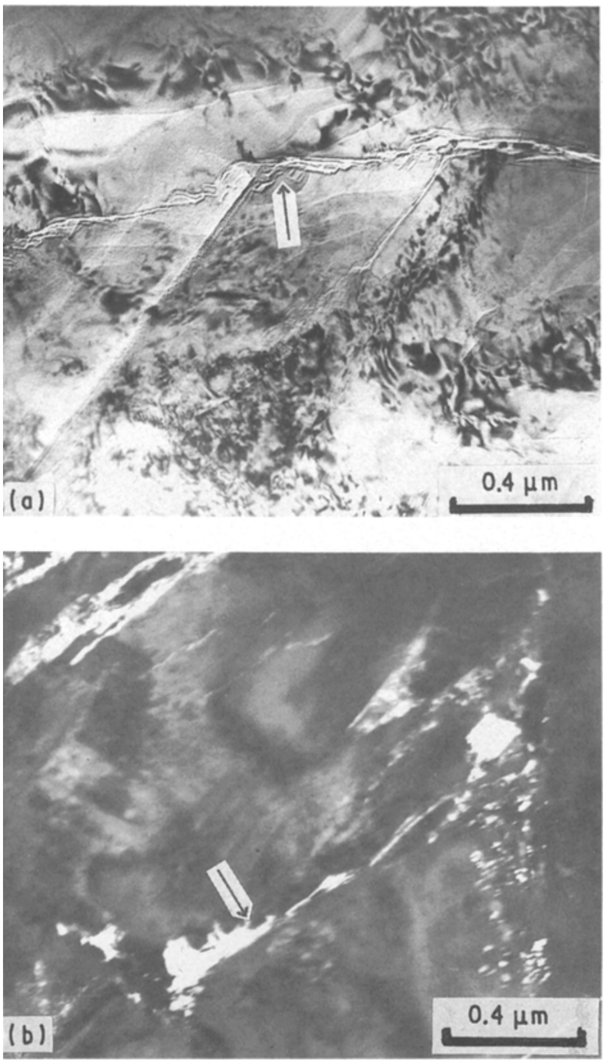

Figure 6 High-temperature substructures ($T = 2500\,^{\circ}\mathrm{C}$). (a) Crack in a diamond grain (indicated by arrow), (b) graphite segregations (dark-field image).

In the high-temperature range of diamond deformation, the temperature region above 2300 °C may be especially marked out. In this region new mechanisms of heavily deformed grain structure relaxation are observed, namely, crack formation and diamond–graphite phase transformation (Fig. 6). Transformation is a crystal-oriented one – planes (0 0 0 1) graphite and (1 1 1) diamond are parallel. The graphite formed is characterized by a microlaminated substructure. This may be correlated with the fact that the point at $T = 2300\,^{\circ}\mathrm{C}$ and $P = 7.7$ GPa is in the vicinity of diamond–graphite phase equilibrium. Therfore, at higher temperatures, the plastic flow overlaps the initial stages of phase transformation.

4. Conclusion

Deformation substructure in grains of polycrystalline diamond samples sintered over a wide temperature range was studied by TEM. The change in the grain substructure with increasing sintering temperature was found to be due to the change in diamond plastic deformation mechanisms. This change is due not only to the intensification of thermally activated processes, but also to the change in the stressed state of the polycrystalline sample during compacting, as well as to defect structure formation in the grains during temperature rise up to the desired temperature (pre-treatment substructure). The sequence of mechanisms responsible for grain deformation during sintering temperature rise with simultaneous increase in powder compact density, was found to be as follows. Light basal sliding with SPD participation and microtwinning in the low-temperature stage (700–1400 °C) are replaced by multiple sliding. This results in barrier formation as intersecting twins and a dislocation forest. The mechanism of perfect dislocation sliding is the basic one in the 1400–1900 °C stage. At higher temperatures (1900–2200 °C), slow dynamic rearrangement of the dislocation structure takes place. Up to 2500 °C, dynamic recovery with point defect participation is not intensive. A high defect density appearing during the temperature rise and a low recovery velocity are responsible for the grain substructure characteristics, similar to the defect density, type and distribution over a wide temperature range (1400–2500 °C). At 2300 °C and higher, relaxation processes take place via crack formation and diamond–graphite phase transformation observed not only on the grain boundaries but also in the bulk.

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