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Microstructure features of polycrystalline diamond synthesized directly from graphite under static high pressure

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Recently, ultra-hard polycrystalline diamond was synthesized from graphite by direct conversion under static high pressure. This paper describes the microstructure features of thus formed polycrystalline diamond. Transmission electron microscopy and electron diffraction have revealed that the polycrystalline diamond has a mixed texture of a homogeneous fine structure and a lamellar structure. The former structure consists of fine-grained diamond particles of several tens of nanometers across, which are randomly oriented. The latter structure has bending diamond layers, which may reflect deformed shapes of locally layered graphite of starting material. The experimental results suggest that diamond particles in the homogeneous fine structure are transformed from graphite in the diffusion process, while diamond layers in the lamellar structure are formed in the martensitic process from graphite via the hexagonal diamond phase. It is also noted that significant grain growth occurred at a high temperature of ∼2700°C, and the lamellar structure was segmentalized to form new grain boundaries.

1. Introduction

Polycrystalline diamond has been used for a wide range of industrial applications, such as cutting tools, drill bits and wire-drawing dies. Conventional polycrystalline diamond, however, contains binder materials of metal (Co, Ni) or ceramic (SiC). These binder materials affect the mechanical properties and thermal stability in varying degrees.

It is known that diamond can be synthesized from graphitic carbon by direct conversion without any catalysts under high pressure and high temperature. This method has been thought to be the most effective to produce pure-polycrystalline diamond containing no binder material or sintered agency. Attempts to obtain a pure-polycrystalline diamond with such direct conversion method using various graphitic carbon were made by shock compression [1], direct heating under static high-pressure [2–5] and Laser heated Diamond anvil cell [6, 7]. High-purity massive sintered polycrystalline diamond, however, has not been obtained because of the evitable problems of residual graphitic carbon and inhomogeneous sintering.

More recently we succeeded in the synthesis of high-pure massive well-sintered polycrystalline diamond by indirect-heating of high-pure graphite under static pressures above 12 GPa and temperatures above 2000°C using the Kawai-type multi-anvil apparatus [8]. The polycrystalline diamond consists of very fine diamond grains of tens of nanometers containing no graphitic carbon phases, and has considerably high hardness equivalent to or even higher than that of single crystal diamond. It is of great interest to characterize the super hard polycrystalline diamond. In the present paper, we investigate the microstructure features of the material in detail by transmission electron microscopy, and discuss the conversion mechanism from graphite and the formation process of the nano-crystalline structure. This study is significant as fundamental research to develop industrial applications of the new material, because the microstructure of the material reflects its physical and mechanical properties. Little information has been available on the microstructures of the massive polycrystalline diamond sintered body formed from graphite under static high pressure. This work is also important as a probe into the origin of natural polycrystalline diamond.

2. Experimental

Well-sintered polycrystalline diamond specimens were synthesized from graphite by direct conversion method under static high pressure and high temperature. An isotropic polycrystalline graphite rod (99.9995%, Nilaco Co. Ltd), consisting of hexagonal graphite particles of several micrometers oriented in a random direction, was used as the starting material. The graphite rod with typical dimensions of 1.5 mm diameter and 1.0 mm length was enclosed in a Re tube heater, and converted to polycrystalline diamond under high pressure and high temperature conditions of 15–18 GPa and 2300–2700°C for 10–10000 s. The high-pressure and high-temperature were generated using a Kawai-type multi-anvil apparatus operated in a 2000-ton hydraulic ram (Orange-2000 at GRC, Ehime University). The details of the high-pressure experimental method were given in our previous paper [9].

The microstructure of polycrystalline diamond was investigated by transmission electron microscopy (TEM). Thin plates of 10 μm × 10 μm × ~0.1 μm were carved out from the polished surface of the respective polycrystalline diamonds by using a focused ion beam (FIB) for TEM observation. The microstructure of the thin film was characterized with a high-resolution electron microscope (Hitachi, H-9000) at an accelerating voltage of 300 kV.

3. Results

Fig. 1 shows a typical transmission electron micrograph of a polycrystalline diamond specimen at a synthetic condition of 18 GPa and 2500°C for 10 s. The microstructure of the polycrystalline diamond consists of two distinct patterns; a homogeneous fine structure and a lamellar structure, marked as A and B in Fig. 1, respectively. Figs 2 and 3 show respective enlarged views. The homogeneous fine structure consists of small and uniform polyhedral granular crystals, typically 10–20 nm across (Fig. 2). The lamellar structure is formed from layer crystals of 100–200 nm length banking up with a slight bending (Fig. 3).

The electron diffraction patterns observed in the respective structures are shown in the insets of Figs 2 and 3. In the homogeneous fine structure, no diffractions from graphite or other phases expect those from cubic diamond are detected, suggesting that the structure is a phase-pure polycrystalline cubic diamond. The diffractions from diamond particles are distributed randomly along the electron reflection rings, forming ring-like diffraction patterns, indicating that each diamond particle is oriented in a random direction. On the contrary, symmetric diffraction spots from the cubic diamond (c-dia) phase were observed in the lamellar structure. The direction of the strong (111) c-dia reflection

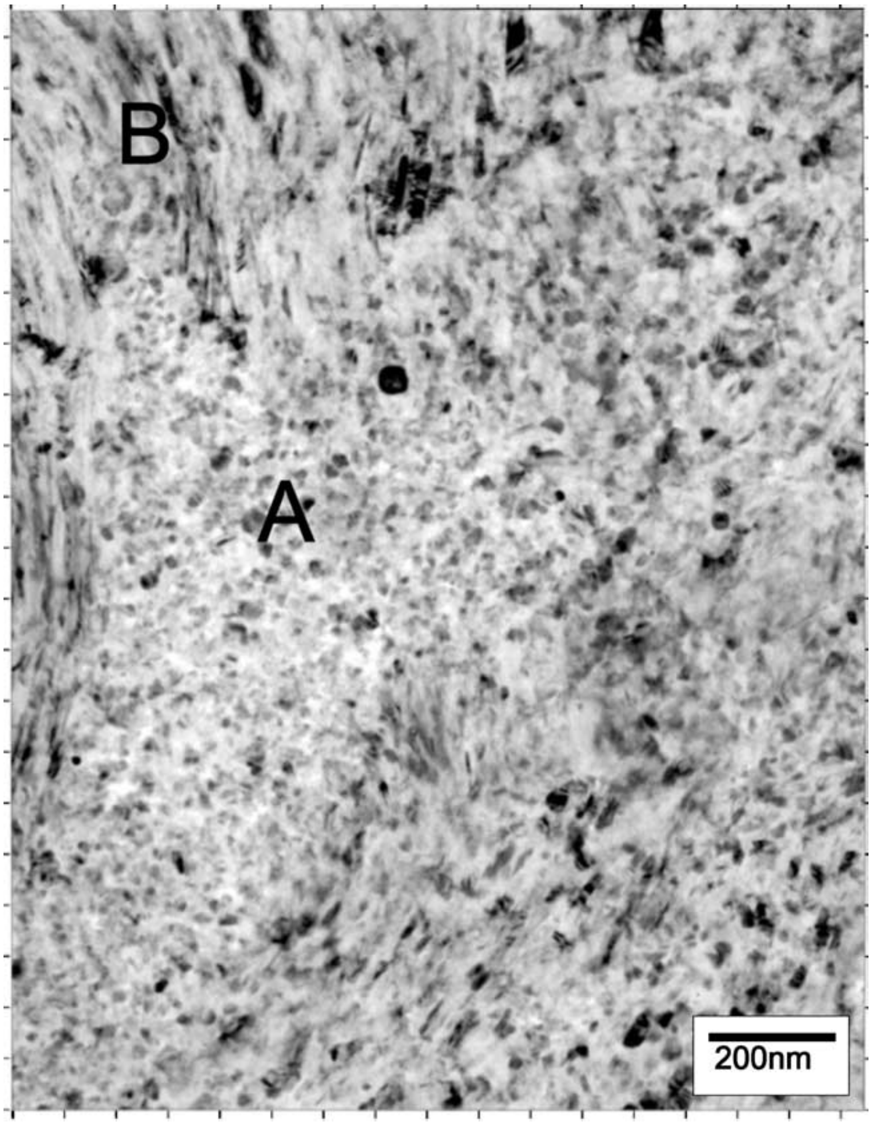

Figure 1 Transmission electron micrograph (×50000) of polycrystalline diamond formed directly from graphite at 18 GPa and 2500°C for 10 s.

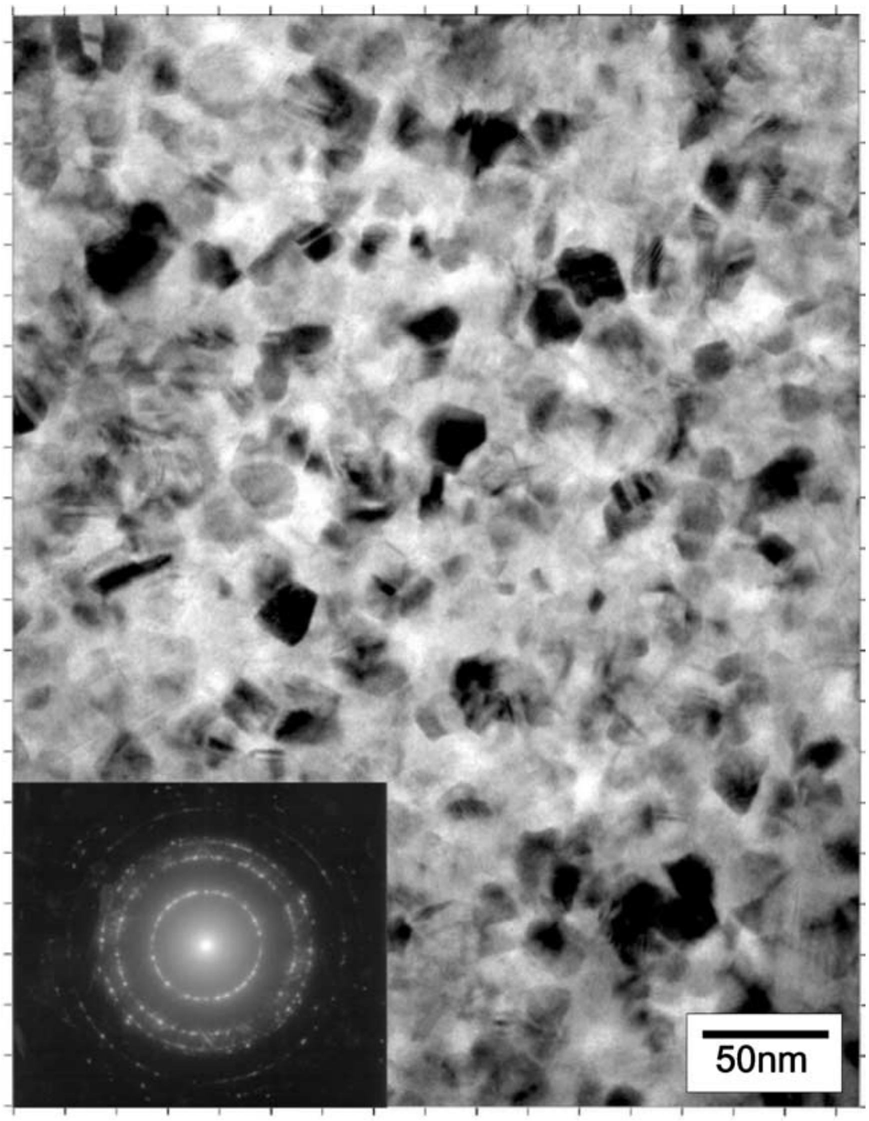

Figure 2 Enlarged transmission electron micrograph (×200000) and electron diffraction pattern of region A (homogeneous fine structure) shown in Fig. 1, taken within the field of 400 nm diameter.

corresponds to the direction of the layers, showing that the lamellar diamond crystal is parallel to the (111) plane. In the lamellar structure, very weak diffraction spots of (100) hexagonal diamond (hex-dia) were occasionally detected near the diffraction spots of (111) c-dia. Fig. 4 shows an enlarged view of the electron diffraction diagram of the lamellar structure. The (100) hex-dia diffraction spots are found to lie on the same radius as the (111) c-dia diffraction spots. This indicates that the mutual orientation of the phases is (111)c-dia// (100)hex-dia.

All of the specimens we investigated in this study showed basically the same mixed microstructure as mentioned above. The diamond particle sizes in the homogeneous fine structure of various specimens are summarized in Table I. The particle size of all specimens obtained below 2500°C was as small as 10–30 nm, and no noticeable grain growth was observed even for a long duration time of 10000 s. However, many larger particles (>30 nm) were observed in a specimen obtained at a high temperature of ∼2700°C (No. 6) as shown in Fig. 5. In the matrix exaggerated growth particles of 100–200 nm were found locally as indicated by an arrow in Fig. 5a. The exaggerated particles have more than six numerous sides on the grain boundaries, while specimens obtained below 2500°C have less than six sides on the grain (Fig. 2). Fig. 6 shows the TEM image of the lamellar structure of the No. 6 specimen. The lamellar structure was found to be segmentalized to produce new grain boundaries. In the electron diffraction pattern for this structure, no diffractions from hex-dia but those from oriented (111) c-dia were detected as shown in the inset of Fig. 6b.

TABLE I Diamond particle sizes in the homogeneous fine structure

No.	*P* (GPa)	*T* (°C)	Time (s)	Particle size (nm)
1	18	2500	15	10–20
2	15	2400	78	10–30
3	18	2300	10	10–30
4	18	2300	1000	10–30
5	18	2300	10000	10–30
6	18	2600–2700[a]	600	30–200

[a] Temperature was estimeted based on a power-temperature relationship at lower temperatures, and may suffer uncertainly of about ±100°C.

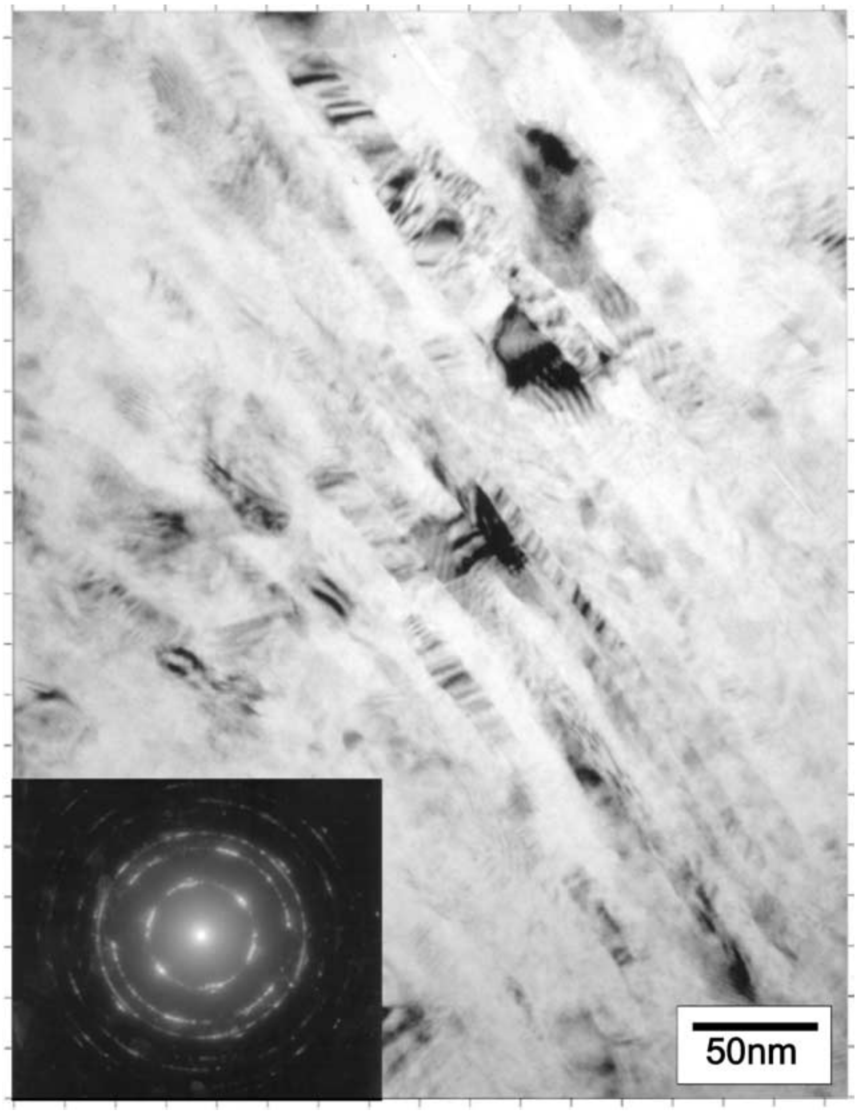

Figure 3 Enlarged transmission electron micrograph (×200000) and electron diffraction pattern of region B (lamellar structure) shown in Fig. 1, taken within the field of 400 nm diameter.

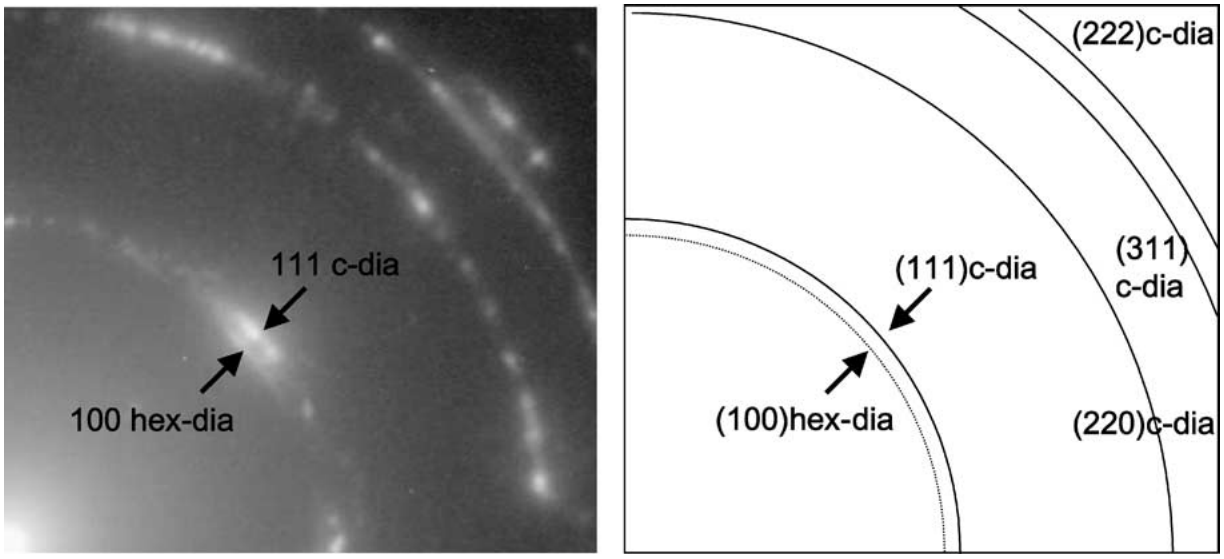

Figure 4 Enlarged view of electron diffraction pattern from lamellar structure shown in Fig. 3.

4. Discussion

TEM observation revealed that the polycrystalline diamond formed by direct conversion from graphite has a mixed texture of a homogeneous fine structure and a lamellar structure. The diamond particles in the homogeneous fine structure are as small as several tens of nanometers across, which are one-hundredth of the typical grain size of raw graphite (Fig. 2). The ring

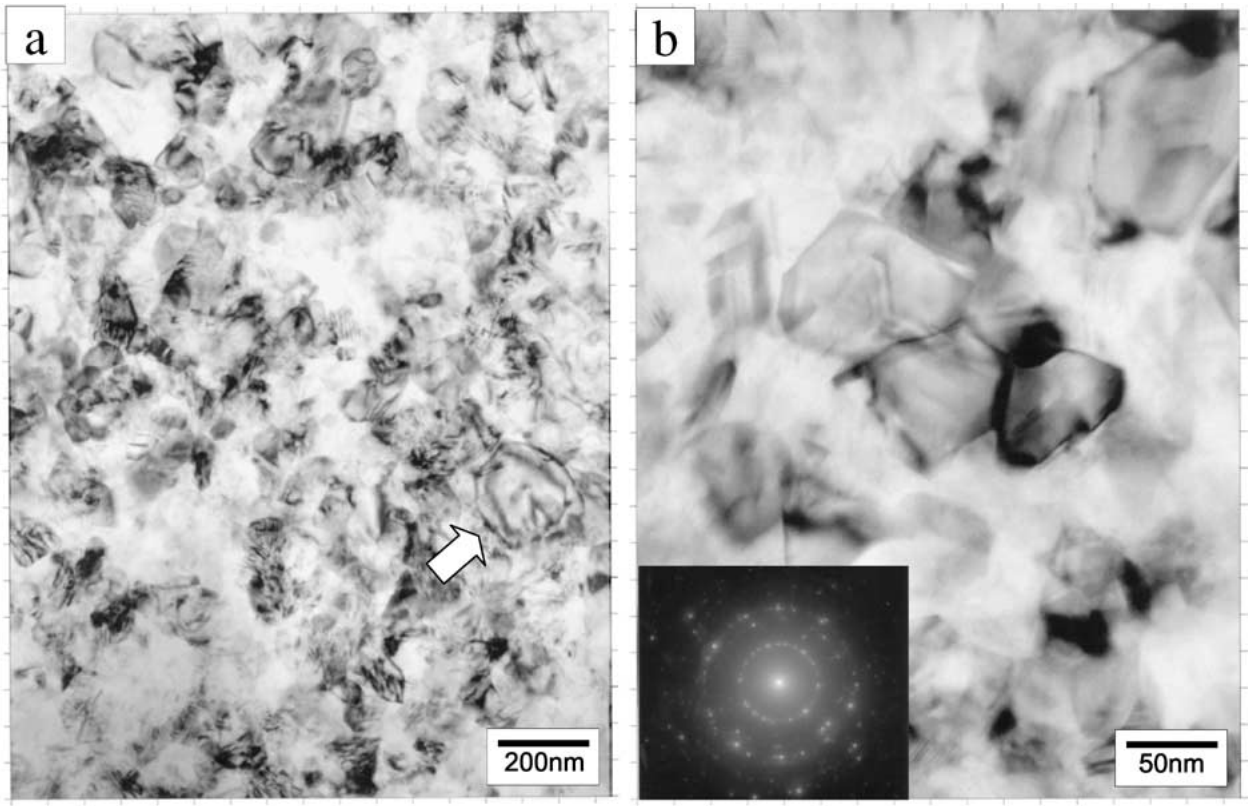

Figure 5 Transmission electron micrographs ((a) ×50000, (b) ×200000) of homogeneous fine structure of polycrystalline diamond formed directly from graphite at 18 GPa and ∼2700°C for 600 s.

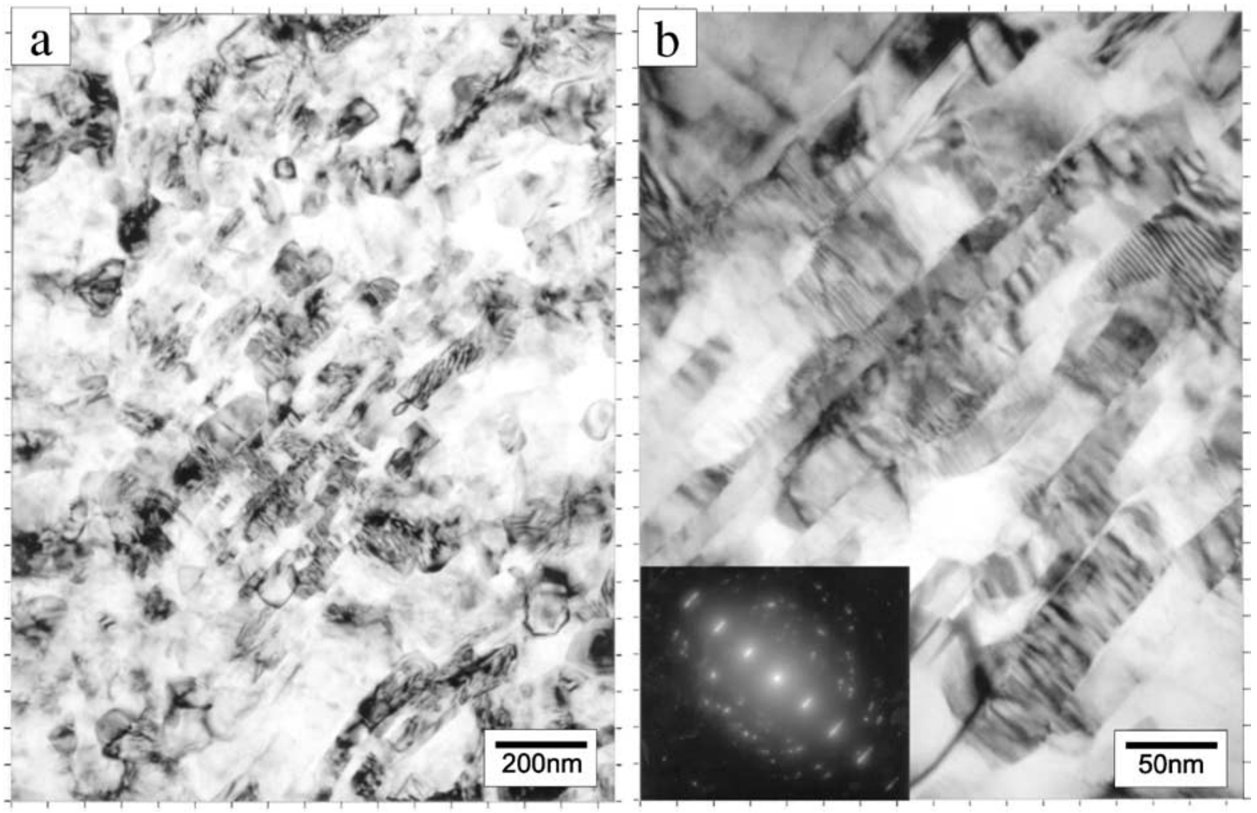

Figure 6 Transmission electron micrographs ((a) ×50000, (b) ×200000) of lamellar structure of polycrystalline diamond formed directly from graphite at 18 GPa and ∼2700°C for 600 s.

diffraction pattern of this structure indicates that each diamond particle orients in a random direction. Namely, the size and the orientation of the diamond particles are not dependent on those of the graphite starting material. This suggests that the diamond particles in this structure have been formed from graphite by the diffusion process accompanied by the breaking of atomic bonds and the reconstruction of the arrangement of the atoms.

The number of sides of each particle is less than six, suggesting that the growth force is relatively small, since the growth force is proportional to (N-6), where N is the number of sides on a particle [10]. Therefore, the particles remain the same size even for a long duration time. However, some particles with more than six sides indicating a high growth force are introduced in the structure as a result of certain local perturbation at a high temperature of 2700°C. They continue to grow, gaining more sides and growing more rapidly as exaggerated grain growth.

The lamellar structure seems to be formed by diamond layers. The electron diffraction patterns of this structure indicate that the diamond layers are stacked in a direction almost parallel to the $\langle 111 \rangle$ of cubic diamond. The diamond layers are not linear but are slightly bending, showing that the lamellar structure is not the micro-twin structure formed by slip deformations in a grain, which is often observed in conventional polycrystalline diamond compacts sintered with a metal binder [11, 12]. The bending diamond layers seem to reflect the original structure in the graphite starting material, which was deformed upon compression.

In the lamellar structure, a few hexagonal diamond crystals occasionally can be seen. The reciprocal relationship of the electron diffraction spots of hex-dia and c-dia (Fig. 4) suggests that the orientation of (100) hex-dia is parallel to the direction of the cubic diamond layer; (111) c-dia. This suggests that the cubic diamond of the lamellar structure has been formed from hexagonal diamond by a martensitic process. The martensitic process with the similar coaxial relationship has been observed in dynamic compression experiment [13]. The hexagonal diamond, which is well known to be formed from graphite martensitically with a directional relationship of (100)h-dia//(001)graphite [14, 15], is dominant at temperatures lower than 2000°C [9]. The lamellar structure in the present sample, therefore, seems to be formed through a two-step martensitic process. First, the graphite converts to the hexagonal diamond with a sliding and bucking process. The hexagonal diamond then converts to the cubic diamond. Namely, the starting material of graphite having a typical layer lattice structure converts to a layered structure of hexagonal diamond, which is secondarily converted to a layered cubic diamond observed in this study (Fig. 3). The mutual orientation of these phases should be (111)c-dia//(100)h-dia//(001)graphite. At a high temperature of ∼2700°C, the lamellar structure is segmentalized to form new grain boundaries with individual crystals oriented in the same direction (Fig. 6).

The graphite rod we used as the starting material has an isotropic texture, in which each hexagonal layered graphite particle of several micrometers orients in a random direction. When the graphite rod is compressed, each graphite particle is deformed in a different way because the direction of the maximum compression force on the graphite lattice differs from one particle to another. The differences of the maximum force direction on the graphite particle seem to create different conversion paths (diffusion and martensitic process) to cubic diamond, leading to the mixed texture of a homogeneous fine structure and a lamellar structure.

5. Conclusions

The microstructure of pure-polycrystalline diamond sintered bodies formed directly from graphite was investigated by using a high-resolution electron microscope. The following conclusions were derived.

(1) The polycrystalline diamond has a mixed texture of a homogeneous fine structure and a lamellar structure.

(2) The homogeneous fine structure consists of fine-grained diamond particles of several tens of nanometers across, which are randomly oriented. In the lamellar structure the bending diamond layers are stacked, which corresponds to deformed original layered of the graphite starting material.

(3) Diamond particles in the homogeneous fine structure are transformed from graphite in a diffusion process, while diamond layers in the lamellar structure are formed from graphite in the two-stage martensitic process via the hexagonal diamond phase.

(4) At a high temperature above 2600°C, an exaggerated or discontinuous grain growth occurs, and the lamellar structure is segmentalized to form new grain boundaries.

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