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Electron microscopic observation of diamond particles grown from the vapour phase

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Diamond particles prepared by chemical vapour deposition from a mixture of methane and hydrogen gases have been examined by electron microscopy. The particles were crystalline with a cubic structure. The typical habit was cubo-octahedron and twinned crystals, i.e. spinel-law twins and multiply-twinned particles, were also observed. Four cage compounds, i.e. bicyclo[2.2.2] octane, tetracyclo[$4.4.0.1^{3,9}.1^{4,8}$] dodecane, hexacyclo[$5.5.1.1^{2,6}.1^{8,12}.0^{3,11}.0^{5,9}$] pentadecane and dodecahedrane are proposed for embryos of twinned crystals.

1. Introduction

Diamond microcrystals with well-defined habits were prepared at pressures lower than 1 atm by Derjaguin and co-workers [1, 2] for the first time by the chemical transport method. Recently, we have also prepared diamond microcrystals by chemical vapour deposition (CVD) from a mixture of methane and hydrogen gases in an open-flow system [3, 4]. The structure of the deposit was identified by reflection electron diffraction [3, 4], Raman spectroscopy [3, 4] and transmission electron energy loss spectroscopy [5]. Scanning electron microscopy (SEM) revealed the crystals habits and the presence of multiple-twinned particles (MTP) [1–4]. The present paper reports the results of electron microscopic observation of the diamond particles obtained by CVD and four cage compounds are proposed for embryos of twinned crystals.

2. Experimental procedures

The apparatus and the method of preparation of diamond particles will be reported elsewhere [4]. Briefly, a mixture of methane (1 vol%) and hydrogen (99 vol%) was heated on non-diamond substrates such as silicon at a temperature of 700 to 1000° C and at a pressure of about 30 torr. Above the substrates, a tungsten filament was placed and heated above 2000° C. After the reaction of 0.5 to 1 h, the resulting deposits were coated with thin amorphous carbon film by vacuum evaporation, and the silicon substrate was dissolved away by hydrofluoric acid. The films supported by mesh sheets were observed by a 100 kV electron microscope (Hitachi H-500) or a 1000 kV electron microscope (Hitachi H-1250).

3. Results

The sizes of the particles were controlled by changing the reaction time. Even particles with a diameter as small as 100 nm had definite facets. The particles of several hundreds of nanometres in size were observed by TEM (transmission electron microscopy) to obtain distinctive diffraction patterns. The ratio of the surface are of $\{111\}$ to that of $\{100\}$ varied with the reaction temperature and methane concentration in the same manner as observed by SEM with larger crystals. The following figures were obtained with the samples prepared under 30 torr of total pressure and at 800° C.

Fig. 1 shows the electron micrograph and electron diffraction pattern of a single-crystalline particle; incident electron beam was parallel to $[110]$. Forbidden reflections 002 and $00\bar{2}$ are caused by double diffraction. Streaks along $\langle 111 \rangle$ in the diffraction pattern indicate the presence of some planar defects parallel to $\{111\}$ planes. Angles between edges in the image suggest that the crystal is surrounded by $\{111\}$ and $\{100\}$ planes.

Fig. 2 gives a typical spinel-law twin whose

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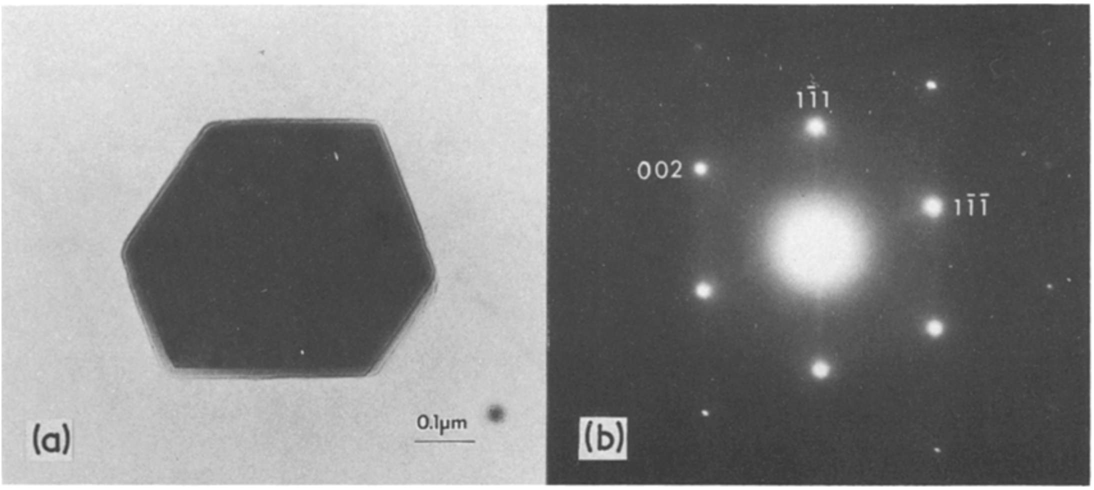

Figure 1 Electron micrograph (a) and diffraction pattern (b) of a single-crystalline particle with the (110) orientation.

[110] direction is parallel to the electron beam. Electron diffraction shows the presence of twinning and dark field images formed with each twin spot (Fig. 3) clearly indicate that the twin plane, $(1\bar{1}1)$ is parallel to the electron beam and divides the particle in two parts. As supposed from the angles between the edges, the particle is also characterized by {111} and {100}; the particle is composed of two half-cubo-octahedra. Further, the lower twin unit contains thin lamellar twins parallel to the $(1\bar{1}1)$ twin plane.

Fig. 4 shows a particle of pentagonal profile. The diffraction pattern and dark field images obtained by using some reflections indicate that this particle is twinned five-fold and is viewed along [110] directions of the twin units. In fcc metal particles, five-fold twinned crystals have the morphology of a pentagonal decahedron bounded by ten {111} faces [6, 7]. The nearly perfect five-fold symmetry of the diffraction pattern indicates that the misfit angle of 7° 20′ of five-fold twinning is nearly equally accommodated in the five twin units or in the five twin boundaries, as is the case for fcc metal particles [8].

In addition to the particles with nearly perfect five-fold symmetry, as shown by an arrow in Fig. 5a, particles with a gap along one of the twin boundaries were frequently observed. The two short edges which form the gap are supposed to be two $(1\bar{1}1)$ planes. The split angle of the diffraction spots marked in Fig. 5b is about 5° and

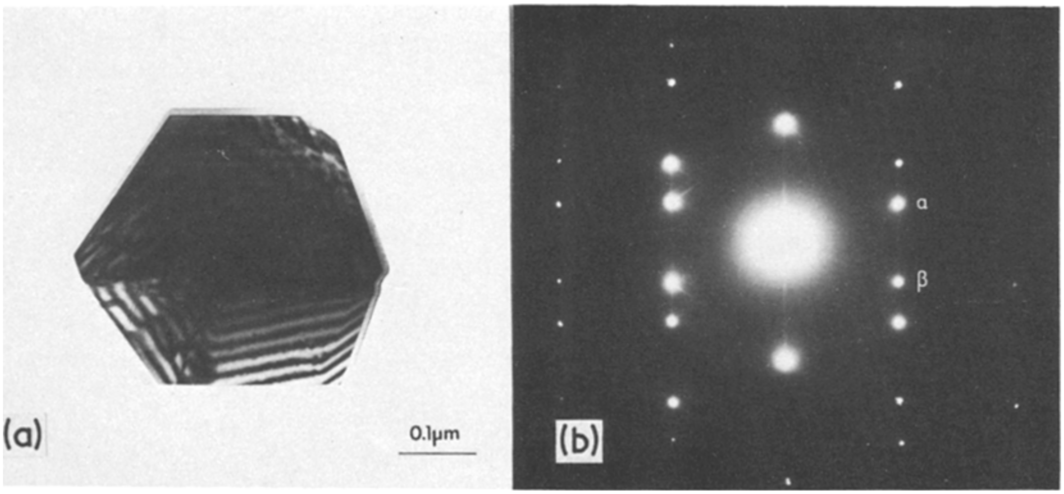

Figure 2 Electron micrograph (a) and diffraction pattern (b) of a spinel-law twin taken along the [110] direction.

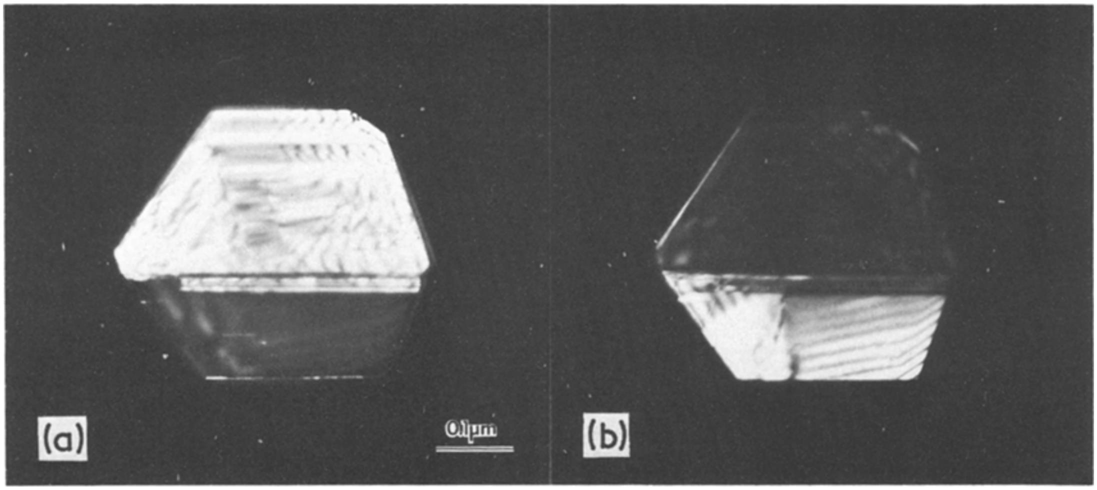

Figure 3 Dark field images formed by reflections in Fig. 2b. (a) Formed by α, (b) formed by β.

is smaller than 7° 20′; this finding suggests that the misfit is accommodated not only at the boundary with a gap but also at other twin boundaries or within twin units. Streaks in the diffraction pattern and dark lines running from the twin boundaries to the particles edges along {1 1 1} planes indicate that the particle in Fig. 5 contains stacking faults or thin lamellar twins. By considering the results of SEM observation, the slightly dark contrast at the lower edge of the particle are thought to be due to another twin grown on one of the five twin units.

Dark contrast near the edges of the particles in Figs. 4 and 5 suggest that, even at the edges, the particles have enough thickness. Another particle with five-fold twinning and a gap gave the electron micrograph shown in Fig. 6, when inclined from the pentagonal profile. This figure, together with SEM images of the corresponding particles indicates that the edges of these particles with a pentagonal profile are presumably truncated by (1 0 0) planes.

These two types of MTP of pentagonal profile with and without a gap have also been found in germanium particles, which have the diamond structure [9]. However, germanium particles are not bounded by {1 1 1} and {1 0 0} planes but by {1 1 1} and {3 1 1} planes. Star-shaped MTP's (5-fold twinned crystals) have also been found in natural and synthetic diamond (up to about 1 mm in size) [10–12]. In these macrocrystals, the misfit angle of 7° 20′ is predominantly located at one of the twin boundaries.

Fig. 7 shows that a MTP composed of 20 twin

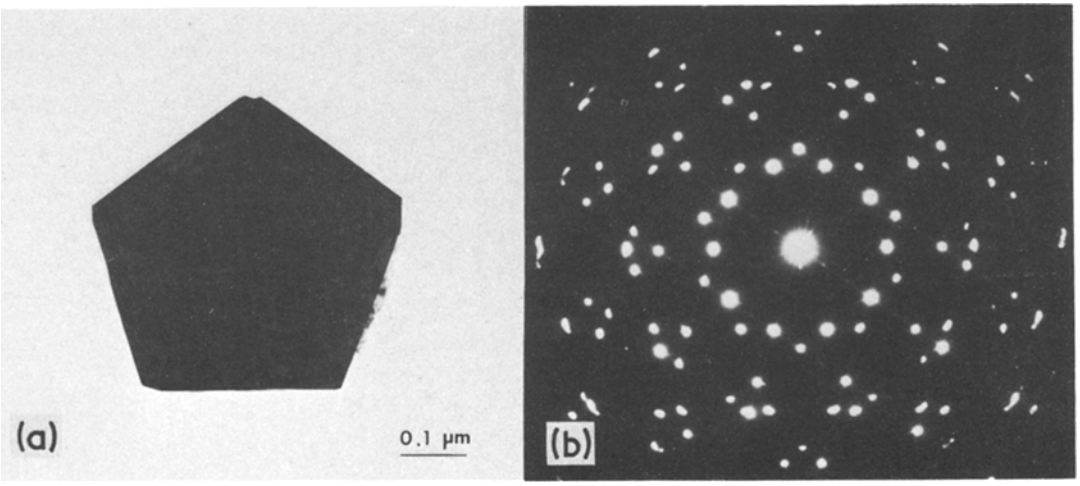

Figure 4 Electron micrograph (a) and diffraction pattern (b) of a 5-fold twinned particle taken along the [1 1 0] direction.

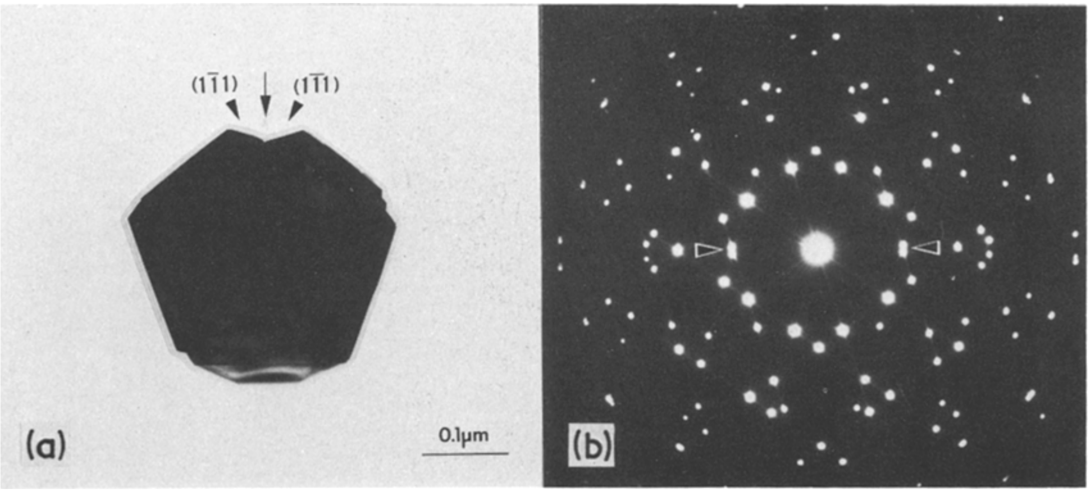

Figure 5 Five-fold twinned particle with a misfit along a twin boundary.

units is in the orientation of five-fold symmetry. This particle corresponds to an icosahedron bounded by twenty (1 1 1) planes which has been found in fcc metal particles [6, 7]. However, the bottom of the particle in Fig. 7 is truncated by the substrate surface. A schematic illustration of this image is given in Fig. 8. Images and diffraction patterns taken with inclination have confirmed that this particle is a MTP of 20-fold twinning. Although this particle has a gap along a twin boundary as shown by an arrow in Fig. 7, many particles with no gap have been found in SEM images.

4. Discussion

The present invesitgation has given evidence that the particles grown by CVD have the diamond structure and their habit planes are {1 1 1} and {1 0 0}. The difference of the reactivity and stability of the surface planes under high concentration of hydrogen seems to specify the morphology of the diamond grown by this method. The experiments of solid–gas interaction using various crystal planes of macrocrystalline diamond are desired.

The above results, together with SEM images, have proved the existence of twins composed of 2, 5 and 20 single crystal units. Fig. 9 is an example of a SEM image for particles larger than those shown in Figs. 1 to 7. Figs. 10a to d summarize the basic morphologies of deposited particles; they are drawn ideally as symmetrical forms. These four will hereafter be called cubo-octahedron, twinned cubo-octahedron, decahedral-Wulff-polyhedron(D-Wulff-polyhedron) and icosahedron, respectively.

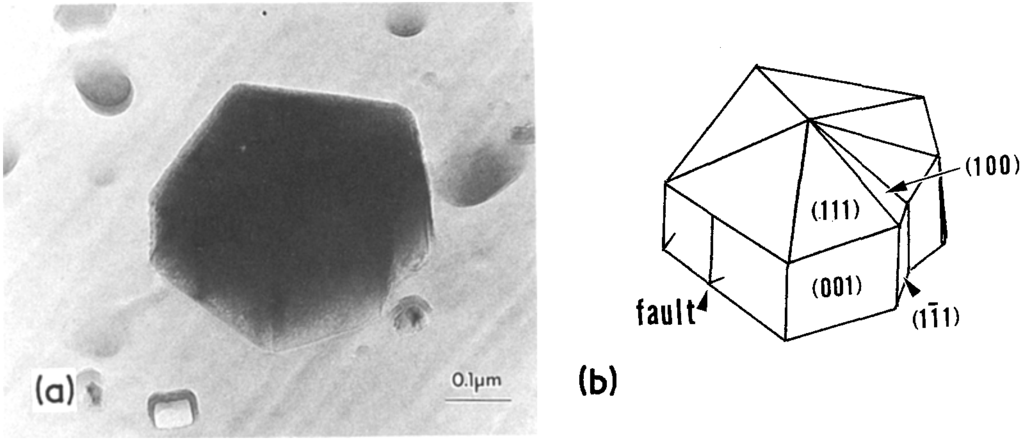

Figure 6 (a) Electron micrograph of a 5-fold twinned particle with a misfit taken with inclination from pentagonal profile and (b) its schematic illustration.

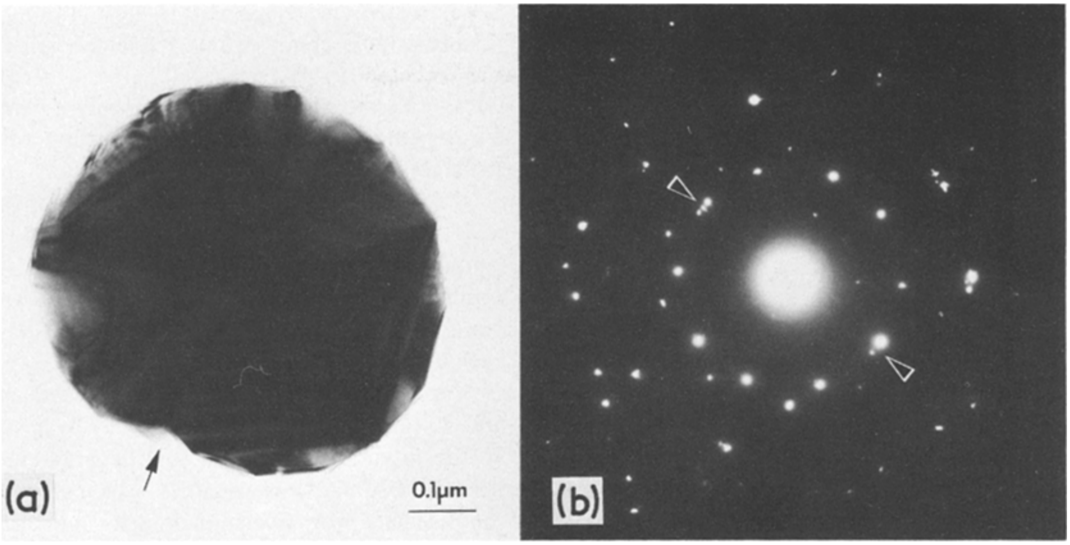

Figure 7 Twenty-fold twinned particle with the orientation of 5-fold symmetry.

The high symmetry of the deposited particles suggests that the above twins are formed at the stage of their nucleation [2], though the twins formed on the growing surfaces are frequently found in the larger crystals. MTP's have been found when the interaction between deposit and substrate is weak (vacuum deposition of fcc metals on alkali halides [6, 7]) or when the particles grow in the gas phase (growth of fcc metals [13] or germanium [9] in argon gas). Since the interaction between the carbon atom and the silicon of the substrate is thought to be strong, the diamond probably nucleates in the gas phase or the nuclei are probably hydrocarbons which have weak interactions with the silicon surface before degradation of the carbon–hydrogen bonds. Saturated hydrocarbons are believed to be stable in comparison with unsaturated or aromatic ones under the present vapour growth conditions: high concentrations of hydrocarbon radicals and atomic hydrogen are supposed to be present and react with the unsaturated carbon atoms. The precursors of diamond nuclei are probably cage compounds of carbon and hydrogen atoms.

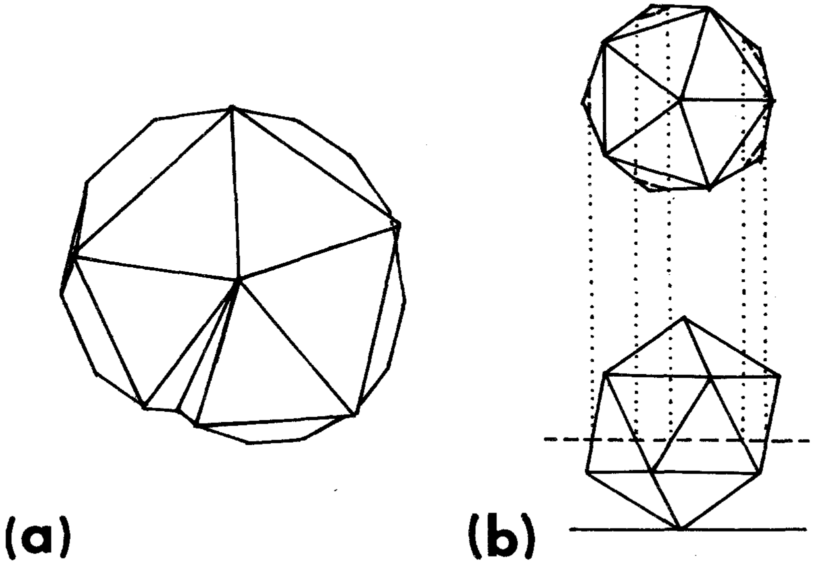

Figure 8 (a) Schematic illustration of Fig. 7a. (b) Top and side views of a truncated icosahedron.

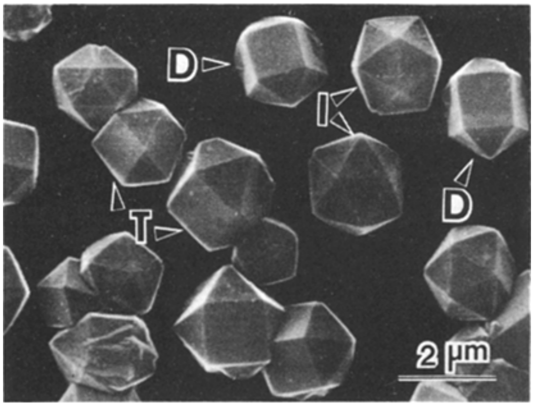

Figure 9 Twins in diamond particles (SEM images). T: twinned cubo-octahedron, D: decahedral-Wulff-polyhedron, I: icosahedron.

As is well known, the smallest compound that has the skeleton of the diamond structure is adamantane (Fig. 10a′, I). A detailed study of the morphologies of the deposited particles suggests that the primitive compounds of twinned cubo-octahedron, D-Wulff-polyhedron and icosahedron are probably bicyclo[2.2.2]octane (Fig. 10b′, II a) or tetracyclo[$4.4.0.1^{3,9}.1^{4,8}$]dodecane (Fig. 10b″, II b), hexacyclo[$5.5.1.1^{2,6}.1^{8,12}.0^{3,11}.0^{5,9}$]pentadecane (Fig. 10c′, III) and dodecahedrane (Fig. 10d′, IV), respectively. In alicyclic hydrocarbons, 5- to 7-membered rings are the most stable [14]. Adamantane is composed of a 6-membered rings and believed to be strain-free. The other four (II to IV) are also composed of only 5- and/or 6-membered rings. Careful consideration of the structures of the above cage compounds leads to the idea that they can be stable compounds with little strain and distortion, though the isolation or synthesis of the last three of these compounds has not been reported to the best of our knowledge. Bicyclo[2.2.2]octane (II a) has been obtained as a stable compound [15].

Since adamantane is not stable above about 500° C [16], compounds II to IV may be unstable at the growth temperature for diamond, i.e. at 600 to 1000° C. However, these cage compounds can probably grow to diamond nuclei under supersaturation of hydrocarbon radicals and atomic hydrogen; they will be hereafter referred to as "embryos".

These embryos already have structures which lead to the formation of the twins described above during growth with the diamond structure. Growth with the cubic diamond structure is most probable because skewed conformation in C–C bond is most stable [14]. Fig. 11 illustrates a model of a small D-Wulff-polyhedron grown from compound III. Carbon–carbon bonds with normal sp^3 struc-

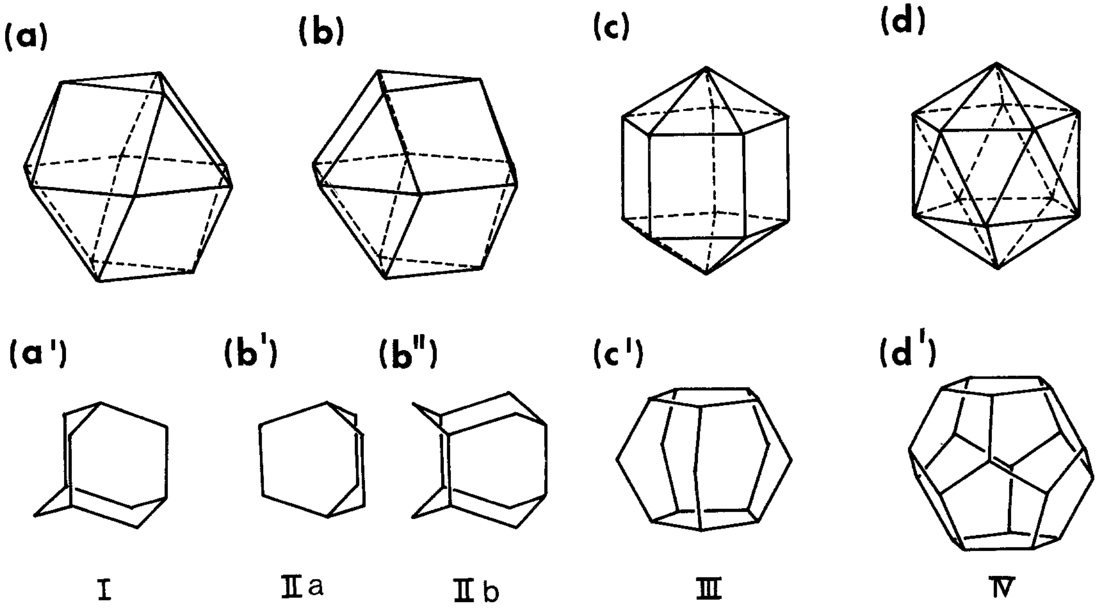

Figure 10 The correspondence between twinned diamond particles and cage compounds. (a) cubo-octahedron (a single crystal), (b) twinned cubo-octahedron, (c) decahedral-Wulff-polyhedron, (d) icosahedron, (a′) adamantane, (b′) bicyclo[2.2.2]octane, (b″) tetracyclo[$4.4.0.1^{3,9}.1^{4,8}$]dodecane, (c′) hexacyclo[$5.5.1.1^{2,6}.1^{8,12}.0^{3,11}.0^{5,9}$]pentadecane, (d′) dodecahedrane. In cage compounds only carbon skeletons are shown.

TABLE I Relations between the cage compounds and diamond particles with various morphologies

Cage compound	Symmetry	N_{ca}*		N_{mp}†	Diamond particle	Symmetry	N_{cp}‡		N_{tp}§	N_{scu}¶
		$-CH_2-$	$\geqslant CH$				(100)	(111)		
I $C_{10}H_{16}$ (Adamantane)	T_d	6	4	0	Cubo-octahedron	O_h	6	8	0	1
II a C_8H_{14}	D_{3h}	6	2	1	Twinned cubo-octahedron	D_{3h}	6	8	1	2
II b $C_{12}H_{18}$	D_{3h}	6	6	1						
III $C_{15}H_{20}$	D_{5h}	5	10	5	D-Wulff-polyhedron	D_{5h}	5	10	5	5
IV $C_{20}H_{20}$ (Dodecahedrane)	I_h	0	20	30/2	Icosahedron	I_h	0	20	30/2	20

*N_{ca}: numbers of carbon atoms.

†N_{mp}: numbers of mirror planes between two carbon atoms bonded each other.

‡N_{cp}: numbers of crystal planes.

§N_{tp}: numbers of twin planes.

¶N_{scu}: numbers of single crystal units.

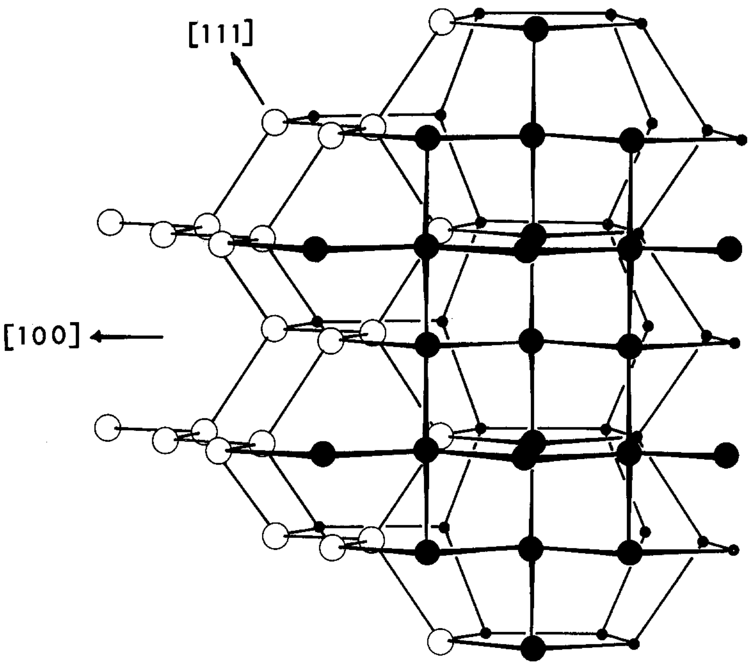

Figure 11 A model of set-up of decahedral-Wulff-polyhedron from compound III. Only two of the single crystal units (white and large black circles) are shown. A twin plane intersects the C–C bonds between the two single crystal units.

ture can be formed with little distortion between two single crystal units. A twin plane perpendicularly bisects the C–C bonds with an eclipsed conformation. These embryos have several methylene and methine groups. The direction of the bisector of the two C–H bonds in a methylene group is [100], and the direction of a C–H bond in a methine group [1 1 1]. Table I shows close relations between the embryos and grown particles with various twins.

As the diamond grows from these embryos, through the nuclei, into crystals, lattice distortion seems to accumulate in the MTP's, because the misfit angle of 7° 20′ between the twin units is incorporated in the C–C bonds. From the results of electron microscopic observations, it is thought that in MTP's of gold this misfit is accommodated by the elastic deformation of each twin and the particles have high stresses towards the centre [17]. Owing to this stress, MTP's of gold above about 400 nm in size transform into the normal fcc structure.

As shown above, both types of MTP, i.e. with and without a gap along the twin boundary have been found in the diamond particles. Even the latter type particle can grow up to 5 μm or above. Growth of MTP up to such a large size seems to be kept by the firmness of C–C bonds in diamond. In this case, the misfit angle may be accommodated not only by elastic deformation but also by defects such as the introduction of dislocations. In addition, these particles do not have a symmetrical form due to the truncation by the substrate. In such particles, the accommodation of stress is considered to be less than in ideally symmetrical particles, if the interaction between the particle and the substrate can be neglected.

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