

Synthesis of prismatic and tabular diamond crystals

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SUMMARY. When diamond is synthesized at conditions of comparatively high temperature and pressure, the nucleation rate is high, as is the growth rate of the nuclei. Consequently the product is usually an aggregate of crystals with dendritic or skeletal structure. In this study the presence of gold or silver as an additive mixed with a catalyst was found to have the effect of suppressing nucleation. When a homogeneous mixture of graphite, catalyst, and additive was treated at conditions where skeletons and dendrites were produced in the absence of additive, euhedral crystals of octahedra were formed. When a special cell assemblage for high pressure experiments, in which the graphite was placed inside a cylinder of catalyst coated with additive, was used, prismatic and tabular crystals were synthesized.

SINGLE crystals of diamond commonly occurring in nature are octahedral, dodecahedral, or cubic in shape, but those with prismatic or tabular morphology have been rarely found (Orlov, 1977). In the laboratory, octahedral, dodecahedral, and cubic crystals are also formed when synthesis is attempted in the diamond-stable region close to the thermodynamic equilibrium between graphite and diamond (Berman and Simon, 1955). If the conditions are far from the equilibrium, the initial rate of nucleation is promoted and the growth rate of these nuclei is accelerated. Consequently the crystals produced are usually dendrites or skeletal structures (Bovenkerk, 1961).

Experimental

A cubic anvil-type device was used for the synthesis experiments (Osugi *et al.*, 1964). Pressures applied to samples were calibrated by the abrupt change of electric conductivities of Bi (2.5 and

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7.7 GPa) and Ba (5.5 GPa). Temperatures were measured by a thermocouple of (Pt/Rh 40·Pt/Rh 20) inserted in the sample but its emf was not corrected for compression, the accuracy in temperature and pressure being ± 30 °C and ± 0.5 GPa² at 1500 °C and 7 GPa.

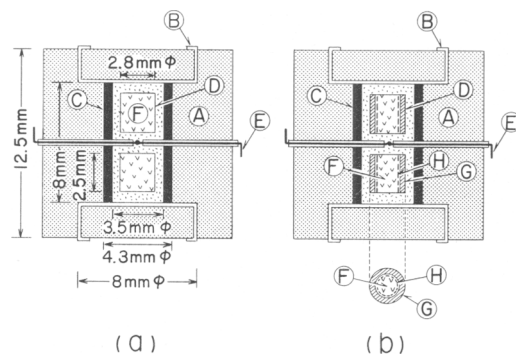


FIG. 1. Cell assemblages for synthesis experiments. (a) Type-1 cell. A, pyrophyllite; B, electrode (Mo metal); C, carbon heater; D, BN sleeve; E, thermocouple; F, starting material (mixed powder of graphite, catalyst, and additive). (b) Type-2 cell. A-E, as in (a); F, starting material (graphite); G, catalyst (Ni-Cr alloy of cylindrical shape); H, additive plated on the inner surface of catalyst.

Two kinds of cell assemblage were used (fig. 1a, b). The starting material charged in the Type-1 cell was composed of mixed powders of graphite, catalyst, and an additive. Graphite was prepared by pulverizing a spectroscopic electrode whose purity was 99.999%. The catalyst was a mixed powder of Ni and Cr metals and the additive was Au or Ag. The mixing ratio of graphite and the catalyst is

² 1 GPa = 10 kbar.

shown in Table I. The experimental conditions were in the range of temperatures between 1600 °C and 2000 °C at 7.0 GPa for 5 min. The sample was rapidly cooled to room temperature and ordinary pressure.

TABLE I. Compositions of starting materials for Type-1 cell assemblage (wt %)

Sample No.	C	Ni	Cr	Au	Ag
1	50	40	10	—	—
2	50	32	8	10	—
3	50	40	9	1	—
4	50	32	8	—	10
5	50	40	9	—	1

The starting material for the Type-2 cell was graphite alone. The catalyst of Ni-Cr alloy was a tube with a wall thickness of 0.06 mm. The tube was inserted inside a carbon heater separated by a BN sleeve. The additive was plated on the inner surface of the catalyst and was about 2000 Å thick. Each sample was maintained at one of the conditions shown in Table II for 5 min and rapidly cooled to room temperature and ordinary pressure.

TABLE II. Conditions of synthesis

Run	Temperature (°C)	Pressure (GPa)
1	1500	6.0
2	1500	6.5
3	1500	7.0
4	1600	6.5
5	1600	7.0
6	1700	7.0
7	1700	7.5
8	1800	7.0

After the syntheses were completed all the products were boiled in mixed acid and then in aqua regia to remove unreacted graphite and metals respectively. The samples obtained in this way were investigated by polarized light and interference contrast microscopes, a scanning electron microscope, and precession and Weissenberg cameras.

Results and discussion

Nucleation observed in Type-1 cell. Numbers of nuclei generated in the Type-1 cell were counted under the microscope. The results are summarized in fig. 2. When starting material No. 1 (Table I) was

used, the nucleation rate was high, even at temperatures higher than 1900 °C where supercooling was slight and the number of nuclei was expected to be small. When an additive was used (sample Nos. 2-5), the number of nuclei decreased, Au having greater effect than Ag. As seen in fig. 2, 1 wt % of Au was equivalent to 10 wt % of Ag in suppressing nucleation at temperatures around 1800 °C at 7 GPa. Skeletons and dendrites were produced in sample No. 1 treated at these conditions, but when the additive was used the skeletons and dendrites disappeared and euhedral octahedra were produced.

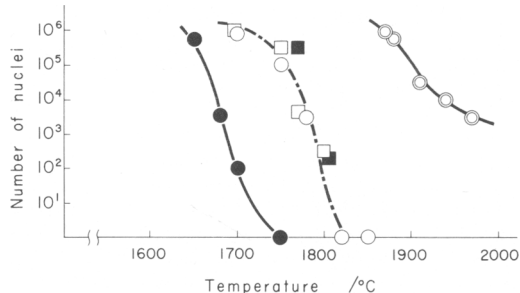
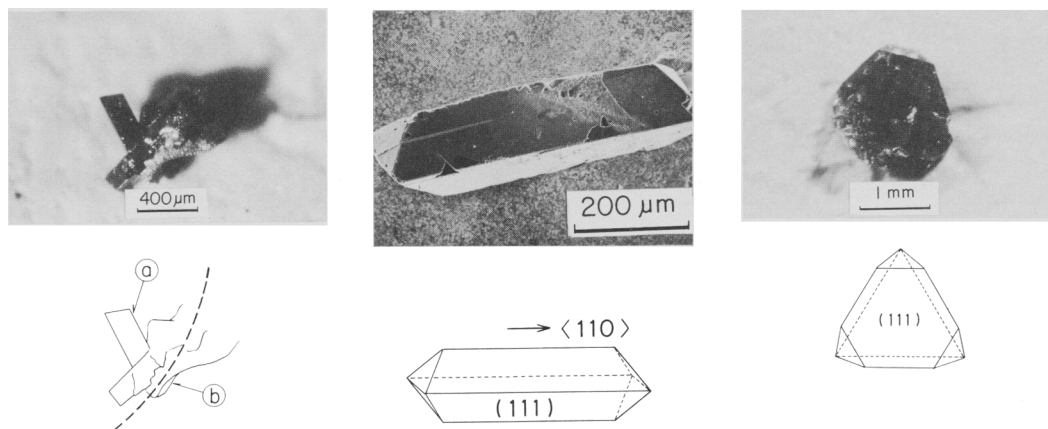


FIG. 2. Relation between temperature of heat treatment and number of nuclei generated at the initial stage of synthesis. Numbers were counted in unit volume (cm³). Pressure, 7 GPa; reaction period, 5 min. ● Starting material No. 1 (Table I). ○ Starting material No. 2. ○ Starting material No. 3. ■ Starting material No. 4. □ Starting material No. 5.

Crystals produced in Type-2 cell. When the syntheses were undertaken at conditions of (1) to (5) and (7) of Table II, octahedral and cubo-octahedral crystals and clusters of these crystals were formed. When the conditions were at (6) and (8), prismatic and tabular crystals were found in an aggregate of small crystals, as seen in fig. 3. Typical examples of individual crystals are shown in figs. 4 and 5. The maximum length of one edge of these crystals is about 1 mm. The ratio of length to width of the prismatic crystals was between 2 and 5. The morphology indicated that all the surface planes were {111} and therefore the axis of elongation of the needles was <110>. Observations by an interference contrast microscope showed that the surfaces of the crystals were smooth and no trace of hopped surface, which is usually found on the skeletal structures, was observed.

The results of X-ray diffractions agreed with those of optical observations. Precession photographs indicated that the long axis of the needles was <110>, and all the diffraction data in Weissenberg photographs may be indexed as a single crystal of diamond.



FIGS. 3-5. FIG. 3 (left): Photomicrograph of product synthesized at 1700 °C and 7 GPa, using the Type-2 cell, showing a prismatic crystal (a) grown on the inner surface of catalyst (b). It is seen that the prism is elongated towards the centre of the cell. FIG. 4 (centre): Scanning electron micrograph of prismatic crystal. FIG. 5 (right): Photomicrograph of tabular crystal.

Twins, which were characterized by a re-entrant angle, were sometimes found as shown in fig. 6. Weissenberg photographs of these twins always had extra diffractions which were located at the positions of mirror symmetry about the $[111]^*$ axis, rendering them easily distinguishable from single crystals.

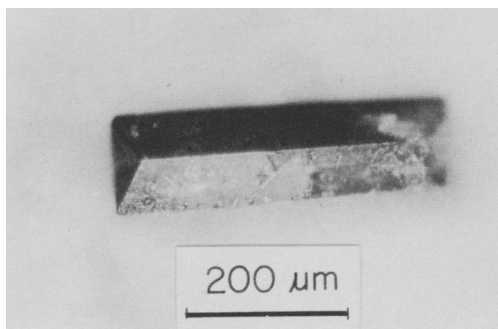


FIG. 6. Twinned prismatic crystal.

The long axes of the prismatic crystals lay parallel to the radius of the catalyst cylinder and the crystals were elongated towards the centre of the cell (fig. 3).

Conclusions

- (1) An additive mixed with graphite and catalyst has the effect of suppressing the nucleation of diamond at comparatively high temperature and pressure.
- (2) Prismatic and tabular crystals only grow in the Type-2 cell but not in the Type-1. The axis of growth of prismatic crystals is towards the centre of the cell. This indicates that a chemical gradient is necessary for uniaxial growth of diamond. The homogeneous mixture of graphite, catalyst, and additive in the Type-1 cell produces euhedral crystals which grow equally in all equivalent directions (e.g. octahedra). It is considered that in order to form an elongated crystal it is necessary to suppress the initial nucleation and to supply material from one direction.

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