Preparation and characterization of ultra-fine diamond powders obtained by using a d.c. arc plasma jet

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Ultra-fine diamond powders were prepared from C_2H_2 and H_2 by quenching a d.c arc plasma jet on a metal disc cooled with water. The powders obtained were agglomerated with very small particles about 20 nm in diameter, with an average size of about 80 nm. Raman spectra, X-ray diffraction, and transmission electron micrographs of them showed that each particle consisted of very small diamond crystals and a small amount of amorphous carbon, and that a single crystal particle had a twin plane. The formation mechanism of the powders has been briefly discussed from the viewpoint of the supersaturation ratio based on the classical theory of homogeneous nucleation.

1. Introduction

Since Eversole [1], Angus *et al.* [2], and Deryagin and Fedoseev [3, 4] considered the possibility of diamond synthesis at a pressure lower than 760 torr (1 torr = 133.322 Pa), diamond films and powders have been prepared by various methods such as a thermal filament [5], microwave plasma [6], r.f plasma [7], and others [8, 9]. Recently, we found a simple method to prepare ultra-fine diamond powders of a smaller size than 300 nm by using a d.c. arc plasma jet [10]. However, their formation mechanism is so complicated that it has not yet been analysed. Thus, in order to obtain information to understand it, an attempt has been made to observe their microstructure mainly with a transmission microscope (TEM). Through the resultant microstructural features, we have attempted to illustrate schematically the formation mechanism of the ultra-fine powders. The preparation method and the microstructure of the powders described, and their formation mechanism is briefly discussed.

2. Experimental procedure

One of the most commonly used plasma-generating devices is a d.c. arc plasma torch. It produces a very high temperature plasma, into which we can introduce reactant gases, such as hydrocarbon and hydrogen, for preparing chemical species with very high energy. The maximum temperature of the plasma is very high, of the order of 15 000 K, and the velocity of the plasma flame is as high as 300 m s^{-1}. Therefore, if the tail flame is quenched with a metal substrate cooled with water, a very high supersaturation can be achieved, which is very effective for rapid nucleation from the chemical species in the plasma.

Fig. 1 shows a schematic illustration of the preparation of ultra-fine diamond powders by using a d.c. arc plasma jet. A d.c. arc plasma was operated under the conditions of a d.c. voltage of 25 V and a d.c. current of 340 A by using argon gas. Reactant gas C_2H_2 was injected into the plasma with a carrier gas, argon, through two orifices in the anode. A sheath gas of H_2 was injected tangentially along the inner wall of the reaction chamber which was maintained at 50–200 torr. The plasma flame containing various chemical species such as C_2H, C_2H_2, CH_3, CH, H, H_2, etc., which partially dissociated in the plasma from the reactant gases of C_2H_2 and H_2, was rapidly quenched on the quenching disc cooled with water. The resulting nucleated materials were transported towards the inner wall of a silica tube around the quenching disc, on which ultra-fine diamond powders were finally deposited. The powders obtained were characterized by X-ray diffraction, laser Raman spectroscopy, scanning electron microscopy, and mainly with detailed TEM. Table I shows the typical experimental conditions required to synthesize the ultra-fine diamond powders.

3. Results and discussion

The d.c. arc plasma was operated for 1 hour to prepare diamond powders under the conditions mentioned above. The powders deposited on the inner wall of a silica tube were always found to be recognized as diamond powders containing a small amount of amorphous carbon as mentioned later. On the other hand, the materials deposited on the copper quenching disc were identified as three kinds of materials, such as an organic material, a diamond-like carbon, and a diamond, depending on the experimental conditions. Raman spectroscopy indicated that the
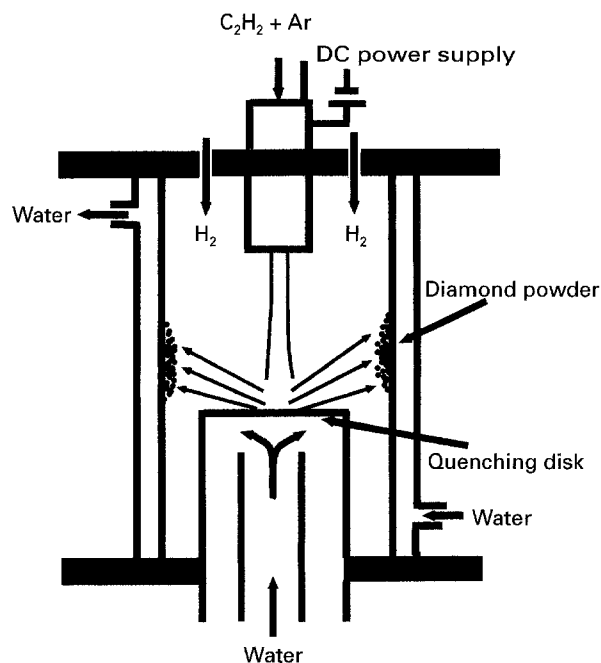
Figure 1 A schematic illustration to prepare ultra-fine diamond powders by using a DC arc plasma jet.

TABLE I Typical experimental conditions for the preparation of diamond powder

D. c. power supply	8.5 KW
Flow rate: plasma gas, argon	$20\,l\,min^{-1}$
sheath gas, hydrogen	$4\,l\,min^{-1}$
C_2H_2 gas	$0.4\,l\,min^{-1}$
carrier gas, argon	$4\,l\,min^{-1}$
Reaction pressure	50–200 torr

products deposited on the inner wall were diamond powders containing a small amount of amorphous carbon, irrespective of the materials deposited on the quenching disc used.

A sharp peak at $1333\,cm^{-1}$ corresponds to diamond and a broad peak around $1540\,cm^{-1}$ to an amorphous carbon, as shown in Fig. 2. That is, the diamond powders obtained consist of diamond and amorphous carbon. Fig. 3 shows electron diffraction rings of the powders which indicate the typical (1 1 1), (2 2 0), and (3 1 1) diffraction, of diamond. However, graphite was not detected by electron diffraction, possibly because it was present in too small a quantity. The diffused rings in the figure may show that diamond particles consist of very small crystals. X-ray diffraction also shows (1 1 1), and (2 2 0) peaks corresponding to the lattice spacings of 0.206 nm and 0.107 nm. The particle size of diamond measured by SEM was less than 300 nm. The conversion yields from the reactant gas of C_2H_2 to diamond powders was very low, about 1%.

Fig. 4 shows a transmission electron micrograph of diamond powders, with an almost spherical particle shape. Their particle size is 20–300 nm, although many particles seem to be agglomerated with small ones. The average size of the particles is about 80 nm. Fig. 5 shows a dark-field image of the powders. The image was obtained by using a diffracted beam, so its contrast is reverse compared to a conventional bright-
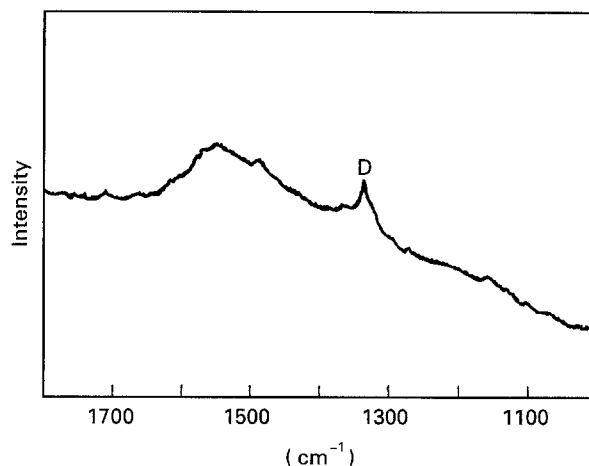

Figure 2 A Raman spectrum of ultra-fine diamond powders. The sharp peak at $1333\,cm^{-1}$ is due to diamond, and the broad peak about $1540\,cm^{-1}$ is due to amorphous carbon.
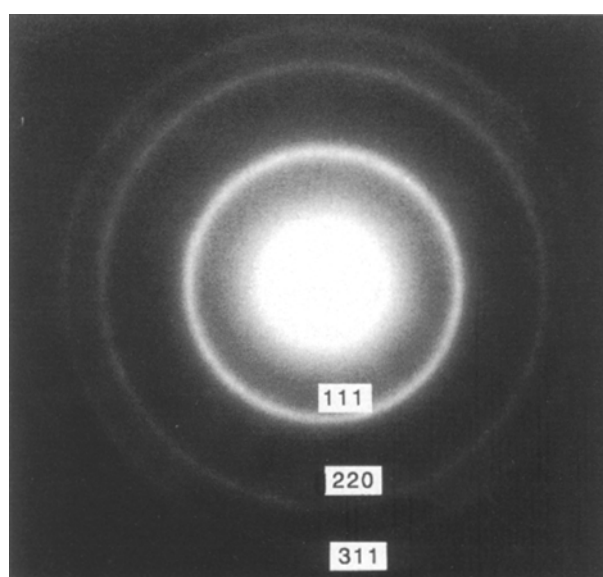

Figure 3 Electron diffraction pattern of ultra-fine diamond powders.
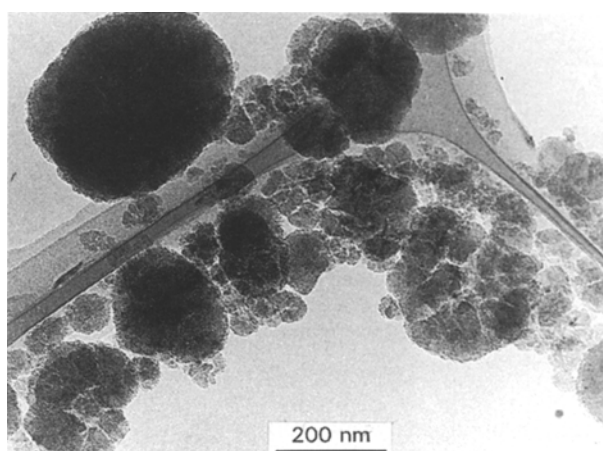

Figure 4 Transmission electron micrograph of ultra-fine diamond powders.

field image. The white contrast in the particle indicating diamond crystals, is from crystals smaller than 10 nm, that is, a particle consists of very small diamond crystals and graphite. As can be seen in Fig. 5b, there is radial contrast, as indicated by arrows, from
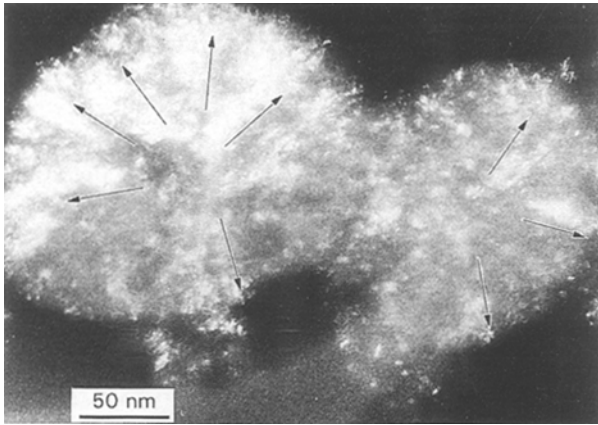
Figure 5 Dark-field image of ultra-fine diamond powders.

Figure 7 A high-resolution transmission electron micrograph of a particle in which a twin plane with zigzag contrast can be seen.
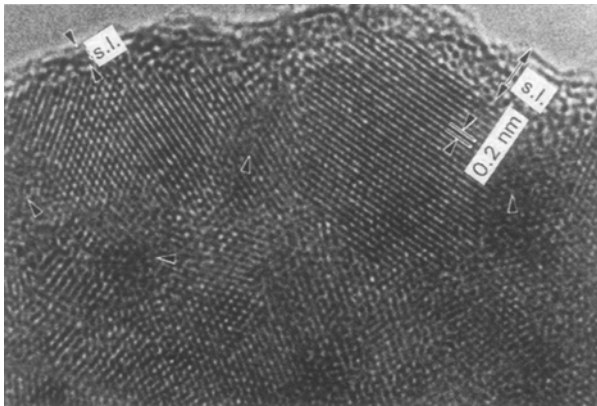

Figure 6 Transmission electron micrograph of ultra-fine diamond powder observed at high magnification. Arrows indicate amorphous carbon layers in the powder; s.l., surface layer.

Figure 8 An optical transformation from the negative film of Fig. 7, showing a typical net pattern of (1 1 0) in a diamond twin. A and B indicate two grains, as shown in Fig. 7.

inside the particles to outside; such radial growth is considered to take place when supersaturation is very high, continuously on one nucleation site which has just been generated. Fig. 6 shows the lattice fringes of 0.206 nm between neighbouring {1 1 1} planes in a particle. As indicated by arrows, the surface layer of the particle and a boundary between two diamond crystals in the particle, have no fringes, due to the existence of amorphous carbon. This is additional evidence that both diamond crystals and amorphous carbon are present in a particle, which agrees with the Raman spectroscopy results. The surface layer of amorphous carbon is estimated to be 1–2 nm thick.

The diamond particles obtained here are generally polycrystals. However, although rare, some smaller particles of diameter less than 40 nm are considered to be single crystals. They are angular in shape. Their electron diffraction pattern was consistent with that of diamond, and was spotty compared with that from polycrystalline particles. In some particles of single crystals, a strange contrast was seen, suggesting the presence of a kind of lattice imperfection. Attempts were made to observe this at high magnification. Fig. 7 shows a transmission electron micrograph of a single crystal of diamond observed at high magnification, in which a zigzag contrast is seen, indicating a lattice imperfection something like a twin plane, TP.
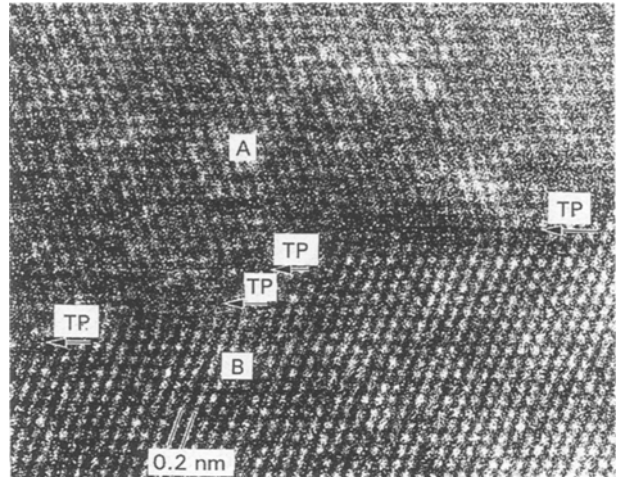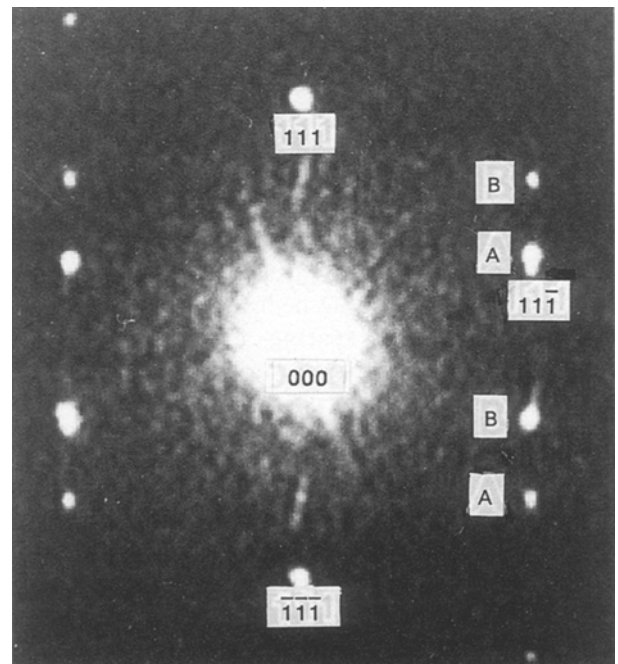
An optical transformation was therefore carried out from the negative film of the micrograph. As a result, the diffraction pattern obtained showed a typical net pattern of (1 1 0) in a diamond twin, as shown in Fig. 8. That is, the zigzag contrast in Fig. 7 indicates the existence of a twin plane. A 180° rotation of the crystal about the [1 1 1] twin axis results in a twinned crystal position; in other words, both these crystals in Fig. 7 are simply mirrored across the (1 1 1) plane. The lattice image as shown in Fig. 7 is not necessarily clear, but we can distinguish a lattice fringe between neighbouring {1 1 1} planes. The spacing between two parallel twin planes is 0.612 nm, and corresponds to three atomic layers of ABC stacking of a diamond along a [1 1 1] direction.

Fig. 9 shows a schematic diagram of the zigzag twin planes. All the twin planes are Σ3, that is, every third
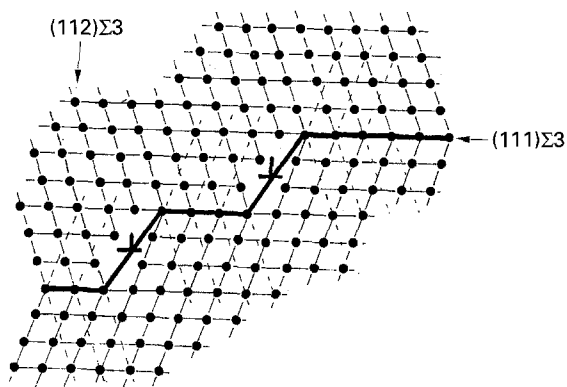
Figure 9 A schematic diagram of a zigzag twin plane.

site is in coincidence. It is interesting that there are relatively large voids at the boundary where a twin plane travels to another twin plane. The lattice spacing of the boundary between parallel twin planes corresponds to three atomic layers of ABC stacking along the [1 1 1] direction as mentioned before. However, the lattice spacing between two parallel twin planes was not found to correspond to one or two atomic layers. This may indicate that these layers between parallel twin planes are unstable in comparison with three atomic layers. In the case of one or two atomic layers, the neighbouring lattice spacing between two parallel twin planes is short compared with that in the three atomic layers observed. Therefore, their strain energy should be higher than in the three layers. As a result, the spacing of the twin planes may be unstable. In other words, three atomic layers between two parallel twin planes are stable. From the view point of periodicity of the lattice, $6, 9, 12, \ldots$, layers, which is the integer times three atomic layers, would also be stable; on the contrary, all the other layers are unstable because of fundamentally the same structure as one and two atomic layers.

According to the classical theory of homogeneous nucleation, the nucleation radius from supersaturated vapour is expressed as

$$R_n = 2\gamma/DRT \ln P/P_o \qquad (1)$$

where γ is the surface energy of spherical solid, D is the density, P is the actual vapour pressure, P_0 is equilibrium vapour pressure, and the supersaturation ratio, S, is defined as

$$S = P/P_o \qquad (2)$$

Because the supersaturation ratio is in the exponential term of Equation 1, the rate of nucleation is sensitive to the degree of supersaturation.

In the case of our experimental data, the plasma temperature decreases very rapidly on the quenching disc; for instance, the temperature decreases from 5000 K at 1 cm above the quenching disc to 1000 K on the quenching disc. As a result, the equilibrium vapour pressure rapidly decreases with temperature, which results in very high supersaturation. Therefore, it has been assumed that the nucleation rate of diamonds from reactant chemical species in the plasma is estimated to be very fast and nucleation would occur instantaneously, because the increasing supersaturation ratio with decreasing plasma temperature is expected dramatically to enhance the nucleation of diamond. The velocity of a d.c. arc plasma is about 300 m s^{-1}. At this velocity, the time to pass through 1 cm in the vicinity of the quenching disc is estimated to be very short, about 3×10^{-5} s; within such a short time the nucleation of diamond crystals is concluded to take place. The nucleated diamond crystals which result would agglomerate to large particles, like the sintering of fine powders, or by Brownian movement during their transportation in the stream of the plasma flame from the quenching disc to the inner wall of the silica tube.

In summary, as a mechanism of the powder formation, it is speculated that diamond crystals are nucleated from the chemical species in the plasma flame on the quenching disc and they are then agglomerated to large particles by a process like sintering, or by Brownian movement during their transportation in the stream of the plasma from the disc to the inner wall of the silica tube, where the ultra-fine powders are deposited.

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