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Studies on synthesis and growth mechanism of high quality sheet cubic diamond crystals under high pressure and high temperature conditions

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ABSTRACT

This paper reported the synthesis of high quality sheet cubic diamond crystals by temperature gradient method under high pressure and high temperature conditions with FeNi alloy as solvent catalyst. The growth mechanisms were discussed by finite element simulation. The synthetic sheet cubic diamond crystals had a higher growth rate in radial direction than that in axial direction. Raman spectrum and Fourier transform infrared spectrum indicated that synthesized sheet cubic diamonds had fewer crystal lattice distortions and nitrogen impurities. Finite element simulations indicated that the solvent metal convection field in the radial direction was stronger than that in the axial direction. A mechanism of sheet cubic diamond crystal growth was proposed and discussed.

Introduction

Diamond, as one of the superhard materials, is of great importance in science and technology with applications in cutting and polishing tools, coatings and abrasives, etc. Since the diamond crystals were synthesized in the 1950s [1], many progresses on diamond synthesis and research have been achieved. Two widely used methods are high pressure and high temperature (HPHT) and chemical vapor deposition (CVD) [2–7]. If some transition metals like Fe, Ni, Co, Mn, and their alloy are used as solvent catalyst, typical growth conditions for diamond synthesis are pressures in the range of 5.0–8.0 GPa and temperatures in the range of 1300–1800 °C [8–11]. Among many synthetic methods, the temperature gradient method (TGM) under high pressure and high temperature conditions to synthesize high quality large diamond crystals has been used for several decades and is one of the effective ways for scientific research and commercial production.

As we all know, natural diamond crystals are mainly composed by (111) and (110) crystal faces, almost no (100) crystal faces. Therefore, cubic diamond crystals composed of (100) crystal faces only can be obtained by synthesis. Generally, in the P-T phase diagram of carbon, the district for diamond growth is a V-shape region bounded by diamond-graphite equilibrium line and solvent-carbon eutectic melting line in the metal solvent-carbon system [12]. In the region, the shape of diamond crystal is mainly affected by synthetic temperature. Because of different crystal shapes, diamond crystals have many different applications. For example, tower shape diamond crystals with (111) crystal faces can be used as the anvil of diamond anvil cell (DAC) or jewelry. High quality large cubic diamonds with sheet shape, which are composed of (100) crystal faces, are widely used in many fields. Many precision and ultra-precision machining tools need regular sheet cubic shape and no inclusions diamond crystals. It has also been used for the heat spreader of the high power laser and windows of infrared instruments.

In this work, we systematically studied the synthesis of high quality cubic diamond crystals using temperature gradient method under high pressure and high temperature conditions with FeNi alloy as solvent catalyst. The diamond crystals were characterized by optical microscopes (OM), Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy. Finite element method (FEM) was used to simulate the solvent metal convection field of the growth cell, and it provided an interesting result to help us understand the growth mechanism of diamond.

Experiments

The diamond synthetic experiments were performed in a China type SPD-6 × 1200 cubic-anvil high pressure apparatus (CHPA). The assembly schematic diagram of high pressure synthesis cell by temperature gradient method is shown in Fig. 1. High purity graphite powder (99.9%, purity) was selected as carbon source, which was placed in the high temperature region of the growth cell. High quality synthetic type Ib diamond crystals were used as seed crystals, with (100) crystal face of about $0.8 \times 0.8\ mm^2$ as the initial growth face, which were placed in the low temperature region of the growth cell. The FeNi alloy (Fe:Ni = 64:36, weight ratio, and 99.9%, purity) was used as the solvent metal. In addition,

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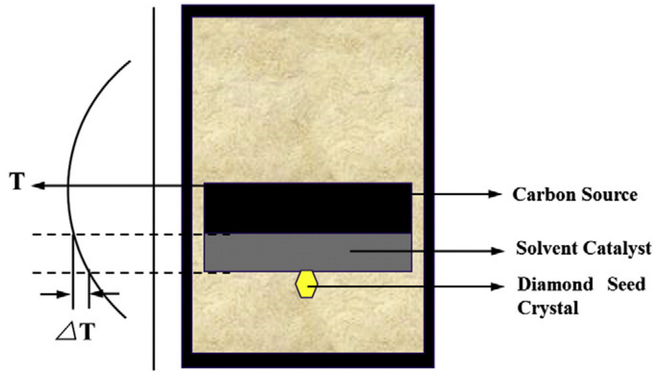

Fig. 1. Sample assembly schematic diagram for diamond growth.

the pressure was estimated by the oil press load, which was calibrated by a curve that was established on the pressure-induced phase transitions of Bi, Tl and Ba; the temperature was determined by a Pt6%Rh–Pt30%Rh thermocouple, respectively [13].

The samples, which taken out from the high pressure apparatus, were put into boiling acids to remove the impurities remaining on these surfaces of diamond crystals. Optical microscope was used to observe the morphology of crystal and inclusion in the diamond crystals. Raman spectrometer and Fourier transform infrared spectrometer were used to characterize the quality of diamond crystals. The solvent metal convection field in the growth cell was simulated by finite element method [14,15]. Using solid 69 and fluid 142 cells in finite element software, thermal–electrical-fluid finite element analyses were carried out in the whole model of the growth cell, respectively.

Results and discussion

Synthesis of sheet cubic diamond crystals

Experiments in the FeNi alloy–carbon system for diamond synthesis were performed at pressures in the range of 5.5–5.8 GPa and temperatures in the range of 1300–1360 °C. The obtained results are summarized in Table 1. During the diamond growth process by TGM, the morphology of diamond changes from cubic crystal mainly with (100) crystal faces, cubo-octahedral crystal mainly with (100) and (111) crystal faces, to octahedral crystals mainly with (111) crystal faces with the increase of synthetic temperature.

If the synthetic temperature is too low, that is to say, the region of diamond crystal is close to the left of V-shape region, then, the skeleton crystals may appear (S1). However, if the synthetic temperature is a little higher, the synthesized diamond crystals may show cubo-octahedral shape (S5, S6). From Table 1, sheet cubic diamond crystals are synthesized in our self-designed FeNi alloy–carbon systems at temperature of 1310–1325 °C (S2–S4). It shows that the growth region of high quality sheet cubic diamond crystals is very narrow in the P-T regions of diamond synthesis.

Table 1
Experimental results of sheet cubic diamond crystal synthesis.

Sample	Pressure (GPa)	Temperature (°C)	Morphology	*Rr* (mm/h)	*Ra* (mm/h)	*Rr*/*Ra*
S1	5.5	1300	/	/	/	/
S2	5.5	1310	(100)	0.21	0.08	2.63
S3	5.5	1315	(100)	0.21	0.09	2.33
S4	5.5	1325	(100)	0.20	0.10	2.00
S5	5.5	1330	(100),(111)	0.19	0.11	1.73
S6	5.5	1340	(100),(111)	0.18	0.15	1.20
S7	5.5	1360	(111)	0.18	0.16	1.13
S8	5.7	1315	(100)	0.23	0.14	1.64
S9	5.8	1315	(100)	0.24	0.17	1.41

Rr: Radial growth rate, *Ra*: Axial growth rate.

It is clearly shown in Fig. 2 that the synthesized diamond crystals in the FeNi alloy–carbon system are predominantly composed by (100) crystal faces. Most of those crystals are sheet cubic shape with the color of light yellow and few inclusions.

Growth rate of sheet cubic diamond crystals

Based on the theory of temperature gradient method of diamond synthesis, the growth rate is mainly affected by the temperature gradient [16,17]. Meanwhile, temperature gradient of diamond synthesis can be adjusted by the growth cell assembly freely. According to the relationship between the morphology of diamond crystal and V-shape regions of diamond synthesis, low temperature section of V-shape regions is suitable for the cubic diamond crystal synthesis by temperature gradient method under HPHT. High growth rate can reduce the synthetic time and cost. However, the growth rate cannot be enhanced without precondition and must be controlled within certain limits. Based on previous studies [18], too high growth rate is not good for the quality of crystal.

In addition, the P-T regions of diamond synthesis in the metallic solvent catalyst-carbon systems appeared significantly broader with the increase of pressures. However, the ratio of radial growth rate (*Rr*) to axial growth rate (*Ra*) decreases (S8 and S9) with increases of synthetic pressure. In other words, a higher synthesized pressure is not suitable for synthesizing diamond crystals with the high ratio of *Rr* to *Ra*.

Characterization of sheet cubic diamond crystals by Raman and FTIR spectroscopies

Raman spectroscopy was used to characterize crystal lattice distortion or crystalline quality of diamond crystals. For comparison, two diamond crystals synthesized from our lab (a) and purchased from commercial company (b) were selected to be analyzed by Raman spectroscopy. Fig. 3 shows Raman spectra recorded from diamond crystals. The Raman peak values and the full width at half maximum (FWHM) indicated the relative quality of those crystals.

The diamond Raman peaks values of those diamond crystals are near 1332 cm^{-1}. However, the FWHM of 1332 cm^{-1} peak of our diamond sample (a) is smaller than that of the commercial diamond (b). It is supposed that the observed features of the Raman spectrum of diamond are related to the increasing concentrations of micro-crystallites in boundary, impurities, residual stress, or defects, etc. Therefore, it illustrates that the sheet cubic diamond crystals synthesized in this paper have less lattice distortion and with high quality.

On the other hand, nitrogen is one of the main impurities in diamond crystal and nitrogen concentration is determined to be in substitutional form based on the shape of spectrum in the one phonon region (800–1400 cm^{-1}) [19]. FTIR spectrum of diamond crystal is shown in Fig. 4. This spectrum shows that the absorption intensity of sheet cubic diamond crystal is in one phonon region. Generally, the nitrogen concentration of normal diamond crystal is about 200–800 ppm. The nitrogen concentration of our samples is about 240 ppm. Compared with normal diamond crystals, our sample has less nitrogen impurity, and it is of high quality.

Simulation of growth mechanism by FEM

In order to analyze the growth mechanism of sheet cubic diamonds, FEM was used to simulate the growth process of diamond crystal. As shown in Fig. 5, the solvent metal convection field of the growth cell of sheet cubic diamond crystal was simulated by FEM. Diffusion and convection in crystal growth cell provide carbon transport from the source to the crystal surface, and it is the governing driving force of crystal growth.

The results of theoretical simulation indicate that distribution of solvent metal convection field shows visible difference in diamond growth