Effects of carbon convection field on large diamond growth under high-pressure high-temperature conditions*

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(Received 1 August 2011; revised manuscript received 30 October 2011)

Large diamond crystals were successfully synthesized by FeNi–C system using temperature gradient method under high-pressure high-temperature conditions. The assembly of the growth cell was improved and the growth process of diamond was investigated. Effects of the symmetry of carbon convection field around the growing diamond crystal were investigated systematically by adjusting the position of seed crystal in the melted catalyst/solvent. The results indicate that morphologies and metal inclusion distributions of the synthetic diamond crystals vary obviously in both symmetric and non-symmetric carbon convection fields with temperature. Moreover, finite element method was applied to analyze carbon convection mode of the melted catalyst/solvent around the diamond crystal. This work is helpful for understanding the growth mechanism of diamond.

Keywords: diamond, high pressure and high temperature, temperature gradient method, carbon convection field

PACS: 81.05.ug, 61.72.Lk, 07.35.+k, 07.20.Ka **DOI:** 10.1088/1674-1056/21/9/098101

1. Introduction

Diamond crystal growth mechanisms and engineering of high-pressure apparatus have been utilized efficiently in most of the world's research and commercial organizations. High-quality large diamond crystals and abrasive diamond grits have been synthesized for commercial and scientific uses.[1−11] Large single-crystal diamonds can be synthesized by low-pressure microwave plasma chemical vapor deposition (MPCVD) and temperature gradient growth methods (TGM) under high pressure and high temperature (HPHT), respectively. Recently, single-crystal diamond synthesis by MPCVD has made much progress at the Carnegie Institution of Washington.[12,13] However, in most of research and commercial organizations throughout the world, the widespread use of chemical vapor deposition (CVD) diamonds in many applications has not been successful because of the slow growth rates and the grain boundaries of polycrystalline diamonds that are produced.[14] Thus, until now, TGM under HPHT is also one of the most effective methods to synthesize large, gem-quality, single-crystal diamonds.

The driving force of diamond growth by TGM is provided by the solubility difference resulting from the temperature gradient in the growth cell. The growth rate is affected by the carbon diffusion through the molten catalyst metal film between the carbon source and the seed diamond crystal.[15−17] The temperature gradient is indispensable to the carbon diffusion and growth of diamond. Generally, the growth cell in a cylinder shape is used for large diamond growth, where the seed crystal is embedded in the seed bed center. During the crystal growth process, the carbon convection field around the growing diamond crystal symmetry distributes in the melted catalyst/solvent in the growth cell. When a solution flow exists around a growing crystal, the distribution of carbon convection field around the growing diamond crystal may have

*Project supported by the National Natural Science Foundation of China (Grant Nos. 50572032, 50731006, and 50801030) and the Young Scientists Fund of the National Natural Science Foundation of China (Grant Nos. 51001042 and 51002045).

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significant effects on the morphology and the growth rate of diamond.[18] In other words, the characteristics of the synthesized diamond embedded in the growth cell may be affected by the changes of seed crystal position. Until now, there are very few reports about systematic investigations on the changes of carbon convection field around the growing diamond, which is symmetric and non-symmetric. Meanwhile, as the commercial production of large gem-quality diamonds, one of the most challenging problems is to optimize the growth cell assembly to create a suitable growth environment based on different requirements using, for example, the multi-seed method. However, there is a lack of effective basis for the adjustment of the diamond growth conditions.

In the present work, large diamond crystals were synthesized using FeNi–C system by TGM under HPHT conditions. Effects of morphologies and metal inclusions of the diamond were investigated systematically by symmetric and non-symmetric carbon convection field. These results should be helpful for improving diamond growth cell assembly and understanding the growth mechanism of the large diamond synthesized at HPHT conditions.

2. Experimental details

The experiments on the diamond crystal growth were carried out in a China-type large volume cubic high-pressure apparatus (CHPA) (SPD-6×1200) at pressure range of 5.5–5.7 GPa and temperature range of 1280–1350 °C. The high-purity graphite powder used as carbon source and the $Fe_{64}Ni_{36}$ alloy used as solvent/catalyst were raw materials in the experiment. The diamond with well faceted {100} crystal face of 0.5×0.5 mm^2 was used as diamond seed. The high pressure apparatus and sample assembly for diamond synthesis are shown in Fig. 1. 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 detected by a Pt6%Rh–Pt30%Rh thermocouple.[19]

Carbon convection field of the melted catalyst/solvent was simulated by finite element method (FEM). With the FEM software, 1/2 and 1/4 entity models were set up, respectively. Entity model was simulated and analyzed by calorifics–electrics-liquid coupling analysis using solid 69 and fluid 142 cells. The properties of catalyst/solvent and other substances have been reported previously.[15,20,21] After HPHT synthesis, optical microscope (OM) was used to observe crystal morphologies and inclusions in diamonds.

3. Results and discussion

3.1. Synthesis and morphology of large diamond at different temperatures

As shown in Fig. 1, the heat is generated from the carbon heater and transmitted along vertical and radial directions. The temperature is highest at position A and falls along vertical (H_v) and radial (H_r) directions. Thus, there are vertical and radial temperature gradients along two directions. The carbon convection field, which results from vertical and radial temperature gradients, around the growing diamond changes with the seed position in the growth cell, and we call them symmetric (the diamond seed embedded in center) and non-symmetric (the diamond seed deviated from the center) carbon convection fields, respectively. Generally, the vertical temperature gradient could be changed freely by adjusting the structure of the assembly. In order to reach a suitable growth rate, the vertical temperature gradient is about 40–60 °C. However, the radial temperature gradient results from the heat delivered from the carbon heater to the center of the growth cell. It is affected by the material thermal conductivity. The temperature gradient is about 10 °C or greater, and increases with increasing growth cell size. Figure 2 shows the diamond crystals synthesized at 5.6 GPa and a temperature range of 1280–1320 °C. The experimental results are summarized in Table 1.

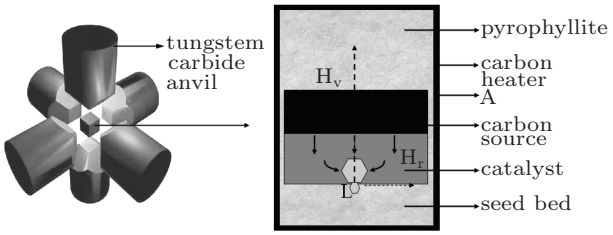


Fig. 1. Schematic diagram of assembly for large diamond synthesis by TGM under HPHT. Hv: high temperature region along the vertical direction; Hr: high temperature region along the radial direction; L: low temperature region.

Table 1. Results of diamond synthesized by TGM at pressure of 5.6 GPa. S denotes the symmetric carbon convection field; N denotes the non-symmetric carbon convection field.

Run	T/°C	Carbon convection field	Diamond morphology	Schematic diagram of diamond
1	1280	S	{100}	
2	1300	S	{100}, {111}	
3	1320	S	{111}	
4	1280	N	{100}	
5	1300	N	{100}, {111}	
6	1320	N	{111}	

First, the seed crystal was embedded in the center of the growth cell to make carbon convection field symmetric around the growing diamond. Figures 2(a), 2(b), and 2(c) show the large diamonds synthesized at 1280, 1300, and 1320 °C (runs 1–3), respectively. The morphologies of diamonds change from the dominated {100} faces to the dominated {111} faces, and few of visible metal inclusions appear in the crystals. The crystals are regular and crystal faces with the same indices of crystal faces are nearly equal in size. Then, we only change the position of seed crystal on the seed bed, and the diamond seed deviates from the center in the growth cell by several millimeters. A series of large diamonds were synthesized at a series of temperatures (runs 4–6). As shown in Figs. 2(d), 2(e), and 2(f), the morphologies of diamonds also change from the dominated {100} faces to the dominated {111} faces. However, it is obviously found from the quality observations that the morphologies of the synthesized diamonds are not regular, and the crystal faces with the same indices of are not equal in size. That is to say, the carbon convection field around the growing crystal changes with the seed position, and the morphology of diamond becomes non-symmetric. The morphologies of diamonds change obviously and do not show symmetrical distribution along the vertical direction through the diamond seed.

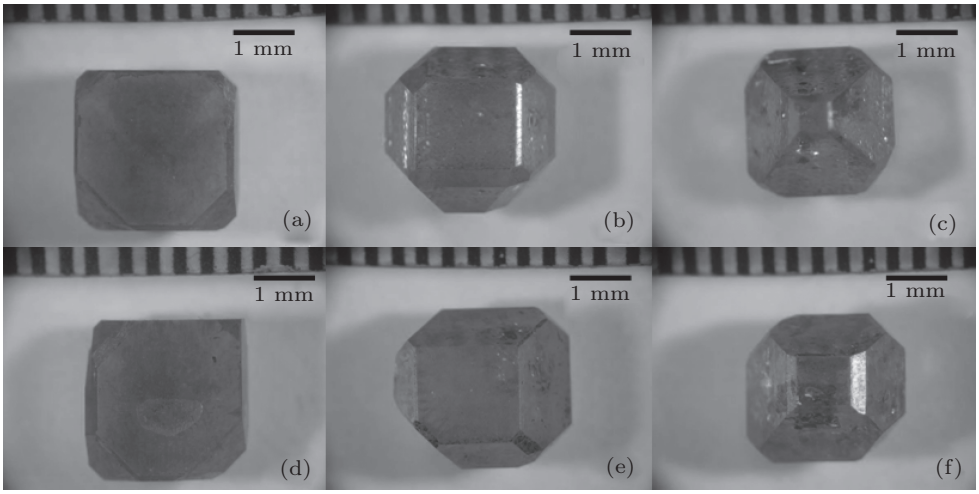


Fig. 2. OM photographs of large diamond crystals synthesized at 1280 °C (a and d), 1300 °C (b and e), and 1320 °C (c and f) in symmetric and non-symmetric carbon convection fields.

In order to analyze the crystal morphology change along the radial direction, a series of experiments in which we change the distance of diamond seed from the center to the edge of growth cell were performed, which are shown in Fig. 3. It is clear that the angle α increases with the distance from the center to the seed position in seed bed. We also found that the quality of diamond crystal deteriorates along the radial direction.

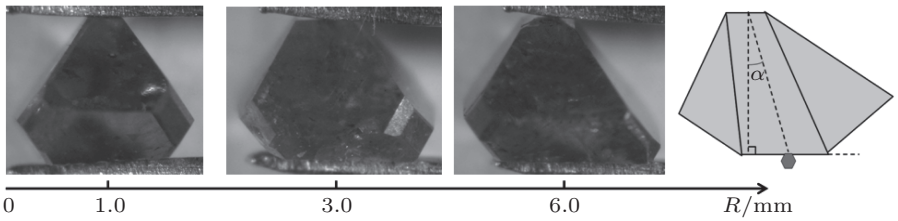


Fig. 3. Diamond crystal morphology changes along the radial direction. The α is the angle between the vertical direction and the center connection line of crystal faces.

3.2. Effects of the carbon convection field on the metal inclusion distribution in the diamond

Usually, metal inclusions were easily trapped in diamond crystal when the crystal growth conditions were not appropriate, such as high growth rate.[21] In order to investigate the distribution of metal inclusions in diamond, a series of diamond crystals with metal inclusions were selected, which were synthesized in the symmetric and non-symmetric carbon convection fields.

Figures 4(a), 4(b), and 4(c) show the OM photographs of large diamond crystals which were synthesized in the symmetric carbon convection field. It can be found that metal inclusions always exist in the vertical direction of diamonds, although the amounts are different. Figure 5(a) shows the schematic diagram of inclusion distribution in diamond crystals synthesized in the symmetric carbon convection field. On the contrary, figures 4(d), 4(e), and 4(f) show the OM photographs of large diamond crystals which were synthesized in the non-symmetric carbon convection field. The metal inclusions deviate from the vertical direction of diamonds. Figure 5(b) shows the schematic diagram of inclusion distribution in diamond crystals synthesized in the non-symmetric carbon convection field.

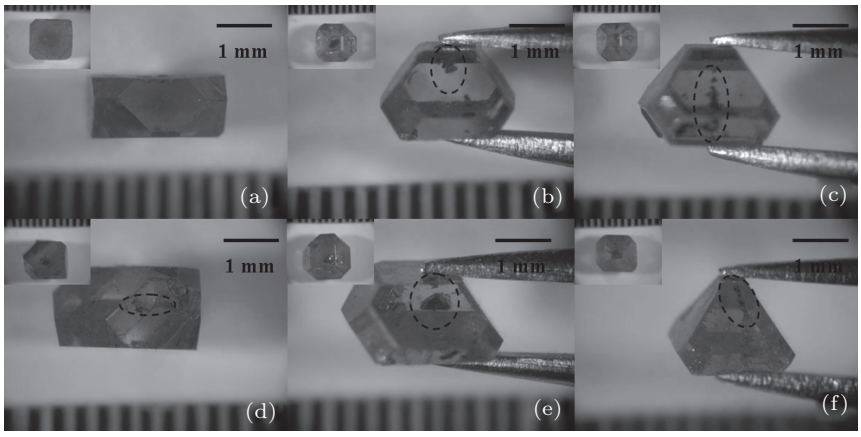


Fig. 4. OM photographs of morphologies and metal inclusions of diamonds synthesized at 1280 °C (a and d), 1300 °C (b and e), and 1320 °C (c and f). Metal inclusions are denoted by dashed ellipses.

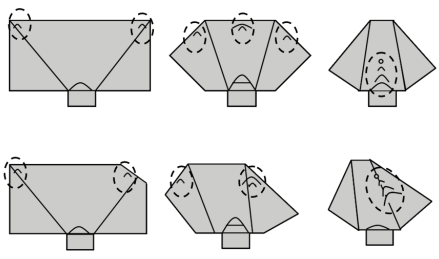


Fig. 5. Schematic diagrams of morphologies and metal inclusions of synthesized diamonds. Metal inclusions are denoted by dashed ellipses.

By comparing the morphologies of diamonds, the distributions of metal inclusions are obviously different for different carbon convection fields. In addition, it is can be found that the metal inclusions were easily trapped in the diamonds, and the amounts of metal inclusions increase with increasing temperature.

3.3. FEM simulation and analysis of the diamond growth

Taking the diamond synthetic temperature of

1300 °C as an example, we explain the diamond growth phenomena. As shown in Fig. 1, the heat is generated from the carbon heater and flows out of the cell, which makes the vertical temperature gradient exist in the growth cell and remain a concentration difference between the high and low temperature regions. Meanwhile, there is a radial temperature gradient, which is one of the most important factors that affect the carbon convection field around the growing diamond crystal. In order to analyze the diamond growth mechanism, the FEM was used to simulate the diamond crystal growth process. Figure 6(a) shows the section of carbon convection field at the initial stage of the crystal growth in FeNi–C system under HPHT.

As shown in Fig. 6(a), carbon concentration gradient in the growth cell is denoted by the arrows. The carbon concentration gradient is associated with the arrow density. The arrow density and length are symmetrically distributed along the vertical direction. That is to say, the carbon convection field around the seed crystal is symmetrically distributed along the vertical direction.

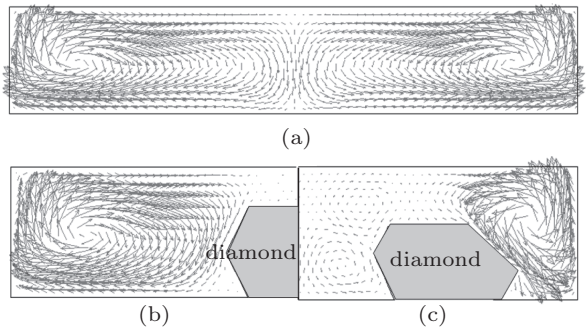


Fig. 6. Carbon convection fields at 5.6 GPa and 1300 °C in the FeNi-C system. (a) Initial stage of the crystal growth; (b) symmetrical distribution around the growing diamond crystal; (c) non-symmetrical distribution around the growing diamond crystal.

Now, we consider that the seeds were embedded in different positions, one is at the center of the growth cell, and another deviates from the center by several millimeters. The diamond crystals grow up with time. Figures 6(b) and 6(c) show half of the carbon convection field. Diamond seed was embedded at different positions in the growth cell. As shown in Fig. 6(b), the carbon convection field around the crystal presents symmetrical distribution. Such symmetrical carbon convection around the growing diamond crystal may lead to the same growth rate on crystal faces with the same indices on the growing diamond crystal. However, as shown in Fig. 6(c), the carbon convection field around the crystal presents non-symmetrical distribution. Such flow structure may provide non-symmetric carbon transport to the crystal faces and lead to different growth rate on crystal faces with the same indices on the growing diamond crystal.

According to the melt–solvent theory, solubility difference resulting from the temperature gradient between the carbon source and diamond seed provides carbon transport from the source to the crystal surface, and is the driving force of diamond growth. The positions of metal inclusions in the diamonds were affected by the symmetry of carbon convection field. Thus, the changes of distribution of seed crystals in the growth cell results in the changes of carbon convection field around the growing diamond crystal, which affects the morphologies and metal inclusion distributions in diamonds significantly.

In fact, with the developments of HPHT apparatuses and large-scale growth cells for diamond synthesis, there are some thorny issues for efficiency in the commercial production. Based on the above investigation, by optimizing the configuration of the assembly cell and adjusting the carbon convection field around the growing diamond crystals, it is promising to synthesize large diamond by TGM and improve the efficiency in the commercial production.

4. Conclusions

We have investigated systematically the effects of the symmetry of carbon convection fields around the growing diamond crystals in the melted catalyst/solvent on large diamond growth. The diamond morphologies and metal inclusion distributions in diamonds were obviously affected by the carbon convection field around the growing diamond crystal. The numerical simulation results were compared with experimental results to explain the diamond growth phenomenon. This work offers a promising route for the adjustment of the diamond growth assembly, and an effective solution for commercial production of large diamond crystals.

References

[1] Burns R C, Hansen J O, Spits R A, Sibanda M, Welbourn C M and Welch D L 1999 *Diamond Relat. Mater.* **8** 1433
[2] Kanda H, Akaishi M and Yamaoka S 1994 *Appl. Phys. Lett.* **65** 784
[3] Zhou L, Jia X P, Ma H A, Zheng Y J and Li Y T 2008 *Chin. Phy.* B **17** 4665

[4] Strong H M and Hanneman R E 1967 *J. Chem. Phys.* **46** 3668

[5] Kanda H, Ohsawa T, Fukunaga O and Sunagawa I 1989 *J. Cryst. Growth* **94** 115

[6] Sumiya H, Toda N and Satoh S 2002 *J. Cryst. Growth* **237** 1281

[7] Li S S, Ma H A, Li X L, Su T C, Huang G F, Li Y and Jia X P 2011 *Chin. Phys.* B **20** 028103

[8] Zhou L, Jia X P, Ma H A, Zheng Y J and Li Y T 2009 *Chin. Phys.* B **18** 333

[9] Qin J M, Zhang Y, Cao J M and Tian L F 2011 *Acta Phys. Sin.* **60** 058102 (in Chinese)

[10] Hu X J, Hu H, Chen X H and Xu B 2011 *Acta Phys. Sin.* **60** 068101 (in Chinese)

[11] Han Q G, Ma H A, Xiao H Y, Li R, Zhang C, Li Z C, Tian Y and Jia X P 2010 *Acta Phys. Sin.* **59** 1923 (in Chinese)

[12] Meng Y F, Yan C S, Lai J, Krasnicki S, Shu H, Yu T, Liang Q, Mao H K and Hemley R J 2008 *PNAS* **105** 17620

[13] Liang Q, Chin C Y, Lai J, Yan C, Meng Y F, Mao H K and Hemley R J 2009 *Appl. Phys. Lett.* **94** 024103

[14] Li R B 2009 *Acta Phys. Sin.* **58** 1287 (in Chinese)

[15] Wentorf R H 1971 *J. Phys. Chem.* **75** 1833

[16] Strong H M and Chrenko R M 1971 *J. Phys. Chem.* **75** 1838

[17] Demina S E, Kalaev V V, Lysakovskyi V V, Serga M A, Kovalenko T V and Ivahnenko S A 2009 *J. Cryst. Growth* **311** 680

[18] Tian Y, Jia X P, Zang C Y, Li R, Li S S, Xiao H Y, Zhang Y F, Huang G F, Han Q G, Ma L Q, Li Y, Chen X Z, Zhang C and Ma H A 2009 *Chin. Phys. Lett.* **26** 028104

[19] Ma H A, Jia X P, Chen LX, Zhu P W, Guo W L, Guo X B, Wang Y D, Li S Q, Zou G T, Zhang G and Phillip B 2002 *J. Phys.: Condens. Matter* **14** 11269

[20] Sato Y, Sugisawa K, Aoki D and Yamamura T 2005 *Meas. Sci. Technol.* **16** 363

[21] Ma Q F 1986 *Handbook of Practical Thermo-Physical Property* (Beijing: China Agricultural Machinery Publishing House) p. 1110 (in Chinese)