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Effects of catalyst height on diamond crystal morphology under high pressure and high temperature*

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The effect of the catalyst height on the morphology of diamond crystal is investigated by means of temperature gradient growth (TGG) under high pressure and high temperature (HPHT) conditions with using Ni-based catalyst in this article. The experimental results show that the morphology of diamond changes from octahedral shape to cub-octahedral shape as the catalyst height rises. Moreover, finite element method (FEM) is used to simulate the temperature field of the melted catalyst/solvent. The results show that the temperature at the location of seed diamond continues to decrease with the increase of catalyst height, which is conducive to changing the morphology of diamond. This work provides a new way to change the diamond crystal morphology.

Keywords: diamond crystal, morphology, catalyst, finite element method

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1. Introduction

Diamond, as the hardest substance in natural world, is of great importance in science and technology with many applications, such as fine grinding material, high hardness cutting tools and parts of precision instrument. Since diamond was first synthesized in a metal catalyst/solvent and graphite system by using the high pressure and high temperature (HPHT) method in 1954,[1] numerous studies of growth mechanism and outstanding properties have been conducted. According to the abundant research results of pioneers, the catalyst and solvent have been recognized to play a critical role in synthesizing diamond when using the HPHT method.[2–4] Different kinds of catalysts have been found and studied to explore the influence on diamond synthesis with using the HPHT method. The non-metallic catalysts generally require the HPHT conditions and thus the obtained diamond is of lower quality. However, metallic solvent catalysts could obtain sufficiently large crystals of synthetic diamond with high purity and high quality in a relative mild condition.[5–16] Nevertheless, little attention has been paid to the research on the effect of height of the catalyst itself on the growth process of diamond. In consideration of the important role of catalyst, we here focus on the catalyst based on Ni-based alloy to explore the effect of catalyst height on the growth process of diamond crystal.

It was well known that the temperature gradient growth (TGG) under HPHT conditions was an effective method to synthesize large single crystal diamond.[17–22] We also knew that the temperature gradient was a driving force of diamond growth. However, it is very difficult to ascertain the dependence of the temperature characteristic in the catalyst on the catalyst height. Therefore, the understanding of the temperature fields of different heights of catalyst is the key to investigating the effect on diamond perfection and morphology. The finite element method (FEM) is a powerful calculation tool[23,24] for understanding the temperature characteristic in high-pressure synthesis cells.

In this study, large diamond crystals are synthesized by using different heights of catalyst by TGG under HPHT conditions. Our work is to clarify the effect of catalyst height on crystal morphology of diamond. The FEM is used to simulate the melted catalyst and solvent temperature field of the growth cell, and thus explaining the growth mechanism of diamond crystals. We believe that our work would be helpful and meaningful for synthesizing different shapes of single crystal diamonds, which are used for industrial production and scientific research.

2. Experimental details

Experiments on diamond crystallization were carried out in a china-type large cubic high-pressure apparatus (CHPA)

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with a sample assembly of 38 mm×38 mm×38 mm at a pressure of 5.7 GPa. The sample assembly for synthesizing diamond by temperature gradient method (TGM) is shown in Fig. 1. As shown in Fig. 1, the growth diamond cell was heated when voltage V_1 was applied to the base of the up steel ring and V_2 was set to be 0 V as it was grounded. The voltage V_1 was set to be 2.5 V in all experiments. High purity graphite powder (mesh 200) and NiMnCo alloy (70:25:5 by wt%) were used as the carbon source and the catalyst/solvent, respectively. The diamond with well faceted {100} crystal face of 0.5 mm×0.5 mm was used as the diamond seed. The pressure was estimated by the oil press load, which was calibrated by a curve that had been established on the pressure-induced phase transitions of Bi, Tl, and Ba.

After the HPHT experiments, the products were dissolved in a hot mixture of HNO_3 and H_2SO_4 to remove the impurities remaining on the surfaces of the crystals. Morphologies of the synthesized samples were characterized by optical microscope.

The distribution of temperature field in the melted catalyst and solvent of the growth assembly was simulated by FEM. We chose solid 69 for thermal-electrical analysis. Finite element model, boundary conditions, and material parameters were cited from other previous reports.[25,26]

3. Results and discussion

3.1. Synthesis and morphology of diamond crystal

Figure 1 shows a cell assembly used in synthesis experiment. Carbon source, a seed crystal and metal solvent and catalyst are essential parts for the growth. They are placed in a carbon heater so that the carbon source is located in a higher temperature region than the seed diamond crystal. In order to study the effect of the catalyst height on the morphology of the diamond crystal, several synthesis experiments were carried out by using 2.0-mm, 2.4-mm, and 2.8-mm catalyst height respectively.

Figure 2(a)–2(c) show the optical microscope photographs of the synthesized large diamond crystals in Ni-based catalyst with different heights (2.0 mm, 2.4 mm, 2.8 mm). It can be found that the morphologies of the diamonds have changed. First of all, it is clear that the morphology of the diamond synthesized in 2.0-mm catalyst shows octahedral crystals shape with the dominating {111} crystal faces in Fig. 2(a). Additionally, it is important to find that the diamond has a cuboctahedral shape in Figs. 2(b) and 2(c) with the dominating {100} and {111} crystal faces. Therefore, our results indicate that using different heights of the catalyst, the different morphologies of the diamond crystals are synthesized.

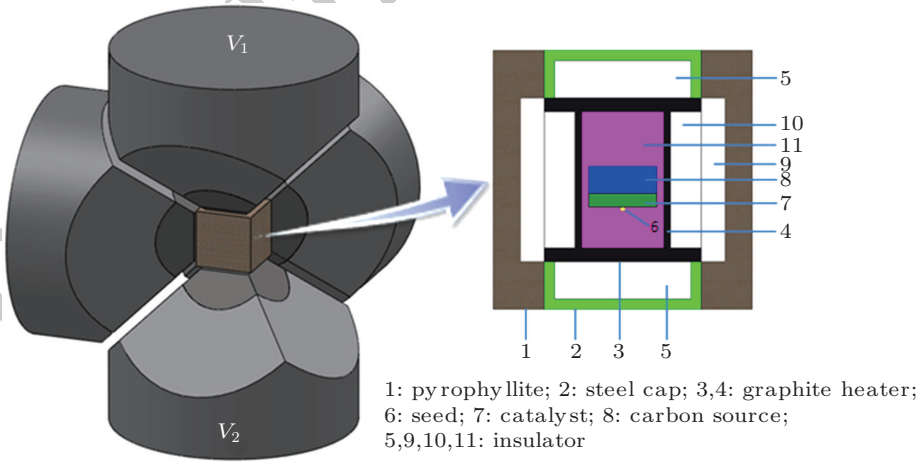

Fig. 1. (color online) Sample assembly for diamond synthesized by HPHT.

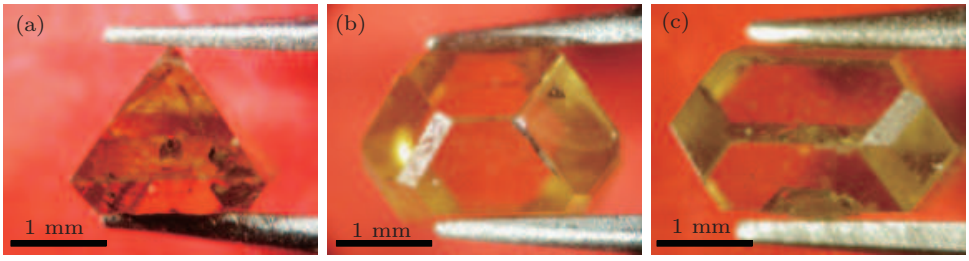

Fig. 2. (color online) Synthesized diamond crystals in different heights of Ni-based catalyst: (a) 2.0 mm, (b) 2.4 mm, (c) 2.8 mm.

It is well known that the morphology of diamond changes from cubic crystal mainly with {100} crystal faces, cub-octahedral crystal mainly with {100} and {111} crystal faces to octahedral crystals mainly with {111} crystal faces with the increase of synthetic temperature in the diamond process by TGG under HPHT. In the pressure–temperature (*P*–*T*) phase diagram of carbon, the region for diamond growth is a V-shape region bounded by a growth-graphite equilibrium line and solvent and carbon eutectic melting line in the metal solvent-carbon system. As shown in Fig. 3, it can be seen that the *P*–*T* regions of diamond synthesis in the metallic solvent and catalyst-carbon systems appear to become significantly broader with the increase of the pressure. Experiments on the diamond synthesized in the Ni–Mn–Co–C system are conducted at a pressure of 5.7 GPa. Our synthesized diamond crystals can be obtained in region A.

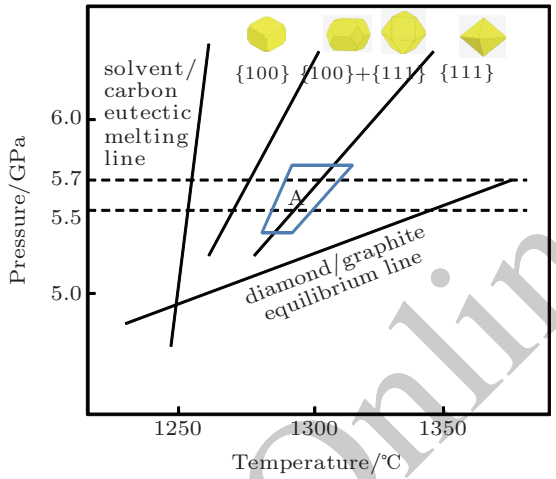

Fig. 3. (color online) *P*–*T* phase diagrams of diamond and graphite crystallization in the Ni–Mn–Co–C system (Region A: *P* and *T* for our obtained diamond crystals by the HPHT method).

Region A in Fig. 3 shows that if the synthesis temperature is high, the region of diamond is close to the right of V-shape region showing octahedral shape. However, if the temperature is a little lower, the cub-octahedral shape may occur. In addition, in the *P*–*T* phase diagram of carbon (under 5.7 GPa),[27] the region of growing diamond crystal is a 30-°C range only in a V-shaped region bounded by the diamond-graphite equilibrium line and the metal-diamond eutectic line in the solvent-graphite system. Hence, the change of the catalyst height in the growth cell results in the change of synthesis temperature around the growing diamond crystal, which affects the morphology of the diamond significantly.

As is well known, based on the TGG under HPHT conditions of diamond growth process, graphite powder is placed in the high temperature region, and diamond seed is embedded in the low temperature region. When the cell is heated electrically by the graphite heater, the graphite powder is converted into diamond in a few minutes after a given temperature has been reached under the high pressure. We also know that diamond has a high thermal conductivity of about 2000 W/m·K, which is much higher than the Ni-based catalyst. When the pressure, voltage, and dimension of the graphite heater are fixed, the heat quantities generated by the graphite heater are the same in experiments. Owing to the high thermal conductivity of diamond, the temperatures in carbon source are almost the same. Furthermore, when using thick catalyst, temperature difference between the carbon source and the surface of the seed diamond is larger than using thin catalyst. Thus, as the temperature of carbon source in high temperature region is almost unchanged, it leads to the lower temperature of seed diamond in low temperature region. That is to say, the synthesis temperature decreases with the increase of catalyst height.

3.2. FEM simulation and verification process

Based on the above experimental results, the morphologies of diamond crystals change as the catalyst height changes. In order to analyze the effect of height of catalyst on the morphology of diamond, FEM is used to simulate the temperature field of catalyst in the process of diamond growth. As shown in Fig. 4, the temperature fields in catalyst with different heights are uneven. The high-temperature region is near to the insulated tube and carbon source. And the lower-temperature region is located in the bottom area of the melted catalyst, especially near the surface of the seed crystal. It could be noticed from the color of the cloud charts that the temperature in the bottom area of the catalyst decreases with catalyst height increasing.

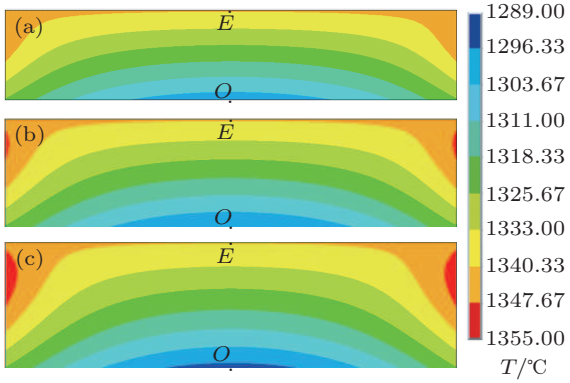

Fig. 4. (color online) Distributions of temperature field on different heights of catalyst (*E*: contact with the carbon source location; *O*: contact with the seed crystal location). (a) 2.0 mm, (b) 2.4 mm, (c) 2.8 mm.

Figure 5 shows the values of temperatures in the top area of the catalyst at location *E* (contact carbon source) and the bottom area of the catalyst at location *O* (contact seed diamond) under different catalyst heights. It is observed obviously that the temperatures of location E are almost unchanged

and the highest value at location *O* is 1298 °C when the height of catalyst is 2.0 mm, and the lowest value is 1288 °C when the height of catalyst is 2.8 mm. Theoretical calculation results suggest that synthesize temperature of the growth cell decreases gradually with the increase of catalyst height. The results show that the simulation results are consistent with the experimental ones. From the experimental and simulated results above, we believe that the temperature in the center of the growth region decreases with catalyst/solvent increasing, which is conducive to changing the morphology of diamond.

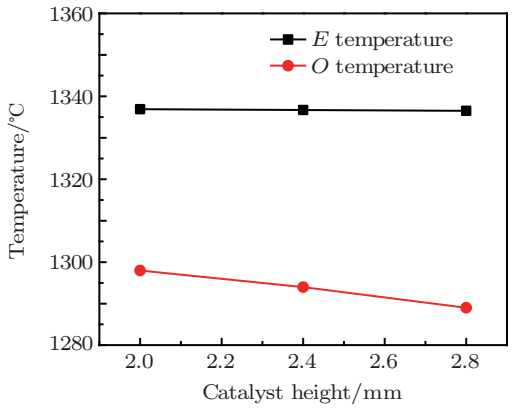

Fig. 5. (color online) Temperatures on locations O and E under different catalyst heights.

4. Conclusions

The diamond morphology is obviously affected by the melted catalyst and solvent heights in the large diamond growth process. The experimental results show that the morphology of the diamond changes from octahedral shape to cub-octahedral shape as catalyst height rises. Numerical simulation results show that the temperature in the seed diamond continues to decrease with the increase of catalyst height. The numerical simulation results can be used to explain some details of the diamond growth process. Our results not only provide a promising route to the adjustment of diamond synthesis assembly, but also offer an effective solution for commercial production of different shapes of large diamond crystals.

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