Research on the Restricted Growth of High-Quality Large Cubic Gem Diamond Crystals

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Abstract. In this paper, cubic gem diamond crystal was grown via the temperature gradient under high pressure and high temperature, with self-made alloy solvent and through adjusting the process of assembling and synthesis appropriately. Crystal characters of large hexahedral cubic diamond crystals grown during different times were researched, and the results show that, the radial growth rate of the synthetic crystal is larger than that of the axial growth rate under the experimental conditions. The radial growth rate of the synthesis of the crystal is 3.75 times than that of the axial growth rate within 20 hours. The synthesized high quality diamond crystal has cubic hexahedral morphology and high repeatability, which will be beneficial to the industrialization of high quality cubic hexahedral diamond crystal.

1. Introduction

Single-crystal diamond tools made of high-quality large-size synthetic diamonds not only solve the problem of scarce and expensive natural diamonds, but also expand the application of diamond tools to many fields such as aviation, aerospace, automotive, and electronics [1-7].

The artificial synthesis of diamond crystal is a physio-chemical process of a complex multiphase system. High temperature and high pressure temperature gradient method is still an effective method to synthesize high quality large-grain diamond single crystals [8-9]. Crystal plane exposed is mainly determined by the competition of the growth rates of different crystal planes based on extensive literature and Wulff criteria [10-16].

The restricted growth method mentioned in this study refers to: according to the growth law and diffusion mechanism of diamond, artificially restrict the growth in one direction by certain means or methods. For cubic hexahedral diamond crystal, the growth rate in the direction of the {111} crystal plane is greater than the {100} crystal plane in the low temperature region. But with the temperature in growth system gradually increases, the growth rate of {111} crystal plane is less than that of the {100} crystal plane normal direction, which shown in figure 1.

The experiment used homemade catalysts to broaden the crystal growth area in the low temperature region. Then, according to the growth characteristics of the hexahedral diamond single crystal, reasonable process adjustment and high-precision control of temperature, the axial growth rate of the crystal is limited.
2. Experiment

This experiment uses homemade catalyst alloy of Fe\textsubscript{x}Ni\textsubscript{y}Co\textsubscript{z}, and the cavity reaction vessel material with a\%ZrO\textsubscript{2}+b\%MgO+c\%MgCaCO\textsubscript{3}+d\%Al\textsubscript{2}O\textsubscript{3}. The synthetic cavity assembly schematic diagram shown in figure 2. The test select a small seed crystal with a diameter of 0.8 mm and the crystal growth surface about 0.5 × 0.5 mm\textsuperscript{2}, and the crystal bed height is 5 mm. Crystal synthesis in the high-pressure equipment with domestic six-sided top hydraulic machine, the synthesis pressure is 5.4 GPa, and the temperature is 1350-1380 °C at different times within 8-36 hour. The sample was treated with dilute nitric acid to remove the metal catalyst on the surface of the crystal, and then the crystal was cleaned for a long time with a mixture of slightly boiling concentrated sulfuric acid and concentrated nitric acid.

3. Results and Discussion

The crystal characters of large hexahedral cubic diamond crystals grown during different times shown in table 1. It shown that the particle size and weight of the crystals become larger with the synthesis time increases. In different growth times from 8 to 36 hours, the radial growth rate of the hexagonal hexahedral crystals formed is greater than the axial growth rate. The curve of the radial growth rate and the axial growth rate is shown in figure 3. The diagonal particle size of the crystals increased from 5.0 mm to 7.6 mm, and weight of the crystal increased from 0.4 Carats to 1.4 Carats, the weight gain rate increased from 5.3 mg/h to 7.8 mg/h, and the size has increased from 3.5 × 3.4 × 0.45 to 5.4 × 5.4 × 3.17 with a cubic hexahedral morphology shown in figure 4. When the synthesis time is increased from 15 hours to 36 hours. It can meet the requirements of industrial large-grain diamond single crystal.
Table 1. Crystal characters of large hexahedral cubic diamond crystals grown during different times.

| Growth times (h) | Crystal weight (carat) | Crystal size (mm) | Diagonal particle size (mm) | Radial growth rate (mm/h) | Axial growth rate (mm/h) | Weight gain rate (mg/h) |
|------------------|------------------------|-------------------|----------------------------|--------------------------|--------------------------|-------------------------|
| 8                | 0.19                   | 2.8×2.6×0.21      | 3.8                        | 0.48                     | 0.026                    | 4.75                    |
| 12               | 0.31                   | 3.2×3.0×0.36      | 4.4                        | 0.37                     | 0.03                     | 5.17                    |
| 15               | 0.40                   | 3.5×3.4×0.45      | 5.0                        | 0.33                     | 0.03                     | 5.30                    |
| 20               | 0.70                   | 4.3×4.2×1.60      | 6.0                        | 0.30                     | 0.08                     | 7.0                     |
| 22               | 0.80                   | 4.4×4.3×1.76      | 6.2                        | 0.28                     | 0.08                     | 7.2                     |
| 25               | 0.90                   | 4.5×4.5×2.05      | 6.4                        | 0.26                     | 0.082                    | 7.2                     |
| 28               | 1.03                   | 4.8×4.8×2.35      | 6.8                        | 0.24                     | 0.084                    | 7.3                     |
| 33               | 1.20                   | 5.2×5.2×2.64      | 7.3                        | 0.22                     | 0.08                     | 7.3                     |
| 36               | 1.40                   | 5.4×5.4×3.17      | 7.6                        | 0.21                     | 0.088                    | 7.8                     |

Figure 3. The radial growth rate and axial growth rate of diamond crystal at different times.

Figure 4. Photographs of diamond crystal: (a) Temperature: 1352 °C, growth time: 15h, growth rate: 5.3 mg/h; (b) Temperature: 1372 °C, growth time: 36h, growth rate: 7.8 mg/h.

In this experiment, through the adjustment of the assembly method and the production process, the crystal growth rate was artificially controlled, that is, the axial growth rate of the crystal was suppressed, and the radial growth rate was accelerated.

It can be seen from figure 3, the radial growth rate of the synthetic crystal is greater than its axial growth rate. Taking crystals synthesized within 20 hours as an example, the radial growth rate is 3.75 times the axial growth rate. However, with the increase of the synthesis time, the radial growth rate of the crystal has slowed down, and accordingly, its axial growth rate has increased slightly. There are two points to analyze the cause of this phenomenon:

(1) It is related to the crystal growth mechanism. We known that the synthetic diamond single crystal large particles under high temperature and pressure are seeded method. When the melt of the carbon source and the metal catalyst reaches saturation, the diamond begins to nucleate and crystallize,
and then it grows layer by layer. With the prolongation of the synthesis time, it is inevitable that the axial growth rate of the crystal will increase, that is, the crystal will increase in thickness.

(2) It is related to the cavity size of the synthetic block used. When the cavity of the synthetic block used is fixed, the area of the carbon source used is also limited to extent. During the synthesis process, since the early carbon source is sufficient, the radial growth rate can be better controlled. For example, during the synthesis time of 8 to 12 hours, the radial growth rate of the crystal reaches from 0.48mm / h to 0.37mm / h, with the increase of the synthesis time, the remainder due to the consumption of the previous carbon source causes the remaining As the number of carbon sources decreases, the conversion rate of the carbon source will become slower and slower, so the radial growth rate of the crystal will also slow down.

According to literature reports [8-10, 17], Japan’s Sumitomo Corporation has adopted high temperature and high pressure temperature gradient method to synthesize high-quality large-particle Ib type diamond crystal, which has reached a very high level. When using small 0.5 × 0.5 mm² seed crystals and Fe-Co alloy catalysts, the growth rate of the Ib type diamond crystal is about 4 mg/h in 120 hours. From the table 1, it can be seen the growth rate of our synthesized high-quality cubic hexahedral diamond crystal reached to 7.3mg/h within 33 hours. Compared with the synthetic crystals of Japan’s Sumitomo in weight, it takes about 64 hours to synthesize a single carat diamond crystal with a 0.5 × 0.5 mm² small seed method. At this time, the crystal growth rate is about 3.2 mg/h. Similarly, in this study, it takes 28 hours to grow a 1.03 Carat with a small seed method of 0.5×0.5 mm², and the crystal growth rate is 7.3 mg/h.

It can be seen that the growth rate of synthetic crystals in this study not only has high reproducibility, but its growth rate has reached a leading level, which will be conducive to the industrialization of producing high-quality diamond large single crystals.

4. Conclusion

(1) The radial growth rate of synthetic crystals is greater than its axial growth rate from 8 to 36 hours.

(2) When the height of the crystal bed is selected to be 5 mm, the maximum growth rate of the synthesized crystal in 28 hours reaches 7.3 mm/h, and the weight of the crystal exceeds 1 Carat.

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