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Thermal analysis of the growth process of synthetic diamond in the large volume cubic press apparatus with large deformation of high pressure cell

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ABSTRACT

The temperature-field in diamond synthesis cell was simulated by a finite element method. A three-dimensional model of the China-type cubic press with large deformation of the synthesis cell was established successfully, which has been verified by situ measurements of synthesis cell. In addition, the distributions of temperature and its gradient in the synthesis sample were described. We found there is a large temperature drop in the synthesis sample, which brings some uncertainties in a synthesis process, such as the phenomenon of "wasteland, on which there is no nucleation and growth of diamond". Furthermore, the formation mechanism of wasteland was studied in detail. It indicates that the wasteland is inevitably exists in the synthesis sample, the distribution of growth region of the diamond with hex-octahedral is move to the center of the synthesis sample from near the heater as the power increasing, and the growth conditions of high quality diamond is locate at the center of the synthesis sample. This work can offer suggestion and advice to the development and optimization of a diamond production process.

1. Introduction

It is well known that diamond, with its outstanding physical and chemical properties, is a promising material for mechanical and electrical applications [1,2]. By 2013, annual output of industrial diamond production was about 151×10^9 carats in China, which can be attributed to the use of the China-type large volume cubic press [3–5]. Nowadays, the synthesis sample is up to 34 mm in diameter, which brings about a more homogeneous temperature distribution in the sample. The axial temperature gradient is largely reduced to about 15 °C/mm (200 °C/mm of early one) [6,7]. Heating of the sample is achieved when a current passes through the graphite-tube, which is separated with the sample by an insulating medium [8].

In the P-T phase diagram of carbon, the district for diamond synthesis is a V-shape region bounded by diamond–graphite equilibrium line and metal–diamond eutectic line in the metal solvent-carbon system [1,9]. Diamond growth interval $\Delta T_V^{5\text{–}5.5\ \mathrm{GPa}} > 250\ ^\circ\mathrm{C}$ when the pressure is 5.0–5.5 GPa. Empirically, it is often found that some regions of the synthesis sample are outside the V-shape region in a diamond synthesis process. There is no nucleation and growth of diamond in these regions, which are called "wasteland" in this paper. The wasteland largely reduces efficiency of mass production.

The temperature distribution in synthesis sample plays a crucial role on the diamonds synthesis process, for instance, it is closely connected with the formation of the wasteland. Today, numerical simulation has already become a helpful tool for revealing temperature distribution of crystal growth systems [10–12]. In the past, Gu et al. have simulated the temperature field of diamond high-pressure synthesis system and revealed the temperature distribution in synthesis cell. However, their simulated results showed that the temperature drop $\Delta T_{sample}^{Gu} = 43.9\ ^\circ\mathrm{C}$, axial temperature gradient was 1 °C/mm in the synthesis sample [13]. Obviously, Gu has largely underestimated the temperature drop (ΔT_{sample}^{Gu}), which was less than both the situ measurement results [6] and the $\Delta T_V^{5\text{–}5.5\ \mathrm{GPa}}$. Otherwise, the wasteland would be easily avoided. In fact, the wasteland often takes place in the mass production.

The main deficiency of Gu's work was that they have neglected the deformation of pyrophyllite cube. In the large volume cubic press, six cubic anvils, each with a square anvil tip, are actuated by three pairs of hydraulic rams, forming a cubic cell, within which the sample assembly is compressed [14,15]. During compression, part of the pyrophyllite cube is squeezed to the gap between the sloping sides of the anvils to form gaskets [8,16]. The influences of

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this large deformation and the gaskets on temperature distribution cannot be ignored.

In this paper, simulations are based on the model of the large volume cubic press with large deformation of high pressure cell. The model was improved according to the results obtained in the situ measurements. Large temperature drop was discovered in the synthesis sample, which resulted in some uncertainties in a synthesis process. For that reason, the formation mechanism of wasteland was studied in detail. Selecting diamond with hex-octahedral as an example, we showed its diverse growth regions in the synthesis sample under different powers (3400–3700 W).

2. Modeling and situ measurement

The sizes of component of the deformed synthesis cell are adopted from high-pressure experiments performed on the large volume cubic press under pressure of 5.2 GPa. The pyrophyllite cube is 50.8 mm in side length (55 mm without deformation) and the gaskets are 12 mm in length. The synthesis sample, insulator and heater have height of 26.8 mm, 28.8 mm and 30.8 mm, respectively. Owing to the symmetry, the simulation is carried out on the 1/4 model. Electro-thermal coupling element SOLID69 is used in the model for mapping mesh, as shown in Fig. 1. The mesh size is $1 \times 1 \times 1$ mm^3.

The temperature drop is very large (about 500 °C under synthesis power) in the pyrophyllite cube, which serves as both the pressure-transmitting medium and the insulation material. For the pyrophyllite, different thermal conductivity values depending on the temperature were adopted in the model, as shown in Table 1. Other property parameters referred to Ref. [13].

We ignored the effect of crystal growth on temperature distribution. Since diamond has very high thermal conductivity, the growth of diamond increases the thermal conductivity of part region in the synthesis sample. In addition, the latent heat during the crystal growth procedure will be released. Both of these will decrease the temperature gradient in the cell. But they still cannot effectively diminish the wasteland, and it has been verified in high pressure synthesis experiments.

Situ measurements of temperature were performed in the synthesis cell with gasket size of 12 mm. Points A and B were selected as measuring points, and they were separately located in the center and the end-surface of the synthesis sample (see Fig. 1(c)). K-type nickel–chromium thermocouples with measuring range of −40 °C to 1000 °C and error less than 2.5 °C were used in the situ measurements. The measurements of two points were synchronous. The measurement results showed that the temperatures were 930 °C (A) and 830 °C (B) under the power of 2000 W; axial temperature drop was 100 °C. The simulation results obtained based on our model are 929 °C (A) and 832 °C (B) under the power of 2000 W, which correspond fairly well with the situ measurement results. That means the model is able to predict temperature distribution under higher powers (3400–3800 W).

3. Results and discussion

Temperature contour of the synthesis sample is shown in Fig. 2 (obtained under the power of 3400 W). The temperature gradients are larger in the regions near the heater and the end-surfaces, the contours are denser in these region. By comparison, it is smaller in the center. The yellow, orange and red areas (1330–1422 °C) are in diamond growth temperature region (1330–1550 °C) under 5.2 GPa. Our simulations are in accordance with the experiments. Some synthesis experiments were carried out under 5.2 GPa and showed that diamonds can grow in the synthesis sample when the power is in range of 3400–3800 W.

Fig. 3 shows the temperature distributions on the paths marked in Fig. 2. Temperature reduces from the center to the end-surfaces on axial path 1 and increases from the center to the heater on radial path 2, 3, 4. That means heat transfers from the heater to the center and loses from the end-surfaces of the sample. According to the slope of the four curves, temperature gradients on path 1, 2, 3 and 4 decrease orderly.

We also see from Fig. 3 that heat in the cell is intensively lost from the both ends of the cell. This is an important reason of forming large temperature drop and temperature gradient in the synthesis sample. We predict that the heat loss might be bated by installing heat source

Table 1
Thermal conductivity of pyrophyllite under the pressure of 5.2 GPa.

Temperature T/(°C)	Thermal conductivity κ/W/(m K)
30	4.162
200	4.183
400	4.267
600	3.178
800	3.262
1000	2.571
1200	1.755

* Thermal conductivity increases 0.12 W/(m K) per 1 GPa increment of pressure.

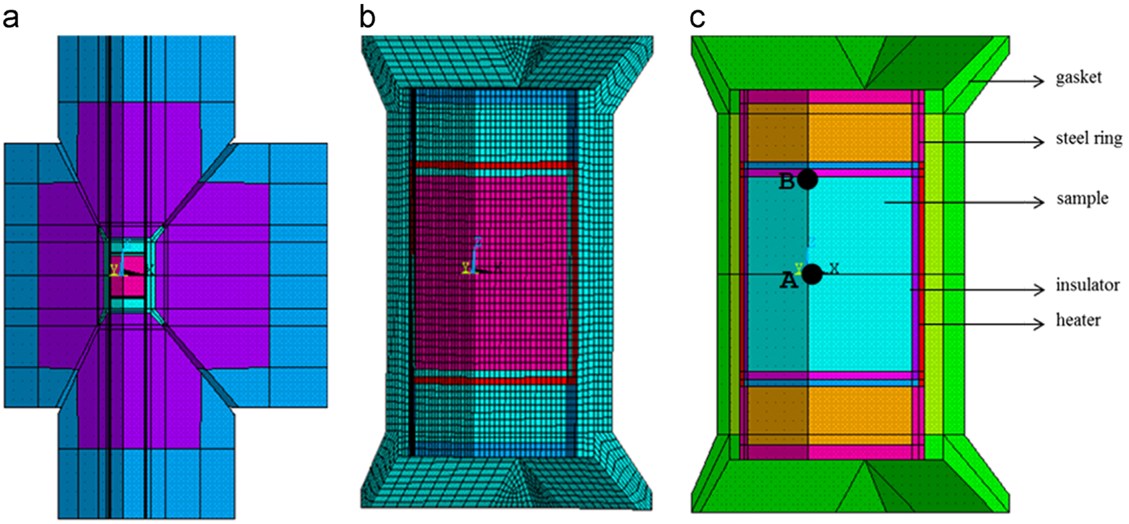

Fig. 1. Geometric model of simplified 1/4 pressure apparatus: (a) overall assembly; (b) and (c) separately refers to the diamond synthesis cell with and without mesh.