The Evaluation of Pressure during Diamond Synthesis in a High Pressure Apparatus

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In this work it was used the system of four die displacement sensors for anvils clearance measurement with the aim to keep watch on pressure variation in "anvil with hollow" type of high pressure apparatus during diamond synthesis. It was shown that natural direct connection between pressure inside reactive cell and height of deformed gasket exists independently of the cause of pressure change. The special inserts and previously sintered metal-catalyst were used to stabilize the process of diamond single crystals synthesis. Their application allowed to reduce pressure fall in a reactionary cell from 0.13GPa/min to 0.02GPa/min, and also to raise yield of high quality diamond crystals.

[Diamond synthesis, high pressure, pressure evaluation, stabilization, displacement sensors]

1. Introduction

The "anvil with hollow" type high pressure apparatus (HPA) makes it possible to create pressures as high as 5GPa and is commonly used both for scientific aims and in industrial production of super hard materials [1,2]. Existing methods of pressure measurement are concerned normally with a lot of practical restrictions and labor-consuming operations because of difficulties in provision of reliable entrance of sensors in the reaction cell of HPA. The tension in the stressed layer (gasket) of the container tears often the sensor leads. This makes the direct measurement of pressure in the range of 5GPa, in this type of apparatus, extremely difficult [3]. This is why indirect methods are normally used. The evaluation of generating pressure is possible by the calibration of cell using reference materials, but only at low temperatures and if there are no processes in the cell which involve a change of volume, related to heating, phase transfer, chemical interaction and so on. At high temperature few methods of high-pressure measurement may be used [4,5]. The mentioned methods of pressure measurement are also labor consuming since it requires input of gauges or sensors in a high-pressure cell. That is why we offer to apply measurements of elastic deformation of a gasket for estimation and monitoring of pressure in a cell. It is known, that during the first stage of HPA loading the extrusion of the gasket material into the clearance between the anvils takes place, but at a certain moment extrusion stops because of the high value of friction forces on the boundary gasket-HPA and the so-called "lock" forms. Further HPA loading leads to elastic strains in the container, gasket and to the generation of pressure in the cell. If any process with change of volume takes place in the cell a redistribution of the pressure between container and gasket arises which leads to an increase or decrease in gasket deformation (increase or decrease in h - clearance between anvils) depending of the sign of volume variation (ΔV) in the cell. If some type of dependence between pressure in the cell and gasket deformation exists it may be used for pressure evaluation by cell deformation measurement. It was determined that at a certain moment after HPA loading, the deformation of the compressible gasket may be described by equations for the elastic strains of matter, particularly by the Murnaghan equation. The latter can be used for high-pressure evaluation by the measurement

of gasket thickness (clearance between anvils).

The problem of high-pressure control during diamond synthesis is very important because of great influence of pressure on the yield and shape of diamond crystals [6]. So, at constant temperature, the averaged yield of diamond crystals grows up exponentially and the quantity of crystals with regular shape has maximum. Diamonds morphology also depends on pressure, varying from octahedrons to cubes as the pressure grows [7]. This is why the problem of high-pressure stabilization during diamond synthesis is also of great interest. It is necessary to note that "anvil with hollow" type of high-pressure apparatus (HPA) has no generally provision for pressure regulation (and stabilization, respectively) during diamond synthesis within sufficient pressure range. It is known that the same problem exists also in the "BELT" type of HPA [8]. So the reaction cell assemblage modifications may be used successfully to reduce non-controllable pressure variation in the cell during diamond synthesis

2. Experimental techniques and results

Experimental data about pressure in the cell at room temperature were obtained using reference materials Bi (I-II 2.55GPa, II-III 2.69GPa), Ti (3.67GPa) and PbSe (4.30GPa). The error in this method of high-pressure measurement is normally no more then 0.05 - 0.08GPa. Data at high temperature (1200 - 1250°C) for the interval 3.5-5.0GPa were obtained through the registration of Cu (copper) melting point by the method of thermal analysis under high pressure [4,9]. The measurements of the gasket height were performed using as die displacement sensors four pairs of digital micrometers installed around the periphery of the dies.

If it is assumed that the HPA operates in the interval of elastic strains of gasket, the area of the gasket does not change after "lock" formation and if the frame and HPA deformation are ignored, than the pressure in the cell as the function on gasket height (h) may be represented as follows:

$$P(\text{GPa}) = 9.5 (X^7 - X^5) (1 - X(X^2 - 1)), \quad (1)$$

$$\text{where } X = (4.19 / (2.14 + h))^{1/3}$$

Function (1) was determined on the base of

Murnaghan's equation [10], which is widely used in geophysics for description of stressed matter behavior. The values of function (1) coefficients are valid for container with initial volume 3.86cm^3 and initial height of gasket 1.45mm . For other type of camera and container they should be determined experimentally. Figure 1 shows a model-input specifications according to function (1) in the interval $0.400 < h < 1.450$ (mm) and experimental data on P-h-dependence.

Fig.1. Relation between pressure in the cell and height of gasket (— theoretic curve, + - calibration points at room temperature, O - experimental points at 1200-1250°C).

It is known, that after achievement of the required value of pressure in HPA, during its operation at high temperature, there are the processes in the cell, connected to change of volume of assembly elements, that results in change of pressure in a reactionary zone. In initial period there is small pressure increment, caused by thermal expansion of assembly elements, and then the fall of pressure, connected to phase transitions in a material of the container. With the aim of stabilize the pressure during diamond synthesis, some different types of reaction cell assemblage were prepared (Figure 2). It was taken into account that the phase transformation in the container material nearby the high temperature zone of reaction cell and fusion of metal-catalyst in the first stage of diamond synthesis make the basic contribution in pressure fall.

Fig.2. Schematic drawing of high-pressure cell assembly; a- standard, b- with insulating insert. 1-container; 2- graphite current leads; 3- heat insulator; 4- metal-solvent; 5- graphite; 6- insulating insert.

The special inserts preventing phase transition in container material were prepared by compacting of zirconium oxide and sodium chloride powder mixtures, and also the

previously sintered metal-catalyst disks with porosity $22\%(\pm 1\%)$ were used.

The initial pressure in all experiments was identical. Temperature was supervised on heating current power, using preliminary calibration of a cell in axes: current power - temperature in a reactionary zone. For each type of high-pressure cell assembly it was made 50 experiments. After extraction of diamonds from a product of synthesis the analysis of their granularity and strength measurements of crystals have carried out.

3. Discussion

Let us note first of all, that the points of curve P on h (Fig. 1), which were obtained as a result of the calibration the HPA both at room temperature and at high temperatures, are rather closely spaced. This means that a natural direct connection between pressure inside HPA and height of the stressed layer exists, independently of the cause of the pressure change - either variation of press-power or heat extension and phase transfer of the cell's elements. Furthermore there were investigated conditions when the press-power is constant and as a consequence of heating, some processes such as phase transfer with change of volume take place in the cell (including graphite-diamond transformation). In this case the change of pressure leads to the redistribution of the pressure between reaction cell and gasket, which leads to variation of the gasket's height, but the sign of "h" reverses, and instead of the function $P=f(h)$ we should use the function $P(H)=f(2a-h)$, where "a" is the value of "h" at the beginning of heating. Experimental data shows that a correlation between h and P also exists in this case (Figure 3).

Fig.3. The variation of pressure in the cell and the height of gasket in the period of heating (press-power is constant).

The maximum on the P-t, H-t (or minimum on h-t) curves at the second minute is connected with the process of heat extension of the cell's elements, which leads to increase of pressure in the cell. The process of phase transition in the cell's elements then begins and pressure ($H=2a-h$, respectively) decreases in the standard cell with rate about 0.13GPa/min . When special inserts and compact metal-catalyst were used, the pressure fall value decrease to 0.02GPa/min (Figure 4). Experimental data shows that performed method of die

displacement measurement (h) is rather sensitive to pressure change in reactive zone and allows to monitor the diamond synthesis. The current pressure may be determined from h - t curves using P - h dependence (Figure 1.) or equation (1) with change of value " h " on $H=2a-h$.

Fig. 4. The variation of gasket height in the period of heating (press-power is constant). 1- standard cell, 2- cell with insulating insert, 3- cell with insulating insert and compact metal-solvent.

Some data, describing process of synthesis and quality of synthesized diamond crystals, are brought in Table 1. One may note that the change of the average output, fracture composition and strength of crystals is in qualitative connection with curves P - t and h - t character.

Table 1. Performance data of synthesis process and diamonds strength

Type of cell assemblage		Average yield (g)	Basic fraction (μm)	Average strength (variance) of fracture 400/315 μm (N)
1	Standard	3.040	400/315	62.9 (± 23.5)
2	With insulating insert	2.504	500/400	78.3 (± 24.6)
3	With insulating insert and compact metal-solvent	2.471	500/400	117.8 (± 20.2)

Really, the less h (P) variation is during synthesis period, the less average yield of crystals and better their quality (size of the basic fracture, average strength). The

raised average yield of diamonds in case of standard assemblage of the container is explained by substantial pressure growth in initial period of synthesis, connected with thermal expansion of assembly elements. As the speed of nucleation and growth rate of diamond crystals rises exponentially with increase of pressure, there are more centers of crystallization, the growth rate of crystals is higher and total yield of crystals more in standard case, than in case 2 and 3. At the same time, the relatively quickly growing crystals of diamond get more structural defects and have smaller strength. Plenty of crystallization centers in this case results in displacement of a maximum of crystals sizes distribution (basic fraction) to smaller values (400/315 microns).

Thus, the use of insulating inserts and previously compacted disks of a metal-solvent results in reduction of uncontrollable pressure fall in a reactionary cell and, hence, to stabilization of synthesis and improvement in diamond crystals quality.

As to suggested method of pressure control, we should note that it does not claim to be a standard. It is rather limited and imposes a lot of restrictions on the experimental technique. But with respect to the absence simple and reliable methods of the direct measurement of pressure, it helps to keep watch on processes, which take place in high-pressure apparatus.

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