Nucleation in High-Pressure Chamber as a Result of a Direct Graphite-to-Diamond Transition. Stochastic Approximation.

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Abstract. In the stochastic approach, the model of diamond nucleation in high pressure chamber (HPC) is discussed as a result of direct graphite-to-diamond transition. The presented considerations regarding the distribution of the number of nuclei N depending on the intensive parameters P and T, as well as immediate counting of the formed diamond crystals lead to the opportunity of using the normal distribution (Gaussian distribution). As a result, an analytical expression for N is obtained that allows determining it as a function of the measured pressure $P_{measured}$ at a fixed temperature.

The problem of the formation of critical diamond nucleus is discussed in a number of papers [1-3], which deals with various models of spontaneous origination of critical diamond nucleus from oversaturated carbon solution in a metal-solvent within the diamond (P,T) stability region.

However, it should be noted that according to the results of [4,5] the probability of fluctuation nucleation of new diamond phase is negligible for both homogeneous and heterogeneous for nucleation. Let us also note that traditional experiments in the development of diamond synthesis regimes proceed as follows: at T = const a series of P are examined in increments of 0, 1-0, 2 GPa, and vice versa, at P = const (within the stability region) a series of T are examined in increments specified by the experimenter, typically $50-100^{\circ}C$. Such experiments are aimed at identification of either maximum diamond yield or specific quality indicators of diamond crystals. After fulfilling similar experiments (assuming that diamond nuclei are formed in the first seconds of the synthesis process and then grow, that is their number remains constant in HPC and equal to the number of the grown crystal), we obtain graphs of the number of nuclei N as a function of their intensive parameters P and T (Figs. 1 and 2).



Fig.1. The number of diamond crystals versus T at P = 4.5 GPa

The number of nuclei embryos identified with the number of diamond crystals was determined by immediate counting. Such assumption makes it possible to check the experiments on diamond growth at fixed P and T, for different times of the synthesis process. The experiments have shown that the number of crystals during the synthesis process can be considered the same at the same P and T, and the weight increases due to the crystals growth, i.e. build-up of their mass.



Fig.2. The number of diamond crystals versus P at T = 1500K

Let us consider nucleation of diamond as a consequence of the possible realization of the conditions of direct graphite-to-diamond transition [7,8] arising in local contact regions, surface imperfections of graphite particles in HPC [8]. Since the current methods of (P, T) parameters measurement (reference elements and compounds, thermocouples) don't provide their measurements in $V >> 4\pi r_{kr}^3/3$, $r \sim 10^{-9} m$, our understanding is limited by averaged macroscopic values of temperature and pressure within HPC.



Fig.3. Characteristic distribution of peak pressure. 1 – measured macroscopic pressure, 2 - random distribution of local pressure peaks in $S \sim \pi r_{kr}^2$ areas, which has the character of some baric "noise" on the background of the measured pressure. Here *L* is a coordinate along any selected direction in HPC

However, in any case there are small contact surfaces in HPC, and it is natural to assume the possibility of peak values of above parameters for the areas with contact surfaces $S \sim \pi r_{kr}^2$. For illustration

purposes, Fig. 3 presents qualitatively the raised suggestion for the pressure in the homogeneous HPC. A similar situation relates to the temperature, since the flow of electric current (for heating the HPC reaction mixture) is caused by the contacts between graphite particles in the presence of the solvent metal (catalyst). Consequently, there are local areas where maximum current densities are realized, and hence maximum temperatures. These areas align with minimum surfaces of grain contacts. The foregoing is shown in Fig. 4.



Fig. 4. Characteristics of the distribution of typical temperatures. 1 – generated temperature "noise" at a level of macroscopic temperature background, 2 - measured temperature.

It should be noted that the above temperature instability may exist very limited time, as the high thermal conductivity of the system quickly brings it to the measured value. The coincidence of peaks of local pressures and temperatures that are randomly distributed in the HPC volume is obvious. For illustration purposes, let us turn the positive temperature axis through 180 degrees and bring in coincidence with Fig. 3, as shows Fig. 5.



Fig. 5. The shaded area is the areas of the local realization of the conditions of direct graphite-to-diamond transition ($P \sim 10-13GPa$, $T \sim 3000$ ⁰K according to [6,7]).

It is obvious from above reasoning that by increasing or decreasing the heating current (i.e. the level of temperature "noise"), it is possible to regulate the number of crystallization centers.

Similar considerations are valid for pressure, the less compliant parameter in industrial environments. From further considerations, we exclude those peak pressure and temperature values lying below the measured values, because they are out of physical interest within the framework of our task. Let us determine the nature of peak pressure distribution. It is known [9] that different graphite types have different L_c and L_a (L_c , L_a are size factors for perfect graphite crystals):

for
$$(C-3)L_a = 475 \text{ Å}$$
, $L_c = 145 \text{ Å}$;
for (GMZ OSCh – 7.3), $L_a = 601, L_c = 160$;
for GSM – 1, $L_a = 1250, L_c = 375$.

Let us choose any of them. Obviously, it is the size factor of a distribution of possible local pressure peaks, and since $L_k \ll D$ (where D is the HPC diameter), the number of probable peaks is sufficiently large, and, therefore, according to the limiting theorem of probability theory [10-12] our distribution of peak values tends to a normal distribution or Gaussian distribution [13].

Let us we write the normal distribution in the adopted symbols for the probability density of the amplitude P values:

$$f(P) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[\frac{\left(P - \mu(P_{measured})\right)^2}{2\sigma^2}\right]$$
(1)

The number of peak pressures $P_{transition}$ or equivalently, the possible number of nuclei (N) is

$$N(P_{measured}) = N_0 \frac{1}{\sigma \sqrt{2\pi}} \int_{P_{per}}^{\infty} \exp\left[\frac{\left(P - \mu(P_{measured})\right)^2}{2\sigma^2}\right] dP, \qquad (2)$$

where $N_0 = V_{graf} / L_a^3$ is a total possible number of peak P, $\mu(P_{measured})$ is a center of symmetry of the normal distribution, σ is dispersion, $P_{transition}$ is pressure of graphite-to-diamond direct phase transition.

The experimental graph of the amount of diamond crystals as a function of pressure (Fig. 2) has an inflection point at 4.5 *GPa*. It is obvious that in the discussed model, when the measured pressure is 4.5 *GPa*, the top of pressure distribution will pass through $P_{transition}$. Let us illustrate this in Fig.6. Integral expression (2) is the shaded part of the area under the distribution curve that lies to the right of $P_{transition}$.

 $\mu(P_{measured})$ - is the function that determines the position of the center of the distribution curve depending on $P_{measured}$ and fulfils the following condition:

$$P_{transition} - \mu \left(P_{\text{inflection}} \right) = 0 \tag{3}$$

Assuming linear dependency in (3), we have

$$\mu = P_{transition} / P_{\text{inflection}} , \qquad (4)$$

where $P_{\text{inflection}}$ is the experimental value on the integral curve (Fig. 2).



Fig. 6. Distribution of peak pressures as a function of the measured macroscopic pressure.

In (2) let us change the variable

$$\frac{P - \mu(P_{\text{inflection}})}{\sigma} = z, \qquad dP = \sigma dz \tag{5}$$

Then the lower limit of integration

$$P_{transition} = \frac{P_{\text{inflection}} - \mu(P_{measured})}{\sigma}.$$
(6)

Consequently,

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$$N\left(u_{measured}\right) = N_0 \frac{1}{\sqrt{2\pi}} \int_{\frac{P_{ransition}}{\sigma} - \mu(P_{measured})}^{\infty} \exp\left(-\frac{z^2}{2}\right) dz = N_0 S\left(\frac{P_{transition} - \mu(P_{measured})}{\sigma}\right)$$
(7)

$$S(x) = \begin{cases} \frac{1}{2} - \Phi(x) & x \ge 0\\ \frac{1}{2} + \Phi(x) & x < 0 \end{cases}$$

$$\tag{8}$$

where $\Phi(x)$ is the error integral [14].

To determine dispersion σ , let us choose two points on experimental integrated curve, P_1 and $P_2 = P_{\text{inflection}} \approx 5$ GPa. For the selected points, we have:

$$\frac{N(P_1,l)}{N(P_2,l)} = \frac{S\left(\frac{P_{transition} - \mu P_1}{\sigma}\right)}{S(0)}$$

where S(0) = 1/2; let us denote $N(P_1)/N(P_2)$ by K, then $K/2 = S(P_{transition} - \mu P_1)/\sigma$, from where

$$S^{-1}\left(\frac{1}{2}K(l)\right) = \frac{P_{transition} - \mu \cdot P_{1}}{\sigma}, \ \sigma = \frac{P_{transition} - \mu \cdot P_{1}}{S^{-1}\left(\frac{1}{2}K(l)\right)}.$$
(9)

Here *K* is a value depending on the mark of graphite. Substituting numerical values, we obtain dispersion of the distribution curve, which determines the shape of the curve for each l. As a structural characteristic of the used graphite, l determines the shape of the curve in Fig. 2 and affects the character of the distribution when using different types of graphite.

The results of the above model agree fairly well with the experimental data, as shown in Figs. 7 and 8.



Fig. 7. Distribution of the number of nuclei vs. pressure for GMZ-OSCh graphite (1 – experiment, 2 - theory).



Fig. 8. Distribution of the number of nuclei as function of pressure tor MG-OSCh graphite. 1 - experimental curve, 2 - theoretical curve.

In the discussed model, the case of close location (in the geometrical sense) of the originated nuclei is obviously realized. After passing into the stage of diffusion growth, they interfere with each other. Images in Figs. 9, 10, and 11 present typical situations.



Fig. 9. Synthetic diamond crystals.



Fig. 10. Synthetic diamond crystals. Arrows indicate typical situations of incomplete crystallization.



Fig. 11. Synthetic diamond crystal. The arrow shows the crystal surface oriented to the nearest neighbor, i.e. the surface of a defective imperfect growth.

Finally, analyzing the experimental results, we come to the unequivocal conclusion that the nucleation of diamond during synthesis in a high-pressure chamber can be described as a direct "graphite-to-diamond" first order phase transition, whereas the subsequent growth of critical nuclei in the region of thermodynamic stability of diamond as a diffusion process in the solution-melt model.

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