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# Mechanism for diamond single crystal synthesis from diamond nanoparticles at high pressures and temperatures

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A mechanism for the formation of submicron diamond single crystals from diamond nanoparticles under high pressure and high temperature (HPHT synthesis) in the presence of organic compounds, which contain C–O–H groups, without a metal catalyst is proposed. The mechanism is based on the concept that under certain conditions, an additional pressure (with respect to the applied static one) is produced in the process of pyrolysis of such compounds and ensures the formation of macroscopic single crystals.

**Keywords:** HPHT diamond synthesis, diamond nanoparticles, macroscopic diamond single crystals.

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The authors of [1,2] were the first to demonstrate experimentally the synthesis of diamond single crystals up to 15 $\mu$m in size from a reaction mixture of a powder of detonation diamond nanoparticles with an approximate size of 4 nm (DND4) and additives in the form of compounds containing C−O−H groups, which was subjected to high-pressure (5−8 GPa) high-temperature (1300−1800 °C) processing (HPHT synthesis). The indicated pressure and temperature are insufficient for the well-known method of synthesis of diamond from graphite in the presence of a metal catalyst (see, e.g., [3]).

We know of two hypotheses that explain the synthesis of submicron diamond single crystals (MDSCs) under the specified conditions.

The first one [2] suggests that MDSCs are formed from DND4 nanoparticles via the oriented attachment mechanism, which was discussed in [4]. This mechanism implies „face-to-face“ attachment of DND4 particles to each other. Organic compounds serve in this case as a medium that facilitates the orientation of DND4 nanoparticles relative to each other [2].

The second proposed synthesis mechanism associates the formation of MDSCs with the dissolution of DND4 particles in a supercritical hydrocarbon fluid and subsequent recrystallization [5,6].

None of these hypotheses provides an explanation for the observed spatial nonuniformity of microcrystal formation. The scanning electron microscopy (SEM) data reveal that MDSC synthesis proceeds in separate small (compared to the size of the sample) „pore-nests“ (Figs. 1, *a*, *b*).

Let us examine the synthesis in detail [7,8] in the context of the proposed model (Fig. 2).

The model relies on the hypothesis that the $P-T$ parameters are exceeded in certain local regions (closed pores). In these regions, pressure values $P = P_0 + \Delta P$ are higher than pressure $P_0$ averaged over the volume of the high-pressure chamber and fall within the diamond crystallization region (Fig. 3).

Assessing the values of $P$ and $T$, we assume that the above compounds containing $-$O$-$H groups and introduced into the reaction mixture pass into a supercritical state (fluid) upon reaching a certain temperature. This fluid may be regarded both as a liquid and as a gas in the assessment of pressure.

To obtain a qualitative estimate of the additional pressure, we assume that the fluid is an ideal gas [9,10]. Additional pressure $\Delta P_s$ induced by the introduction of the additive into the reaction mixture is then calculated as

$$\Delta P_s = \frac{\rho}{M} RT.$$

Let us illustrate this by calculating the additional pressure arising in a closed pore at temperature $T \approx 1400\,^{\circ}$C in the case where the additive is pentaerythritol $C(CH_2OH)_4$ with molar mass $M \approx 136$ g/mol. It is assumed that pentaerythritol in such a pore retains density $\rho \approx 1.4$ g/cm$^3$ that it had under normal conditions. Inserting $R \approx 8.3$ J/(mol · K) into the formula, we obtain $\Delta P_s \approx 0.12-0.13$ GPa.

It is evident that the compound containing C−O−H decomposes in the process of heating. There are several possible decomposition options for pentaerythritol:

1) $C(CH_2OH)_4 = 4H_2 + CH_4 + 4CO$ (nine molecules);
2) $C(CH_2OH)_4 = 3CH_4 + 2CO + O_2$ (six molecules);
3) $C(CH_2OH)_4 = 3CH_4 + 2CO_2$ (five molecules).

Naturally, the increase in pressure is directly proportional to the number of molecules; in the examined case of pentaerythritol, this increase after decomposition is $\Delta P = (5-9)\Delta P_s \approx 0.65-0.78$ GPa.

The increase in pressure obtained with ethanol, glycerin, and pentaerythritol additives is indicated in the table. Average pressure values are listed.

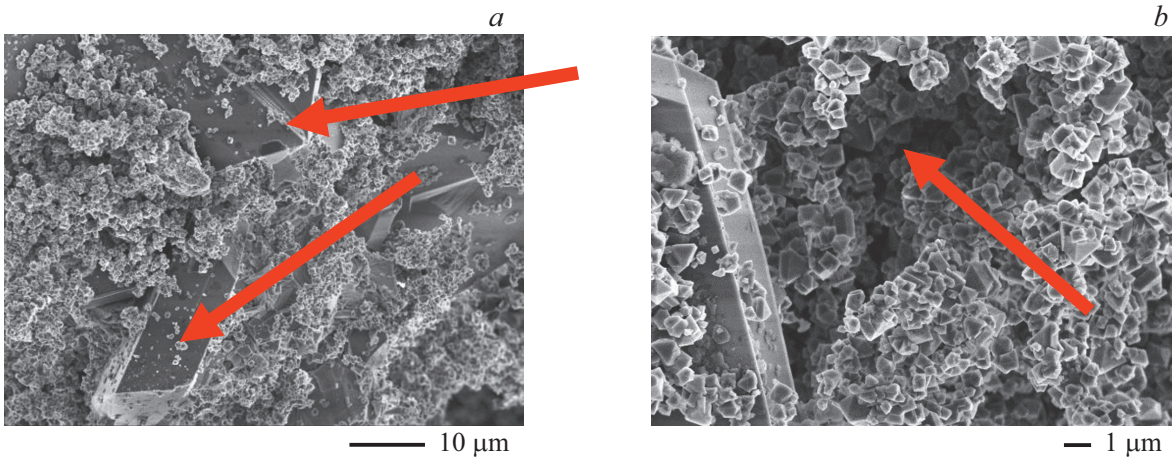


**Figure 1.** SEM images of „pore-nests" surrounded by synthesized micrometer-sized diamond single crystals. Detonation diamonds with a particle size of about 4 nm and pentaerythritol were used as a reaction mixture for synthesis at a pressure of 7 GPa and a temperature of 1400 °C. *a* — Arrows indicate microcrystals larger than 10 $\mu$m; *b* — arrows indicate a macropore the inner surface of which is coated with grown microcrystals.

Pressure increase (in GPa) resulting from the decomposition of certain C−O−H additives

| Parameter | Additive | | | | | |
|---|---|---|---|---|---|---|
| | Ethanol $C_2H_5OH$ | | Glycerol $C_3H_5(OH)_3$ | | Pentaerythritol $C(CH_2OH)_4$ | |
| Density under normal conditions, g/cm$^3$ | 0.79 | | 1.25 | | 1.39 | |
| Increase in the number of molecules after decomposition | 10/3 | | 15/2 (in the presence of $C_2H_4$) | | 6 | |
| $T$, °C | After decomposition at the critical point | After decomposition to individual atoms | After decomposition at the critical point | After decomposition to individual atoms | After decomposition at the critical point | After decomposition to individual atoms |
| 1300 | 0.73 | 2.2 | 1.23 | 2.4 | 0.78 | 2.7 |
| 1500 | 0.96 | 2.9 | 1.50 | 2.8 | 0.95 | 3.1 |
| 1800 | 0.30 | 3.0 | 2.23 | 3.2 | 1.08 | 3.8 |

The $\Delta P$ value given in the table is added to the static pressure. The total pressure may reach (and even exceed) the pressure required for crystallization of diamond from graphite at temperature $T \approx 1200-1800$ °C (Fig. 3).

It can be seen from the decomposition formulae for pentaerythritol that the bulk of compounds containing C−O−H groups remain undecomposed to free carbon atoms at the critical point. However, a small fraction of free carbon atoms does form and becomes involved in the formation of diamond microcrystals. If no free carbon atoms are formed from C−O−H-containing compounds at the $P-T$ parameters set, the proposed model suggests that the formation of diamond microcrystals should be impeded. This was verified experimentally. Diamond microcrystals did not form with a benzene additive, which has a binding energy exceeding those of the compounds listed in the table.

Let us review once again the assumptions made in constructing the proposed model.

At elevated pressure in a closed micropore, its walls were assumed to be impermeable to fluid in the supercritical state. In the contrary case, the static pressure in a pore should not differ from the pressure outside. Notably, the excess pressure in a pore should not exceed the tensile strength of the wall material. This assumption appears to be reasonable, since a high pressure is established before the initiation of heating in actual experiments on HPHT

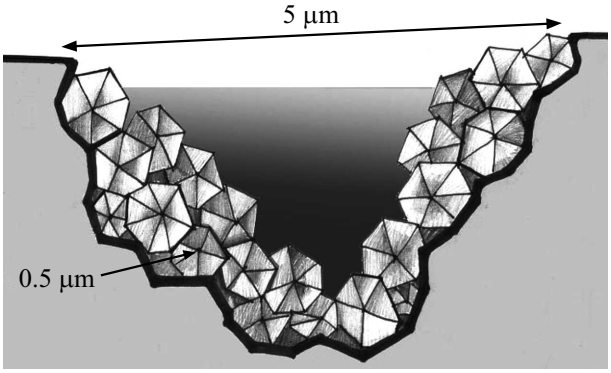


**Figure 2.** Schematic representation of a single micropore with its inner surface coated with synthesized diamond microcrystals.

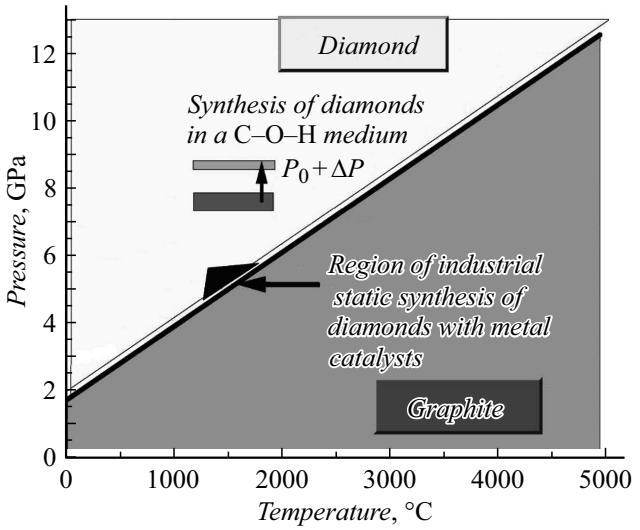


**Figure 3.** Section of the carbon phase diagram showing typical $P-T$ regions of industrial synthesis of diamond from graphite with a metal catalyst and synthesis of MDSCs from DND4 nanoparticles.

diamond synthesis, and the synthesis period is several seconds long [1.6]. This implies that the wall material in (at least a fraction of) pores is a forming diamond phase. This material may be impermeable to supercritical fluid, and its tensile strength is sufficient for the model to remain valid. As is known, the compressive strength of synthetic diamond crystals is close to 17 GPa.

The ideal gas law is used in the model to estimate the excess pressure in a pore. This is the crudest assumption in the proposed model. It remains to be seen how accurate it is for supercritical fluids. We believe that this assumption does not alter the obtained results qualitatively.

Thus, a model for the formation of submicron diamond single crystals from diamond nanoparticles at high pressure and temperature (HPHT synthesis) without a metal catalyst and in the presence of certain compounds containing C−O−H groups was proposed. Notably, natural diamond deposits have the shape of giant pipes.

The model is based on the observed effect of spatial nonuniformity of microcrystal synthesis, which is confined to specific regions („nests“) that are small in size compared to the entire sample, and on the concept of an increase in pressure as a result of decomposition of C−O−H-containing compounds in closed cavities (pores) of the sample.

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### Conflict of interest

The authors declare that they have no conflict of interest.

## References

[1] S.V. Kidalov, F.M. Shakhov, A.V. Shvidchenko, A.N. Smirnov, V.V. Sokolov, M.A. Yagovkina, A.Y. Vul', Tech. Phys. Lett., **43** (1), 53 (2017). DOI: 10.1134/S1063785017010084.
[2] A.T. Dideikin, E.D. Eidelman, S.V. Kidalov, D.A. Kirilenko, A.P. Meilakhs, F.M. Shakhov, A.V. Shvidchenko, V.V. Sokolov, R.A. Babunz, A.Ya. Vul, Diamond Relat. Mater., **75** (3), 85 (2017). DOI: 10.1016/j.diamond.2017.02.009
[3] F.P. Bundy, Science, **137**, 1057 (1962). DOI: 10.1126/science.137.3535.1057
[4] W. Lv, W. He, X. Wang, Y. Niu, H. Cao, J.H. Dickerson, Z. Wang, Nanoscale, **6** (5), 2531 (2014). DOI: 10.1039/C3NR04717B
[5] F.J. Humphreys, M. Hatherly, *Recrystallization and related annealing phenomena* (Elsevier, 2004), p. 451.
[6] F.M. Shakhov, A.M. Abyzov, K. Takai, J. Solid State Chem., **256**, 72 (2017). DOI: 10.1016/j.jssc.2017.08.009
[7] F.M. Shakhov, S.V. Kidalov, P.G. Baranov, R.A. Babunts, D.A. Sakseev, A.E. Aleksenskii, M.V. Baidakova, A.Ya. Vul', *Sposob polucheniya kristallicheskikh almaznykh chastits*, RF Patent No. 2576055 (applied on December 9, 2013; published on February 27, 2016).
[8] F.M. Shakhov, S.V. Kidalov, A.Ya. Vul', *Sposob polucheniya kristallicheskikh almaznykh chastits*, RF Patent No. 2628617 (applied on November 21, 2015; published on August 21, 2017).
[9] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, *Molecular theory of gases and liquids* (Wiley, N.Y., 1954).
[10] L.D. Landau, E.M. Lifshitz. *Statistical physics*, 3rd ed. (Elsevier, 1980), vol. 5, pt. 1.

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