

PRESSURE-DEPENDENT RATES OF DIAMOND NUCLEATION AND CRYSTAL GROWTH IN K-Na-Mg-Ca-C-CARBONATE-CARBON MELT-SOLUTION

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Experimental study of diamond mass crystallization in multi-component K-Na-Mg-Fe-Ca-C-carbonate-carbon melt-solution was earlier carried out at pressure 8.5 GPa and variable temperature in the 1300 - 1720⁰ C range [1]. Thus, such important kinetic characteristics as nucleation density of diamond phase and growth rate of diamond crystals have been studied in dependence of temperature at constant pressure. A certain connection of the kinetic parameters of diamond crystallization with *PT* conditions does not contradict to available estimations [2, 3], is established.

Studying the processes of diamond crystallization in carbonate melts, which are chemically similar to growth environment of natural diamonds [4, 5], has an essential influence on development of synthetic chemistry of diamond. It is caused that efficiency of mass crystallization of «carbonate-synthetic diamond» is close to that of diamond synthesis in the melts of heavy metals (Fe, Ni, Mn, Co, etc.). Possibility of diamond formation in the metallic melt-solutions of carbon has been predicted by the author of the first realistic curve of graphite-diamond equilibrium curve which was calculated using thermodynamic data [6]. This forecast has been experimentally realized in Sweden [7] and the USA [8] in 1950th. High kinetic efficiency of mass crystallization of «metal-synthetic diamond» became a basis for industrial chemical technology of diamond synthesis which has had a wide development.

At the same time, growth features of "carbonate-synthetic" and "metal-synthetic" diamonds as well as physical properties causing their real doped structure are various. Influence of chemical peculiarities of growth melts onto this difference is definable. Similarly, mechanisms of face growth have some distinctions of basic value. In case of "carbonate-synthetic diamond", octahedral faces dominate in crystal morphology and, correspondingly, "octahedral growth layers" are the controlling factor in formation of octahedral faces that is also typical for the natural mantle-derived diamonds (the natural diamonds consist of the octahedral growth pyramids exclusively). It contrast, a cubic-octahedron crystal morphology (the inner crystal structure is presented by combination of octahedron and cubic growth pyramids) is dominating in formation of "metal-synthetic diamond". These features of growth mechanism and chemistry of growth melts define structures and concentration of growth inclusions, structural impurities in diamond crystals and, accordingly, physical and mechanical properties of both the types of synthetic diamonds under consideration. Also, an important point is the radical chemical difference of the carbon solvents in each case. This determines their contrast behavior in the ecological plan in case of industrial application. The heavy metals participating in the technology of «metal-synthetic diamond» become especially dangerous to environment in a finishing stage of a chemical-work cycle. It happens because the heavy metals are translated into soluble forms while diamond fraction is under extraction from the synthesis products. Removal of residual carbonate substance from a technological product (without heavy metals) at extraction of diamond fraction can be carried out in ecologically safe way.

The objective of present experimental research is studying of relation of kinetic parameters of diamond crystallization in carbonate-carbon melts with pressure (lowering in a direction to the graphite-diamond equilibrium curve) at constant temperature. It is expected that formation of diamond fraction with rather larger «carbonate-synthetic diamond» single crystals under conditions of mass crystallization can be realized. At the same time, revealing the regularity of diamond crystallization in carbonate-carbon melt can be of interest not only for synthetic chemistry of diamond as a super-hard material, but also for clearing kinetic features of natural diamond formation in the mantle carbonatite growth environment.

Experimental procedure

As starting materials we have used a homogenized mixture of carbonates of the composition (wt. %): K₂CO₃ 35.0, Na₂CO₃ 10.0, MgCO₃ 25.0, CaCO₃ 30.0, which is a Fe-free version of carbonatite composition studied earlier [1]: K₂CO₃ 27.21, Na₂CO₃ 2.89, MgCO₃ 17.36, CaCO₃ 26.91, FeCO₃ 25.63. To a large degree, both the carbonatite compositions are chemical replicas of the carbonatite

end member for multi-component carbonate-silicate compositions of primary carbonatite inclusions in Botswanian diamonds [9]. Graphite is used as a starting carbon material. The runs were done at high-pressure vessel of the toroidal "anvil with a hole" type and a cell made from lithographic stone. A tubular graphite heater was used at standard temperature of 1610 °C and pressure variable within the 7.0 – 8.5 GPa range for time duration of 5 – 30 min. The accuracy of estimation of pressure and temperature is ± 0.1 GPa and $\pm 20^\circ\text{C}$, correspondingly. Experimental samples were investigated in the IEM RAS with the use of electron microscope Tescan Vega II XMU. Quantity of spontaneously formed diamond crystals in the volume unit of the sample after quenching and solidification of the growth melt was taken as the conventional indicator of nucleation density for diamond phase («survived nucleation centers»).

Experimental results

Conditions of the experiments are presented on the fig. 1. By the PT parameters, all the experimental points are in the field of thermodynamic stability of diamond (in the region of labile carbon solutions oversaturated in respect to diamond [3]. The samples obtained (dark and light phases are diamond and quenching melts, respectively) are represented on figs. 2 – 13. It allows to study the change of crystallization rate of diamond with pressure decrease and estimate a direction of oversaturation reduction for carbon solution in respect to diamond in dependence of PT – parameters. Also, the PT - experimental points of earlier experiments [1] are put on the fig. 1 for the 1300 – 1750°C temperature interval at constant pressure of 8.5 GPa (time duration 30 minute). All this makes evident that degree of carbon oversaturation in respect to diamond in carbonatite melts decreases at direction to the graphite-diamond equilibrium line.

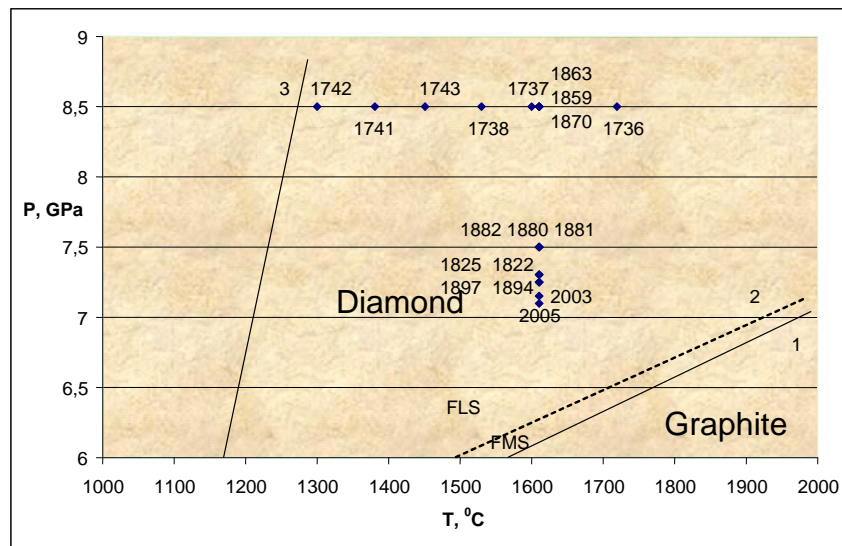


Fig.1. Experimental conditions on the PT -diagram of diamond crystallization (black points and numbers of the runs): 1 - graphite-diamond equilibrium curve, FLS and FMS, respectively, regions of labile and metastable oversaturation of carbon solutions with respect to diamond, 2 - kinetic boundary FLS/FMS, 3 - line of eutectic melting temperature for the carbonate-graphite mixture in dependence of pressure

$P = 8.5$ GPa

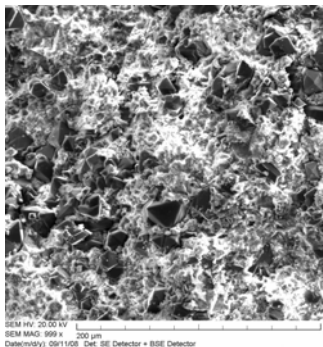


Fig.2. Run №1863 (3 min)

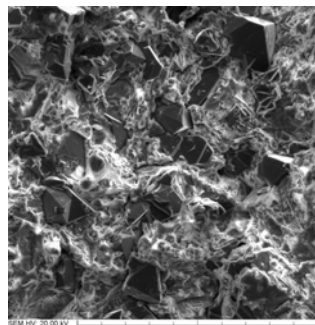


Fig.3. Run №1859 (10 min)

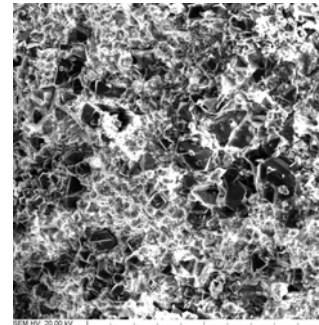


Fig.4. Run №1870 (30 min)

In the experiments 1859, 1863 and 1870 (figs. 2-4), intensive spontaneous diamond nucleation with density value from $1.7 \cdot 10^4$ to $1.0 \cdot 10^5$ grains/mm³ and average linear size of crystals of 30 μ m (the minimal and maximal size are 9 and 45 μ m, correspondingly) is observed.

P = 7.5 GPa

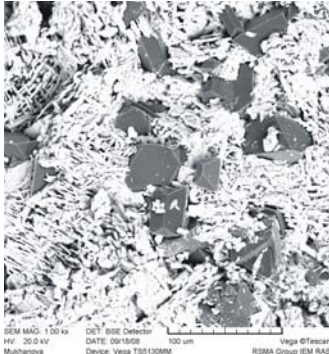


Fig.5. Run №1882 (5 min)

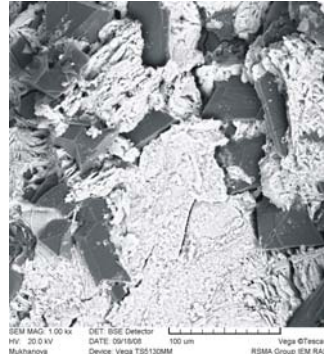


Fig.6. Run №1880 (10 min)

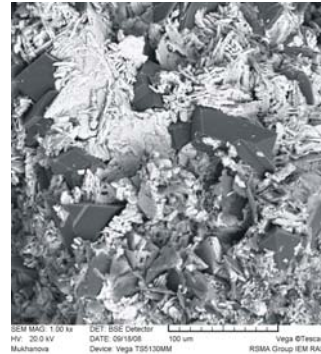


Fig.7. Run №1881 (30 min)

For experiments 1880 - 1882 (figs. 5-7) at lower pressure, the average linear size of crystals is 60 μ m (minimal and maximal sizes are 15 and 160 μ m, correspondingly) and the density nucleation varies from $1.5 \cdot 10^3$ to $5.0 \cdot 10^3$ grains/mm³.

P = 7.3 GPa

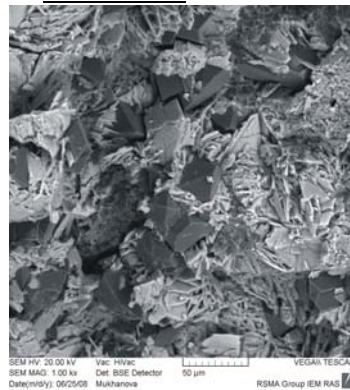


Fig.8. Run №1825 (5 min)

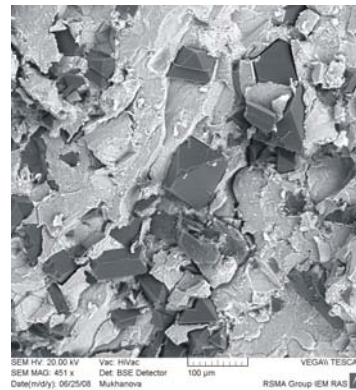


Fig.9. Run №1822 (30 min)

At the further pressure decrease in the experiments 1822 and 1825 (fig. 8, 9), spontaneous nucleation is characterized by values within $1.8 \cdot 10^3$ – $1.0 \cdot 10^4$ grains/mm³, and the average linear size of crystals reaches 80 μ m (minimal and maximal sizes are 18 and 140 μ m, correspondingly).

P = 7.25 GPa

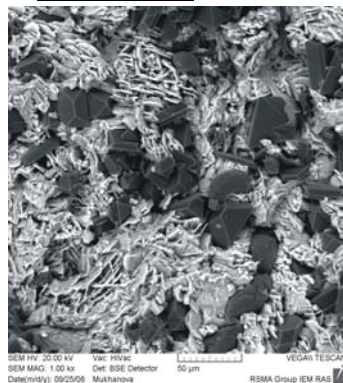


Fig.10. Run №1897 (5 min)

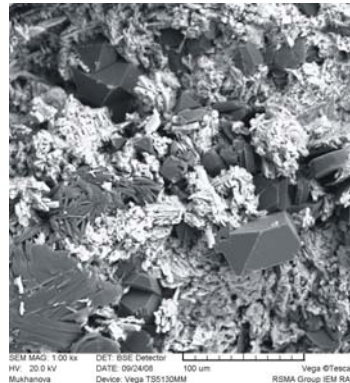


Fig.11. Run №1894 (10 min)

At pressure decrease to 7.25 GPa for experiments 1894 and 1897 (fig. 10, 11), the density of spontaneous nucleation is $2.4 \cdot 10^3$ - $4.2 \cdot 10^3$ grains/mm³, the linear size of crystals – 70 μ m (minimal

and maximal sizes are 13 and 130 μm , correspondingly). Thermodynamically unstable graphite phase (formed as black brilliantly shining single crystalline plates) together with diamond appears in the quenching melt. It is a sort of a special signal that a critical border for a field of spontaneous nucleation of diamond (i.e., region of labile oversaturation of carbonate solution with dissolved carbon in respect to diamond) is approached.

P = 7.15 GPa

P = 7.1 GPa

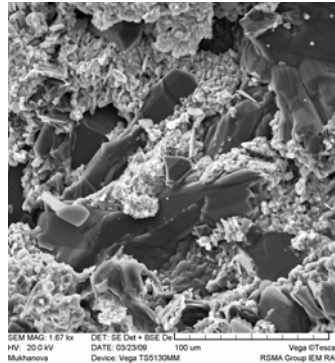


Fig.12. Run №2003 (30 min)

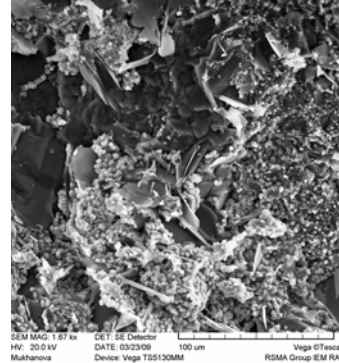


Fig.13. Run №2005 (30 min)

At lowest pressures of 7.15 GPa in the experiment 2003 (fig. 12) and 7.1 GPa in the experiment 2005 (fig. 13), spontaneous diamond nucleation is terminated and diamond seeded growth is only possible (region of metastable oversaturation with respect to diamond of carbon solutions in carbonate melts). Numerous single crystalline plates of thermodynamically unstable graphite which are formed as a result of mass spontaneous crystallization are present in the quenched melt.

Discussion

Diamond nucleation density and single crystal size in dependence of pressure under the conditions of spontaneous mass crystallization within the 7.0 - 8.5 GPa pressure range at constant temperature 1610 °C and time duration 5 – 30 min. are changeable. Linear size of diamond single crystals increases with pressure decrease for each of the time duration value (fig. 14).

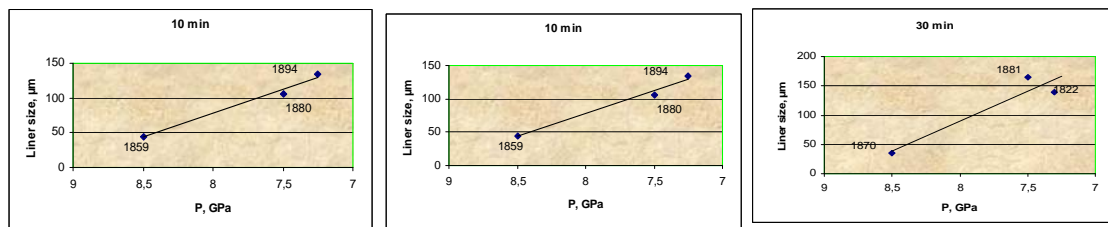


Fig.14. Linear size of diamond crystals in dependence of pressure

Diamond nucleation density decreases with pressure lowering for each of the time duration value (fig. 15). It was also found that the linear size of diamond single crystals increase exponentially in dependence of time duration (fig. 16) that can be explained as the “volume loss” effect.

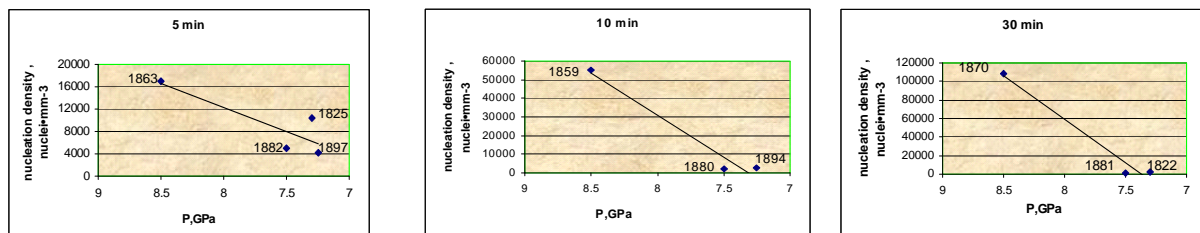


Fig.15. Diamond nucleation density in dependence of pressure

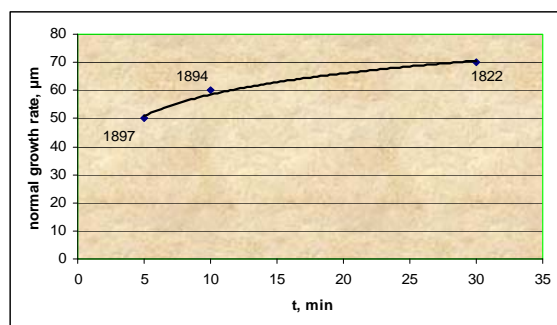


Fig.16. Normal rate of diamond single crystal growth

The effect is a result of transformation of less dense graphite into more dense diamond under the conditions of strong compression of the sample. The transformation leads to local pressure decrease (because the general loading on the sample is fixed) that leads to decrease of carbon oversaturation in the carbonate melt-solution to the point of disappearance at the FLS/FMS boundary conditions. Thus, the maximal size of diamond crystals can be expected in any critical point for the time duration value for which carbon saturation in respect to diamond is realized, and diamond growth is terminated because of that.

Thus, a change of carbon oversaturation in respect to diamond in carbonate growth melt-solution, as the main moving force of the process of diamond crystallization in the PT field of stability, is studied. It is found that the maximal size of spontaneous diamond crystals is expected at a low pressure region (7.25 - 7.3 GPa) for the constant temperature of 1610°C and any critical time duration. The result obtained is important for the further research of diamond mass crystallization and single crystalline seeded growth in the conditions of high pressures and temperatures.

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