

## DIAMOND CRYSTALLIZATION IN CARBONATE-CARBON MELTS OF MULTICOMPONENT NATURAL CHEMISTRY

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The new methods of diamond synthesis in carbonate - carbonic melts of multicomponent natural chemistry reproduce the physical and chemical conditions of diamond formation in experiments. The major purpose of the present experiments is to show high-pressure diamond synthesis as spontaneous crystallization and seeded growth on metal-synthetic single crystals in carbonate - carbonic melts ( $\text{K}_2\text{CO}_3$  -  $\text{Na}_2\text{CO}_3$  -  $\text{CaCO}_3$  -  $\text{MgCO}_3$  -  $\text{FeCO}_3$  - C) equivalent to those of multicomponent natural chemistry. Special attention is given to the elementary development mechanism in layers of newly formed carbonate - synthetic diamond on the seeds (forms and features of early developed growth steps).

The multicomponent carbonate - carbonic melt – solution of system  $\text{K}_2\text{CO}_3$ - $\text{Na}_2\text{CO}_3$ - $\text{CaCO}_3$ - $\text{MgCO}_3$ - $\text{FeCO}_3$ -C was first used in the present experiment on diamond crystallization.

The starting mixture was prepared from a carbonaceous mixture ( $\text{K}_2\text{CO}_3$  – 27,21;  $\text{Na}_2\text{CO}_3$  – 2,89;  $\text{CaCO}_3$  – 26,91;  $\text{MgCO}_3$  – 17,35;  $\text{FeCO}_3$  – 25,63; wt %) mixed with graphite powder. The experiments were performed using an “anvil-with-hole” apparatus with the cell made of lithographic limestone. Pressure was controlled within the accuracy  $\pm 0.1$  GPa. Accuracy of temperature measurement was  $\pm 20^\circ\text{C}$ .

Certain features of these experimental techniques eliminate the possibility for direct observation of growth of diamond crystals. The research of diamond growth mechanism realizes at the analysis of a surface and micromorphology of diamonds facets in situ samples. The experimental samples were studied by SEM with the use of an electron microscope CamScan MV 2300 (IEM RAS, operator – Nekrasov A.N.)

The experiments were carried out under the conditions of diamond stability ( $P=5.5$ - $8.5$  GPa and  $T=1200$ - $2000^\circ\text{C}$ ). These conditions provide high solubility of carbon in carbonate melts. As a result, a carbon solution forms in the melt, the solution is supersaturated with respect to diamond. The following factors determine the formation of such solutions at PT - conditions of diamond thermodynamic stability: (1) the differences in the solubilities of metastable graphite and stable diamond, and (2) the thermal gradient within the heater.

A PT-diagram of diamond crystallization is studied and constructed. The field of diamond crystallization is between the graphite - diamond equilibrium boundary (Kennedy C.S., Kennedy G.C., 1976) on the part of low pressures and the line of melting of the carbonate-carbon mix on the part of low temperatures. Spontaneous nucleation is connected with formation of labile carbonate - carbon melts supersaturated to diamond. The formation of metastable supersaturated melt - solutions is enough for the growth of new layers of diamond on a seed. Combined together at the same time, the processes of spontaneous crystallization and seeded growth are competitive and can negatively influence each other depending on the degree of carbon supersaturation in the melt – solution. (For example, spontaneously formed diamond intergrowths are capable of blocking the entrance of dissolved carbon flows to facets of seeds and, oppositely, seeded growths limit the capabilities of labile supersaturated solutions forming, as a result of which, the spontaneous nucleation of diamond is depressed).

The main feature of diamond crystallization in multicomponent carbonate-carbon systems is intensive spontaneous nucleation at conditions close to the graphite - diamond equilibrium boundary. Rate and density are essential for spontaneous nucleation (accordingly, about  $100\text{ }\mu\text{m}/\text{mine}$  and not less than  $1\cdot 2\cdot 10^3$  crystallization centers  $/\text{mm}^3$ ) and depend upon PT - parameters. Diamonds form only octahedral single crystals, spinel twins, and sometimes polysynthetic twins, with aggregates of mean size up to  $100\text{ }\mu\text{m}$ .

Different mechanisms for new layers of diamond both smooth facets (111) and rough (octahedral micropyrramids) facets (100) were observed on seeds grown on different facets. For seeds, cub-octahedral metal-synthetic diamonds were used.

The growth layers on smooth facets (111) occur at the tops and edges and move in the direction of the facet's center, forming flat steps of different width. The growth layers can sometimes occur at just one top or edge, thus forming twisting fronts moving with trigonal geometry along octahedral facets of seed crystals.

Some growth fronts can arise simultaneously. In that case, either prismatic cavities, ledges, or insulated planes, blocks – crystallites can form having typical trigonal geometry oriented on a facet (111) when crossing or put on of these growth fronts. The new growth layers arise between the steps of layers. They are usually triangles with even or rough edges.

The surface of a facet (100) is practically always rough; smooth segments are formed rarely. Layers can arise on different parts of a facet (100), but the growth layers are oriented facets (111). Formation of a rough surface is the result of the polycentric growth of facets (100). For cubic facets, the most typical elements of a microrelief are: tetrahedral micropylramids and micropylramid-shaped hollows, blocks - crystallites, and assemblies of nano- and microlayers of trigonal geometry oriented over octahedral facets. The growth layers with trigonal symmetry are legibly determinable on all elements of a microrelief of cubic facets.

The growth layers on cubic facets look like a prolongation of growth layers on octahedral facets formed at the border between facets (111) and (100).

All growth layers can be separated by nano- and microlayers (20 - 300 nm and 0,3 - 4  $\mu\text{m}$  accordingly). These microlayers consist of nanolayers, which have arisen practically simultaneously from one top or one edge and moved along and parallel to a seed's facet. Thus, the microlayer (growth step) develops at the same time in tangential and normal directions of growth.

As a result of these experimental researches it is possible to make following conclusions:

1. Multicomponent carbonate - carbonic melts - solutions are growth mediums for natural diamonds (based on mineralogical and experimental data).
2. For crystallization in carbonate - carbonic melts – solutions, diamonds form in octahedral morphology, and the octahedral growth pyramids develop radically.
3. The process of growth of new layers of diamond on facets (111) and (100) was first carried out in multicomponent carbonate - carbonic melts ( $\text{K}_2\text{CO}_3$  –  $\text{Na}_2\text{CO}_3$  –  $\text{CaCO}_3$  –  $\text{MgCO}_3$  –  $\text{FeCO}_3$  – C) simulating natural chemistry.
4. There are tangential and normal mechanisms in seeded growth layers. Newly formed layers of diamond have a typically trigonal geometry oriented over seeded facets (111).
5. Diamond growth nanolayers (20 up to 300 nm) exhibit typical trigonal geometry and are the basic elements for larger growth steps.

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