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Low-Temperature Growth of Diamond Seedings in Acid Solutions

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Abstract

The growth of natural and artificial seedings of diamond from low-temperature hydrothermal aqueous solutions containing mixtures of nitric, sulphuric and acetic acids (~ 20–30 %) at atmospheric pressure and 38–90 °C is studied by means of the direct temperature difference method (~ 10–60 °C) using graphite as the source of carbon. It is shown that a tangential growth of transparent, colourless nearly continuous smooth layers at the faces {111} and {110} is observed while the accelerated growth of the {100} face proceeds practically *via* a normal mechanism. The maximum growth rate of the seedings is achieved at the temperature difference of 50 °C. Different stages of the red-ox graphite to diamond transformation are discussed, as well as the possibility for it to occur in nature in postmagmatic aqueous solutions.

INTRODUCTION

Diamond crystals and films are grown both in the diamond stability region at high temperatures and pressures, and by means of metastable growth from liquid or gas phase at low pressures and intermediate temperatures, as well as from the plasma, atomic or molecular beams [1–3]. In the latter case, simultaneous formation of other carbon-containing products is possible. Because of this, the properties of artificial diamonds differ; these diamonds can be separated into two groups: 1) pure diamonds and films including those of the jewellery or semiconductor quality, 2) diamond-like films with the considerable content of amorphous carbon, graphite and hydrogen [4] which are semitransparent or nontransparent grey, dark grey or black materials.

The formation and growth of diamond from water-salt solutions [5–8] are less known and poorly studied. Polycrystal diamond films 15–40 μm thick were obtained from the solutions of complicated composition at a pressure of 15 kbar and a temperature of 400 °C [5]. The growth of diamond for seeding was conducted in the aqueous solutions of the halides of alkaline metals by means of gradual temperature decrease [6]. Recently, hydrothermal synthesis of diamond has been performed in the metal – carbon – water system at a pressure of 1.4 kbar and temperature of 800 °C in the presence of fine nickel catalyst [7]. Hydrothermal growth of diamond at seedings at atmospheric pressure and temperatures below 100 °C was conducted for the first time by us [8].

On the other hand, the known data on diamond occurrence in nature evidently point to its polygenesis, *i. e.* the possibility of different routes of the formation of polymorphous carbon modifications in natural geological processes and their transformations into each other within a wide range of state parameters [9–11]. Because of this, a detailed investigation of the

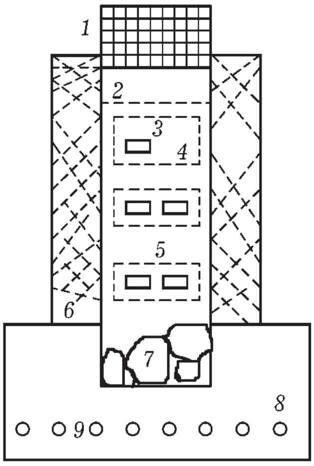

Fig. 1. Scheme of the crystallizer: *1* – cap, *2* – quartz tube, *3* – Teflon grid, *4* – diamond seedings, *5* – aqueous solution of acids, *6* – thermoinsulator cooler, *7* – graphite pieces, *8* – thermostat, *9* – heater.

crystallization and transformation of polymorphous carbon modifications in solutions is of interest for the understanding of the physics and chemistry of the formation of diamond products under natural conditions and in technological experiments, as well as for the application of this knowledge to the design of diamonds with the required dimensions and properties.

In the present paper we describe the results of the growth of natural and artificial seeding diamond crystals in multicomponent acidic solutions and discuss the possible physicochemical mechanisms of graphite to diamond transformations in these solutions at atmospheric pressure and temperatures within 100 °C.

EXPERIMENTAL

We used the method of direct temperature difference which is usually applied to the hydrothermal synthesis and growth of crystals from solutions. The dissolution zone is in the lower part of the vertical vessel and the growth region is in its upper part. The scheme of the set-up is shown in Fig. 1. Test tubes made of transparent quartz were used as the containers. The tube volume was 50 ml. The pieces of ultrapure graphite (with a mass of about 20 g) were put into a Teflon sieve sack and placed in the lower part of a tube. The frames made of Teflon with diamond seedings enclosed in holes were mounted along the tubes. The seedings were preliminarily studied using a microscope, washed in easily flammable solvents, ethanol and distilled water, dried at 100 °C and weighed. The tubes were filled with the mixtures of double-distilled water with ultrapure concentrated acids (sulphuric, nitric, acetic) at different ratios. Then the tubes were closed with Teflon caps and placed in a thermostat at a temperature equal to that of the vessel bottom (dissolution zone) which was 98–99 °C. The temperature of the growth zone was maintained at a point within the range of 38–98 °C for different experiments. After each experiment the tubes were removed from the thermostat and the solution was poured off. The seedings were washed thoroughly by hot distilled water, dried till constant mass and weighed with a precise electron balance (Sartorius, at an accuracy of 10^{-6} g). Then the morphology of different faces of the crystals was studied using an optical binocular microscope and scanning electron microscope.

The measurements were performed in three stages. At the first stage, preliminarily we searched for the compositions of solutions in which crystal growth was carried out. Fine natural and synthetic crystals, or their chippings (with a mass up to 10 mg) were used as seedings. The duration of an experiment varied from 4 to 30 days. The results of this series of experiments are shown in Table 1.

At the second stage we studied the dependence of crystal mass increase on the temperature difference between the upper and lower zones of solution when the composition of the

TABLE 1
The increase of the mass of diamond seedings

Solution composition (in volume fractions)				ΔM, %
HNO_3	H_2SO_4	CH_3COOH	H_2O	
1	1	0.1	3	1
1	1	0.01	3	0.3
1	1	1	3	0.1
0.1	0.1	0.1	5	0
1	1	1	0.5	0
1	0	0.1	3	0
1	1	0	3	0
0	1	0.1	3	0

Note. Temperature of the dissolution zone was 96 °C, growth zone – 76 °C, experiment duration 4 days, the mass of seedings 6–10 mg, ΔM – mass increase per day (in % of the initial mass of seedings).

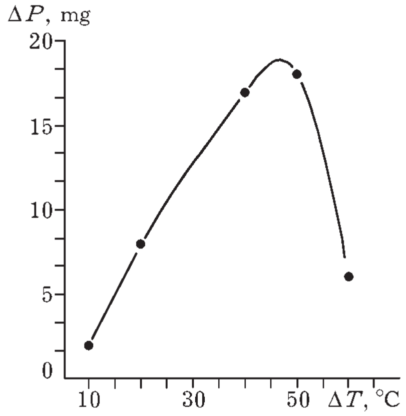

Fig. 2. The dependence of diamond seedings mass increase (ΔP) on temperature difference between the upper and the lower zones of the solution (ΔT). Temperature of dissolution zone 98 °C, composition of the solution (in volume fractions): $HNO_3 : H_2SO_4 : CH_3COOH : H_2O = 1 : 1 : 1 : 3$.

solution was close to optimal one (volume ratio $HNO_3 : H_2SO_4 : CH_3COOH : H_2O = 1 : 1 : 0.1 : 3$). In this case, larger crystals of the octahedron, octahedron-rhombododecahedral and table habitus were used as seedings (with a mass of ~ 0.3 carat and the length of the main face up to 3 mm). These seedings were colourless, transparent, with smooth faces, without any cracks, caverns or scratches. The duration of experiments of this series was 2 to 3 months (Figs. 2 and 3).

At the third stage we performed prolonged experiments at optimal temperatures (~ 50 °C) and solution compositions; the solution was poured off many times and fresh solution was fed every 2 months. Maximum thickness of the grown layers in this case was 0.1 mm and maximum increase in the seeding mass was 70–80 mg.

RESULTS AND DISCUSSION

It was stated that a noticeable oxidative decomposition of graphite in hot solutions containing nitric and sulphuric acids occurs. When temperature is increased till the boiling point, part of the dissolved carbon is released as carbon monoxide or dioxide. The mass of the dissolved graphite under the optimal conditions described was up to 4–5 g.

Even in the experiments with non-optimal solution composition we did not observe the dissolution of diamond, *i. e.* decrease of the mass and changes of the surface of seedings (see Table 1). Diamond is known to be insoluble in acids; only in the presence of special oxidizing agents or in the melts of their salts (for example, Berthollet's salt) it burns. In microscopic studies we also did not observe dissolution shapes of crystals or etching of their faces, even when the solutions of nitric and sulphuric acids were used.

The growth of diamond seedings occurs only when three selected acids and graphite load are used and depends on their concentration (see Table 1). In the absence of any one of the acids, the growth is not observed. This process takes

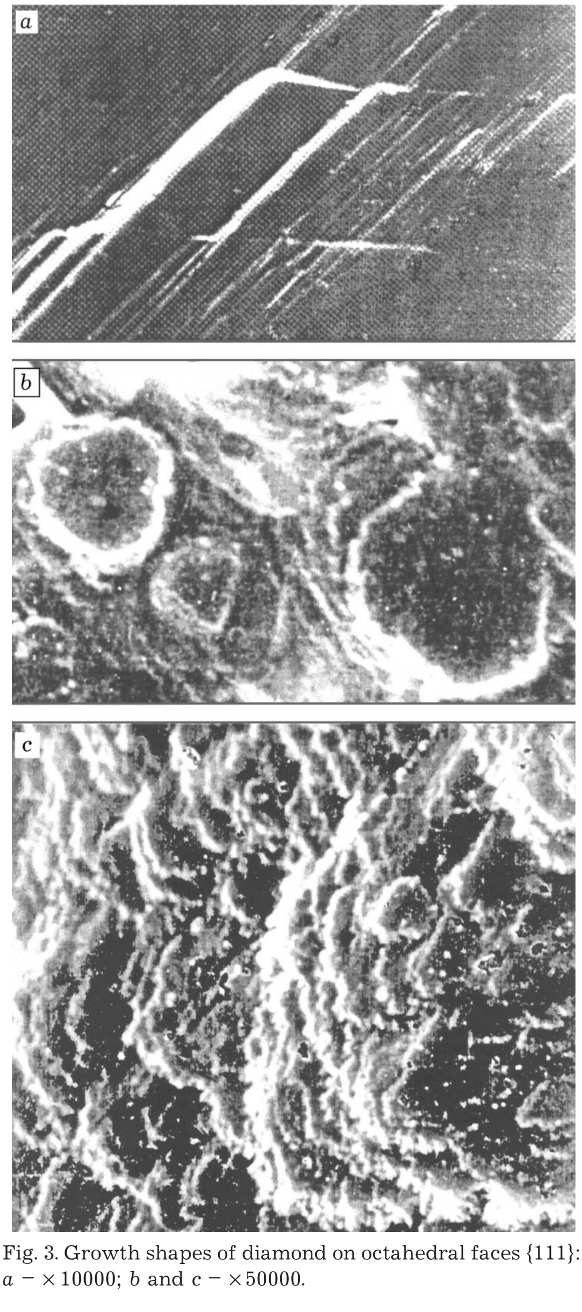

Fig. 3. Growth shapes of diamond on octahedral faces {111}: *a* – × 10000; *b* and *c* – × 50000.

place only at high concentrations of both nitric and sulphuric acids; however, the concentration of acetic acid should be an order of magnitude lower. At the same time, even for low concentrations of acetic acid (unlike other acids), the growth of seedings takes place. When the composition of solution is varied near the optimal concentrations (see the first line of Table 1), the growth rate changes insignificantly.

The dependence of the growth of diamond seedings in the second series of experiments on temperature difference ΔT between the upper and the lower parts of solution at its constant optimal composition, process duration and maximum graphite dissolution temperature (98–99 °C) exhibits a clear extremum at $\Delta T \approx 50$ °C (see Fig. 2). One can see that till $\Delta T = 40$–50 °C growth rate is rather high while with further increase of temperature difference it decreases sharply. According to this fact, the seedings located in different parts of the tube grew at different rates (see Fig. 1). At the beginning of the process, the seedings growth rate is 1–2 μm per day but while the oxidizing acids are consumed for graphite dissolution, the diamond growth rate gradually decreases. When the solution is renewed, the process rate again increases.

Microscopic investigation of crystals shows that the grown layer is absolutely transparent, colourless and its refractive indices do not differ from those of the initial material of seedings. The growth layer on the {111} faces looks nearly continuous and smooth. The shapes of tangential growth on this face are clearly seen in electron microscopic photos. Figure 3, *a* clearly shows rectangular growth steps with the rhombododecahedral faces {110}, and Fig. 3, *b*, *c* – triangular-oval isles of the growing layers. The cubic faces {100} exhibit the shapes of accelerated growth according to practically normal mechanism without obvious steps but with the simultaneous formation of square pits in the sites of decelerated growth.

At long enlargement (abnormal growth) the facing of the initial seedings changes, namely, octahedral and rhombododecahedral faces grow over the cubic faces, then rhombododecahedral faces appear on the edges of octahedron, and octahedral faces {111} are transformed into triads of the trigontrioctahedral faces (*hkl*). So, the rates of diamond faces growth from acidic solutions exhibit the following ratio: $V[100] > V[111] > V[110] \cong V[hkl]$.

X-ray Debye crystallograms before and after growing are similar to each other which means that all the diamond lines are conserved and no new lines appear.

It is essential to note that when the reagents of special purity grade are used and stable thermodynamic regimes are kept, we do not observe deposition of graphite and amorphous carbon deposition in the growth region and other regions of the crystallizer. Since such a deposit is always nontransparent, it is readily seen on the walls of the vessel, even it is slight. In the case if some microadmixtures were added with graphite into the lower zone of the crystallizer, a small amount of plate-like graphite crystals with a size of up to 3–4 mm is formed in the coolest upper part of the vessel.

When the tubes are rapidly cooled till room temperature, a continuous thin non-transparent layer of graphite and amorphous carbon is deposited on the tube walls and the hardware of the crystallizer. In prolonged experiments, when current supply was switched off and the solution was cooled, the intrusions of fine non-transparent hexagonal graphite flakes with a size of up to 1 mm were observed in the grown transparent layers.

The nature of grown layer and the possible mechanism of the hydrothermal process

The results described above allow us to assume that diamond layers are grown on seedings under the conditions described. However, final conclusion can be made only on the basis of X-ray structural analysis of the grown layer after it reaches sufficient thickness for the layer to be removed from the seeding.

This hydrothermal process includes oxidative dissolution of graphite with the formation of various intermediate carbon compounds, carbon transfer into the growth zone and the growth of diamond on the seedings.

Graphite dissolution is a multistage process. It can be represented with the following scheme:

$$\mathrm{G} \Rightarrow^{1} \mathrm{GBS} \Rightarrow^{2} \mathrm{GO} \Rightarrow^{3} \mathrm{MA} + \mathrm{FC} \Rightarrow^{4} \mathrm{C} + \mathrm{CO} + \mathrm{CO_2} \qquad (1)$$

Here G is graphite, GBS is graphite bisulphate, GO is graphite oxide, MA is melilitic acid, FC is free carbon, figures 1 to 4 indicate the stages of the process.

The first stage is intercalation; in the solvent used by us, the product of intercalation is probably graphite bisulphate. Its formation can be represented by a scheme [12]

$$G + n/[O] + H_2SO_4 \Rightarrow C^{n+}(HSO_4)\cdot(H_2SO_4)_x + n/2H_2O \quad (2)$$

where O is an oxidizer, $C^{n+}(HSO_4)\cdot(H_2SO_4)_x$ is graphite bisulphate. In the case under consideration, nitric acid is used as an oxidizer. It supplies oxygen to the intercalate according to the reaction

$$2HNO_3 \Rightarrow 2NO_2 + H_2O + O \quad (2a)$$

The second stage is the hydrolysis of graphite bisulphate with the formation of graphite oxide [13]. The composition of graphite oxide is variable. It changes during consequent destruction of hexagonal graphite grids. Its limit formula is $[C_7H_2O_4]_n$ [12]. The formation of graphite oxide is accompanied by the breakage of C—C bonds inside each hexagonal graphite grid and the formation of covalent C—O bonds that change the grid configuration. The grid becomes not flat, carbon atom bound to the anion gets above the grid thus forming methane-like structure; valence angles are close to tetrahedral ones. This process is very much like the catalytic action of atoms of transition elements in the synthesis of diamond from graphite in their melts: these atoms intercalate into graphite between sp^2 hybrid carbon grids and leave behind them crimped grids with diamond structure [14, 15]. So, the formation of GO is accompanied by the destruction of graphite structural grids and the appearance of the regions with sp^3 hybridization which is characteristic of diamond structure.

The third stage is the formation of melilitic acid $C_6(OH)_6$ and the release of free carbon or its dioxide according to the equations

$$[C_7H_2O_4] + 2H_2O + O_2 \Rightarrow C_6(OH)_6 + CO_2 \quad (3a)$$

$$[C_7H_2O_4] + 2H_2O \Rightarrow C_6(OH)_6 + C \quad (3b)$$

The fourth stage, depending on the oxidative potential of the solution, proceeds either *via* complete oxidation of MA or with the formation of elemental carbon, its monoxide and dioxide:

$$C_6(OH)_6 + 3O_2 \Rightarrow 3CO_2 + 3CO + 3H_2O \quad (4a)$$

$$C_6(OH)_6 \Rightarrow CO_2 + CO + 3H_2O + 4C \quad (4b)$$

So, a wide range of carbon-containing compounds can be formed in the closed system graphite – a mixture of acids – diamond. These carbon species act as carbon carriers from the graphite dissolution zone into the diamond growth zone. Quantitative relations between these compounds are strongly dependent on the oxidative potential and thus on the initial and current composition of the solution. The transport of these carbon forms into the crystallization zone occurs due to the convection stirring of the solution under the conditions of temperature difference. The decomposition of melilitic acid according to reactions (4a) and (4b) occurs on the surface of diamond seedings, mainly at the growth steps and at their fissures. The morphology of the grown diamond layers points to such a tangential, layer-by-layer growth mechanism. This process is to a definite extent similar to the formation of diamond during the decomposition and oxidation of gas-phase hydrocarbons [3]. It takes place in the layers formed by the electrolyte components adsorbed on the surface of diamond. Substituents of different types participate in this process, for example ->C—H, ->C—OH, ->C—COOH, *etc.* [16]. It is clear that some of these types undoubtedly are present in the acidic solutions used in our experiments.

The diamond growth rate is low in this process. It is an order of magnitude lower than that observed for diamond growth from gas phase. However, the growth rate can be increased by broadening the production scale, improving the geometry and structure of installations, increasing the process temperature, choosing other, more optimal compositions of the multicomponent solutions.

Thermodynamic conditions of diamond crystallization

The formation of diamond is known to be observed in very wide temperature and pressure range, both in the region of its thermodynamic

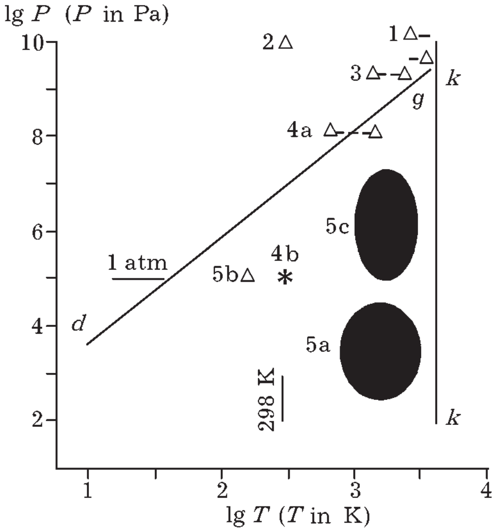

Fig. 4. The known $P-T$ regions of diamond formation with the phase equilibrium line graphite − diamond. Designations: see the text.

stability and outside it. We summed these conditions up in the phase diagram built in logarithmic $P-T$ coordinates (Fig. 4). The designations are: $d-g$ is the line of graphite-to-diamond equilibrium [14, 17]; $k-k$ is the approximate line of diamond kinetic stability within the region of graphite thermodynamic stability [18]. The conditions of the following processes are given: 1 − solid-phase synthesis of diamond from graphite during explosion or high static pressure [1, 2, 19]; 2 − the synthesis of diamond from fullerene at room temperature [20]; 3 − the synthesis in the melts of metals or carbonates [17]; 4a, b − hydrothermal synthesis [5−7]; 5a-c − the synthesis of diamond from the gas phase [3, 21, 22]. Besides, the line corresponding to the pressure of 1 atm and room temperature line are marked. They separate the regions of diamond synthesis under usual and extremal conditions. An asterisk (4b) marks our experimental conditions. It is clearly seen that they fall well within the known metastable regions of synthesis.

The formation of diamond in nature

The results of our investigation are in agreement with the conclusions of many authors (for example, [9−11, 23−25]) that the crystallization of diamond can take place during the metasomatism of kimberlites at the pneumatolytic and hydrothermal stages of the postmagmatic process, as well as in various metamorphic facies from migmatite-gneissic to green shale. Moreover, the crystallization of diamond is possible in carbon-containing rocks at atmospheric pressure and not very high temperatures under the action of acidic solutions (for example, those of volcanic origin).

CONCLUSION

So, further investigation of carbon crystallization from hydrothermal aqueous salt-containing and acidic solutions in the $P-T$ region which is metastable for diamond is of interest both for the understanding of natural processes leading to diamond formation, and for more precise evaluation of the conditions under which different polymorphous carbon modifications are formed.

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