On the Possibility of Bulk Large Diamond Single Crystal Synthesis with Hydrothermal Process*

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ABSTRACT : Analysis of geological data, relating to occurence and formation of diamonds as well as host rocks, inclined author to have different outlook on the diamond genesis and to establish a proposition on their formation at pneumatolytic-hydrothermal conditions near superficial Earth zones. Based on that theoretical foundations and experimental works, the first low-pressure and low-temperature hydrothermal diamond synthesis from water solution in pressure autoclave was executed. As a result, the natural diamond seed crystal grew bigger and coupling of the synthetic diamond single-crystalline grains were obtained. SEM documentation proofs that parallely paragenetic crystallization of quartz and diamond, and nucleation of new octahedral diamond crystals brush take place on the seed crystal surface.

Forecast of nine times growth of diamond industrial application at 2000 and seventeen times at 2010 with reference to 1995, needs technology of large and pure single-crystals diamond synthesis. Growth of the stable and destressed diamond single-crystals in the pseudo-metastable diamond plot, may be realized with processes going through the long time and with participation of free radicals catalysts admixtures only. Sol-gel colloidal processes are an example of environment which form stable crystals in thermodynamically unstable conditions through a long time.

Paper critically discusses a whole way of studies on the diamond synthesis, from high-pressure and high-temperature processes through chemical vapour deposition up to hydrothermal experiments.

INTRODUCTION

Diamond is a mineral which shows a number of extreme properties for different practical applications. It is not only ideally transparent to infrared, ultraviolet and visible light but also the most ideal heat conductor, exceeding the heat conduction of copper by a factor of four, with a very low coefficient of thermal expansion. Diamond is the hardest and strongest of all known minerals, with abrasion strength comparable to that of teflon. Undoped diamond crystals are dielectric. Those with selective admixtures acquire the properties of the best elementary semiconductor with an energy gap of 5.45 eV, making it possible to produce electronic components with performance speed hundreds of times greater than that achieved for single-crystal silicon. In nature, semiconductor diamonds, as a rule with a bluish hue, are extremely rare (type IIb—extremely pure diamond which is given semiconductor properties by doping with trivalent or pentavalent cations) (Table 1). Historically, its extremely high index of refraction and very high dispersion, coupled with its transparency and hardness, have established its position of the jeweller's stone.

The genesis of diamonds of both the kimeberlite and other types, is not fully clear yet. It is basically erroneous to assume the exclusively plutonic origin of these minerals; this assumption

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Table 1. The general classification of the bulk diamond stones.

Type IA	Substantial amounts of nitrogen (about 1 %) which may be aggregated; most natural diamonds are of this type
Type IB	Nitrogen is usually a dispersed substitutional element; nearly all synthetic stones are of this type
Type IIA	Almost nitrogen-free; very rare in the nature; enhanced optical and thermal properties
Type IIB	Very pure diamond; usually semiconducting; boron impurities can render the stones p-type semiconductor

is based on very dubious grounds. Even in the early 20th century some mineralogists assumed that diamond might have been of hydrothermal origin, particularly with respect to large specimens. Analyzing diamond parageneses in quartz veins of Brazilian itacolumite with feldspars, and inter-layers with anatase and hematite as well as the co-occurrence of Australian diamonds with sapphire, ruby, garnets, topaz and tourmaline, that is, minerals of pegmatite origin, Thugutt (1923) assumed the possible diamond genesis at the pneumatolytic stage of magma differentiation. At the same time, he claimed that it was difficult to imagine a hydrothermal process of diamond growth. Today's laboratory and industrial experiments in the hydrosynthesis of crystals of many minerals make it possible to return to the problem of diamond hydrogenesis and hydrosynthesis.

For many years the success of high-pressure and high-temperature syntheses stopped physico-chemical analyses of the diamond genesis (Bundy et al. 1955; Szymański 1978, 1987; Kanda, Fukunaga 1984; Burns et al 1990; Bakoń, Szymański 1992). Researchers returned to them as the diamond phase was achieved in the metastable range of diamond by disintegration of hydrocarbons under subatmospheirc pressure (Eversole 1962; Angus et al. 1968; Deryagin, Fedoseev 1977; Spitsyn et al.

1981; Mitura 1987; Badzian, DeVries 1988; Piekarczyk et al. 1989; Piekarczyk, Yarbrough 1991; Inuzuka 1994). Independently, research work was continued on the possibility of lowering pressures and temperatures in the industrially applied high-pressure processes, gaining positive results when graphite was replaced by vitreous carbon(Figs. 1 and 2a, b). Diamond was obtained at a pressure of 3.8 GPa (Niedbalska, Szymański 1987; Niedbalska et al. 1988; Szymański 1990; DeVries et al. 1993). Miyamoto et al. (1989) and Brannon and McCollum (1991) confirmed these results by synthesizing diamond from vitreous carbon close to the graphite/diamond equilibrium line. The possibility of diamond synthesis in nature by disintegration of liquid hydrocarbons was confirmed by Sobolev and Shatsky (1986), who described diamonds which emerged in liquid inclusions enclosed in garnets of metamorphic rocks. Krasoń et al. (1991) described the possibility of carbonado type polycrystalline diamonds emerging as a result of explosive disintegration of hydrated hydrocarbons which filled rock voids in a frozen state. On the basis of these considerations, a "geode" type camera was developed for diamond synthesis (Szymański 1994a).

It can be concluded from the schematically represented diamond/graphite phase system (Fig. 1) that the course of the process of hydrothermal diamond synthesis, which is essentially a static form of hydrotermal homogeneous liquid phase epitaxy (HHLPE), should be similar to that of the processes of epitaxy from the gaseous phase, i.e., chemical vapour deposition (CVD), in the stable range of the graphite phase and the metastable range of the diamond phase of carbon.

THE ROLE OF HYDROGEN AND WATER IN THE DIAMOND SYNTHESIS PROCESS

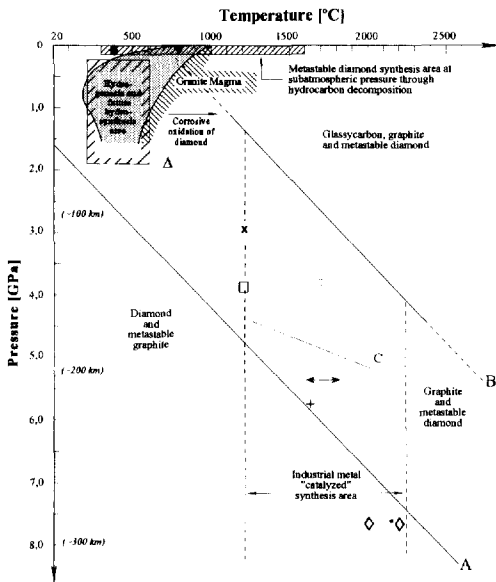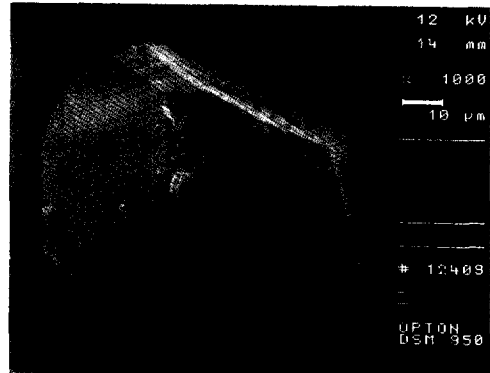As a result of homogeneous or heterogeneous low-pressure epitaxy from the gaseous phase, sin-

Fig. 1. Low- and high-pressure diamond synthesis plots at the pressure-temperature system (depth). Equilibrium lines: A :graphite/diamond (Bundy 1962); B :glassy carbon/diamond (Wiereszczagin et al 1977); C :graphite/diamond for eclogites (Dawson 1980). Point darkened area ‒ plot of the pneumatolytic-hydrothermal processes (Wyllie 1972). Dashed areas: CVD syntheses (top), granite type magma and potential hydrosyntheses (rectangle). Points of the positive experimental syntheses and observed in the nature. [solvent/catalyst]: ▽ :Cherian (1980)[NaOH+Ni], ⊗ :Niedbalska and Szymański (1987)[Co], + :Miyamoto et al (1989)[Co], x :Brannon and McCollum (1991)[Co], ↔ :Kanda et al (1991)[Na$_2$CO$_3$, CaCO$_3$, SrCO$_3$], ● :Akaishi et al (1991)[Li$_2$CO$_3$, Na$_2$CO$_3$ CaCO$_3$, SrCO$_3$, MgCO$_3$, Na$_2$SO$_4$, MgSO$_4$, CaSO$_4$ · 0.5H$_2$O, Mg(OH)$_2$, Ca(OH)$_2$], ◇ :Yamaoka et al (1992)[H$_2$O], △ :in quartz veins of Brasilian itacolumite (Thugutt 1923), ◻ :in post-hydrocarbon inclusions into garnets connected with metamorphic rocks (Sobolev and Shatsky 1986), ◆ :1st positive syntheses in hydrothermal autoclave (Szymański 1994, Szymański et al 1995).

(b)

Fig. 2. Two diamonds obtained by Niedbalska and Szymański (1987) from glassy carbon as precursor.

gle-crystalline grains can be obtained with the dimensions of several micrometers at the most or so can thin diamond or diamond-like layers in crystalline form, inhomogeneous structure, variable properties and limited thickness, through the plasma disintegration of gaseous hydrocarbons or other organic compounds in the presence of atomic hydrogen (H). It is assumed that as a very active free radical atomic hydrogen plays a very essential role in the diamond growth in the stable range of the graphite phase of the carbon phase system, stimulating the diamond growth rate (Spitsyn et al. 1981; Badzian, DeVries 1988). The mechanism of this effect ‒ diamond surface stabilization ‒ consists in securing C-C bonds in sp^3 hybridization configuration. The theory saying that sp^3 C-H bonds act as a diamond growth stabilizer, preventing the addition of elements of the sp^3 graphite structure, is understood and approved for the diamond growth mechanism of the

CVD processes (Angus, Hayman 1988; Szymański 1989a). Another factor of the positive role of hydrogen (both atomic and molecular) in the process of diamond phase growth is its 500-fold preference in the dissolution of the graphite phase (Angus et al. 1968). Researchers at Research Triangle Institute obtained polycrystalline diamond films grown homoepitaxially on the natural diamond replacing hydrogen by water or alcohol. The growth rate was the same, but energy requirement was cut in half per one carat weight. Experiments were conducted in RF source of heating.

The effective static high-pressure diamond synthesis using a carbon precursor which was carbonized phenol-formaldehyde resin (vitreous carbon), containing 3~4.85% of hydrogen, over the pressure range of 3.1~3.8 GPa in the metastable range of diamond (Fig. 1), demonstrate that in this process, too, the presence of hydrogen can act as a factor eliminating co-crystallization of graphite and diamond (Niedbalska, Szymanski 1987, 1994b; Niedbalska et al. 1988; Brannon, McCollum 1991).

Kanda et al. (1989) demonstrated the essential effect of the presence of H_2O in the process of high-pressure and high-temperature synthesis (HP/HT) on the morphology of the growing diamond crystals. Slightly later it was demonstrated that in these syntheses the traditionally applied metallic solvent could be replaced by mineral solvents introduced in the proportion of 20% with respect ot the graphite precursor (Kanda et al. 1991; Akaishi et al. 1991). Carbonates, sulfates and hydroxides were applied as solvents (Fig. 1). On the assumption that over the high pressure range the activity of hydroxide solvents $Mg(OH)_2$ and $Ca(OH)_2$ were related to their resolution into oxide and water, forming together a supercritical solution (Brownlow 1979), Yamaoka et al. (1992) decided to investigate the water-carbon system in the same conditions of pressure and temperature. Graphite with a 12% water addition was applied
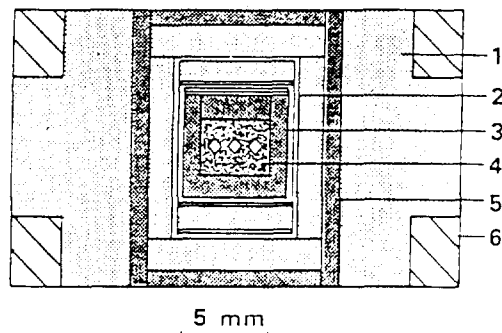

5 mm

Fig. 3. Cross section of the high-pressure/high-temperature chamber for $C-H_2O$ system investigation (Yamaoka et al. 1992): 1:pressure stabilizing medium ($NaCl+ZrO_2$), 2:two-walled tantal capsule, 3:internal graphite capsule, 4:powdered graphite pressed with 12% of water and seed diamond crystals of octahedral habit, 5:graphite heater, 6:steel stabilizing ring.

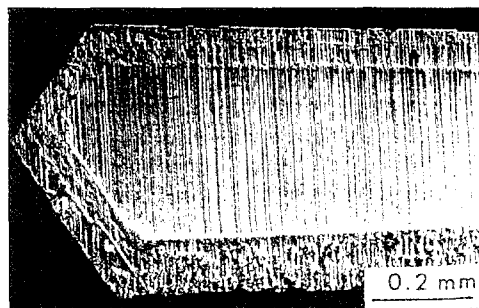0.2 mm

Fig. 4. Section [110] of the seed diamond crystal after synthesis in the system $C-H_2O$ at 2200℃, 7.7 Gpa and 17 minnutes (Yamaoka et al 1992).

in a capsule as the precursor. Diamond seed crystals with octahedral habit and 2 mg weight were placed in a pressed water and graphite capsule (Fig. 3). The system was subjected to a pressure of 7.7 GPa at temperatures of 2000℃ and 2200℃ over 30 min. and 17~20 min., respectively. A 70% increase in the weight of diamond seeds was obtained for the 7.7/2200/17 process, which in linear terms amounted to about 0.1 mm (Fig. 4). These studies showed that diamond could grow by homogeneous epitaxy on the diamond seed surface in the carbon-water system in a very short time

at extremely high pressures and temperatures. As the growing layer contained distinct graphite intrusions it could be presumed that either there was no free hydrogen in the system or graphite microcrystals were taken over from the precursor.

The phase equilibrium calculations taken at given P and T conditions using Taylor's GFLUID Programme (199) for a C–H–O system with excessive carbon indicate that in addition to dissociated water there are small amounts (_5% mole) of CO_2, CH_4 and H_2. Thus, graphite is dissolved in a water–rich liquid, forming CO_2 and CH_4 while carbon is precipitated from the carbon–saturated solution on the diamond surface. The experiments made by Yamaoka et al. (1992) clearly demonstrated that diamond could form in hydrothermal processes. On this basis, it can be presumed that the free hydrogen surplus was too small in the synthesis system or the excessively accelerated growth process prevented graphite elimination (dissolution) from the graphite surface. Just as in the CVD processes the forced high rate of the process generated a faulty structure of the growing diamond layer (Motojima, Iwanaga 1992; Plano 1995).

It turned out that Thugutt (1923) was right in suggesting the hydrothermal origin of large diamonds. Here, it is also interesting to mention the case, cited by Maślankiewicz (1983) after Rehman (1953), which took place as he visited the deep Kimberly mine (about 1000m). Namely, after a pick had struck the rock a hot water source broke out. Thus, breccia kimberlite rocks can hold hot waters in the local voids of the rock formation, sui generis natural autoclaves which could make it possible for diamond crystals to continue their slow growth added by hydrothermal solutions. This would be a hydrometamorphic process which would take place without a substantial pressure increase and at relatively low temperatures (Ryka, Maliszewska 1982; Piekarczyk 1990).

CRYSTALLITE SIZE EFFECT (CSE)

The currently valid system of diamond–graphite phase equilibria (Fig. 1) was considered in terms of the potential phase transitions of solid materials in a solid state and taking into account only the conclusions from diamond synthesis experiments made for HP/HT processes using a static method (Bundy 1962; Kennedy, Kennedy 1976; Vereshchagin et al. 1977). In the synthesis conducted in this way, solid graphite or vitreous carbon disks were applied as the carbon precursor, in alternating configuration with metallic solvent plates (e.g., Co, Ni, Fe, other metals or alloys) (Szymański 1978, 1987, 1989b, 1994b). The transformation of the precursor into diamond involves recrystallization via partial disintegration of the carbon substance in the metal. Diamond crystals up to 1 mm are ususlly obtained using pressures exceeding 3 GPa (usually, 5~8 GPa) and temperatures exceeding $1100°$, with the synthesis time of 20~30 min. In the modified version proposed by Strong and Wentorf (1972), also called the reconstitution method, the feed comprised diamond seed crystals, the intermediate solvent metal layer or a mineral salt capable of dissolving the carbon precursor, which would be disintegrated or transported in an atomized state and deposited on the seed surface (Niedbalska 1987; Crowningshield 1971). The static HP/HT synthesis process, conducted for several to dozen or so days, enables the diamond seed to grow at an average growth rate of about 1 mm per day. The diamond crystals of several millimeters obtained from this process are usually distinctly coloured, as a result of a substantial admixture of nitrogen atoms (Chrenko et al. 1971) and those of metals (Collins, Spear 1982) captured from the solvent medium, showing electric conduction.

The equilibrium between the microcrystals in the metastable and stable phases of solid materials, possibly with the temporary, short–term effect of a different dissolution phase, is achieved for a

specific size proportion between their crystals, with the course of the equilibrium curves depending on the properties of the two phases, in particular, on the size of microcrystals. This results from the compensation for the differences in the volume-specific Gibbs energies occurring as an effect of the different component contributions to the surface energy (Niedbalska, Szymański 1991a).

The size factor of microcrystals, called "the microcrystallite size effect" (CSE), can play an essential role, particularly for low-temperature crystallization of the polymorphous phases of mineral pairs, e.g., in the case of deposit recrystallization, greater particle sizes contained in them and metacolloid formation. Distinctly, the CSE mechanism also depends on the growth rates of the different crystal walls (Sunagawa 1982, 1984; Szymański et al. 1991, 1994a; Tauson, Abramowicz 1988).

It was found that the recrystallization (phase reconstruction) processes for particles with dimensions of about 10 mm took place, irrespective of the kind of crystals, at temperatures which were 2.5-fold to 7-fold lower than those for distinctly thicker crystals and did so under colloidal -capillary conditions over a temperature range equal to 0.7 fusibility (Tauson, Abramowicz 1988). The Oswald law will be satisfied in the system if initially the metastable form does not produce sufficiently large crystals.

If in a colloidal-capillary system of the thermal processes of metasomatic rock metamorphoses, e.g., under the impact of solutions with higher partial pressures migrating in pores and microcracks, there emerge conditions for hydrothermal metamorphosis and seed diamond embryo crystals existed earlier in the phase composition of the rock matrix, they are able to block the growth of stable-phase crystallites-graphite. On the basis of the CSE, such a system generates material diffusion over the phase boundaries to the phase which dominates in terms of volume, the crystals of which are larger than the critical size of em-

bryo crystals. The minimum free energy of crystals in a given volume corresponds to their equilibrium forms and is different for the diamond and graphite phases. Where crystals grow the local free-energy minimum will reach the level of the absolute free energy. Therefore, the conditions favouring the transformation from the graphite phase to the diamond one at low pressures and temperatures occur in the environment as the degree of dispersion of crystallites increases in the initial system. Calculations show that for crystallites the radius of which is greater than 100 mm a high-pressure and high-temperature equilibrium is valid (A, Fig. 1), whereas for smaller crystallites their stability ranges are perturbed and can show stability over different temperature ranges. In the nanomolecular range non-measurable intermolecular forces play a very significant role, shaping the system of phase equilibria in a different way (Moy, Neumann 1996; Szymański 1994b, 1996a, 1997). Milashev (1989) demonstrates that the emergence of embryo crystals in the system with dimensions below 10 nm may result from the local heating of the precursor without a simultaneous increase in pressure. He believes that for colloidal solutions it would be useful to introduce an additional third factor in the calculations of the phase system, i.e., the size of crystallites.

In the light of the above considerations, it should be assumed that the individual crystallization of large diamonds did not take place in the original kimberlite rocks but, rather, after their displacement, in a secondary deposit under colloidal-hydrothermal conditions, from embryo crystals which had formed earlier, through homogeneous epitaxy from the liquid phase (water solution), in the composition of which hydrogen dominated methane in the presence of nitrogen. Cebulak and John (1996) believe that in such an environment kerogen may have been the source of vitreous substance.

Therefore, in order for the seed crystallization

of graphite to develop as a stable phase with respect to diamond in the process of hydrothermal synthesis, over a given P and T range, formally metastable for diamond, in the presence of seed diamonds, embryo graphite crystals need to reach a specific size, such that they could become centres of heterogeneous nucleation. Therefore, as its embryo crystals dominate in size the metastable diamond can persist in the system for a very long time. The changes taking place in such a system, e.g. the phase decay, are affected by differences in the bulk and surface free energies of the two phases. When graphite is not used in the projected process of hydrothermal diamond synthesis (Szymański 1993, 1994b), under P and T conditions corresponding to those of colloidal-capillary metasomatic metamorphism, and it is replaced by precursors, the chemical structure of which, after thermal disintegration, will naturally form elements of the diamond structure; with these elements being complexes of carbon atoms connected in the sp³ hybridization configuration, suspended in a water solution in the form of water gas; there should be no barriers to the growth of these diamond seeds when placed in this system. It will take place, although over this P and T range the diamond polymorph is a metastable crystalline phase of carbon.

The significant role of the CSE in the crystallization processes taking place in nanometric colloidal-capillary systems was traced for a number of polymorphous pairs of minerals in natural conditions (e.g., calcite and aragonite) and in laboratory processes (Tauson, Abramowicz 1988). A distinct drop in the phase equilibrium range of polymorphs was observed. It is too early to define strictly the magnitude of the CSE impact. The transition of a mineral into a metastable phase in a solid state should take place for the crystallite size corresponding to given conditions, irrespective or partly irrespective of the environment. For homogeneous natural water environments the tension on the crystal surface depends on pH or
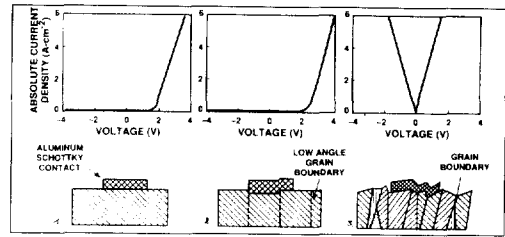

Fig. 5. Electrical characterization of single-crystal (1), CVD seeded blocks (2) and CVD seeded polycrystalline diamonds (Plano 1995). Seeded blocky diamond (2) has unstable electrical properties and in many thermal processes, which take place in the electronic chip circuit bonding, undergo a change to polycrystalline state (3).

the variable composition of salts which saturate solutions. Therefore, microminerals of metastable polymorphous modifications can emerge in such systems where a geochemical capillary system can form. From the point of view of the transition to stable macrocrystals it is necessary for the structure of the crystallizing material to include admixtures which could activate phase transitions in a solid state, and the solution should show a low ability to dissolve phases and slight saturation (Szternberg 1968; Kuznetsov 1968). The time factor takes care of the rest.

THE POTENTIAL DIAMOND GROWTH MODEL

In the course of the diamond crystallization from the gaseous phase (CVD), a tendency can be observed for polycrystalline layers with a heterogeneous structure to grow (Plano 1995) (Fig. 5). Similarly, it can be assumed that in the hydrothermal process the homegeneous crystallization which theoretically takes place in the metastable range of diamond will occur through a microblock growth of crystals – the formation of holomorphous aggregates from a non-ideal colloidal, microheterogeneous solution. The "block-mosaic" structure of the fragments which build
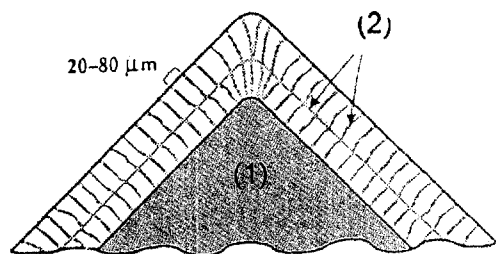
Fig. 6. Schematic cross-section of a coated diamond from Zaire showing a core of clear diamond (1), surrounded by a rims (2) of fibrous diamond. Turbid layers contain inclusions of the typical hydrothermal fluids (Guthrie et al 1991).

Fig. 7. Probable schematic system of the sp^3 organized carbon diffusion from host-rocks, through pneumatolytic fluids, on the interface of the diamond seed crystals; *x*-carbon enriched colloidal fluid (Szymański 1996a).

successive epitaxial layers on a seed crystal will probably be regulated by the CSE, therefore, in order to prevent the possible simultaneous crystallization of graphite "blocks", it seems well-advised to saturate the solution in a hydrogen-atomized autoclave.

A thin lonsdaleite layer, which is a hexagonal variety of diamond, was observed on the surface of some large cystals of natural diamonds (the Premier Mine in South Africa, the scattered deposits in Ukraine) (Frondel, Marvin 1967). This could indicate (Niedbalska, Szymański 1991a) that under the natural conditions of the epitaxial growth of successive layers it is the "intermediate" microblock one with the lonsdaleite structure between diamond and graphite that is the first to form; with the passage of time, after successive layers have grown, it coalesces as the polycrystalline lonsdaleite structure slowly rebuilds into a homogeneous diamond crystal. The diamonds from Zaire (Fig. 6) described by Guthrie et al (1991) also show the layered, transitionally polycrystalline growth of natural diamonds. Thin layers of fibrous diamond, from several dozen to several hundred micrometers thick, were found on their surface, superimposed on one another. These small fibres, with 2~80 mm cross-section, lie parallel to one another and are prependicular to the monocrystalline inside of
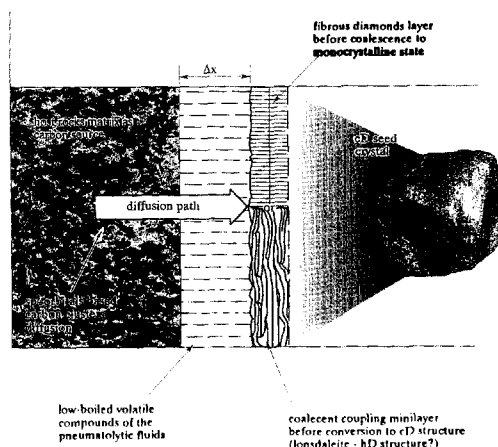
the diamond crystal. A large number of closed off inclusions, enriched with K, Si, Ca, Fe, H_2O and CO_3^{2-}, were found between these fibres which fogged the diamond surface. This composition indicates that their origin is related to the metasomatic solutions of the upper part of the mantle of the Earth. A schematic model of the gradual diamond growth within the mother rock can be derived from the above observations (Szymański 1996a, b) (Fig. 7).

Kimberlite magma, particularly at greater depth, contained large amounts of water, gaseous CO_2 and other volatile components with low boiling points (Milashev 1989; Navon 1991; Boyd et al. 1992; Turner et al. 1990). As a result of high fluidity, it could freely migrate through the rock cracks surrounding the inclusion, destroying the surrounding rocks (often xenoliths of carbonates, sandstones or even granites) and forming different types of kimberlite breccias. Therefore, the diamonds contained in kimberlites should not be connected in genetic terms exclusively with the deep crystallization of kimberlite magma. As
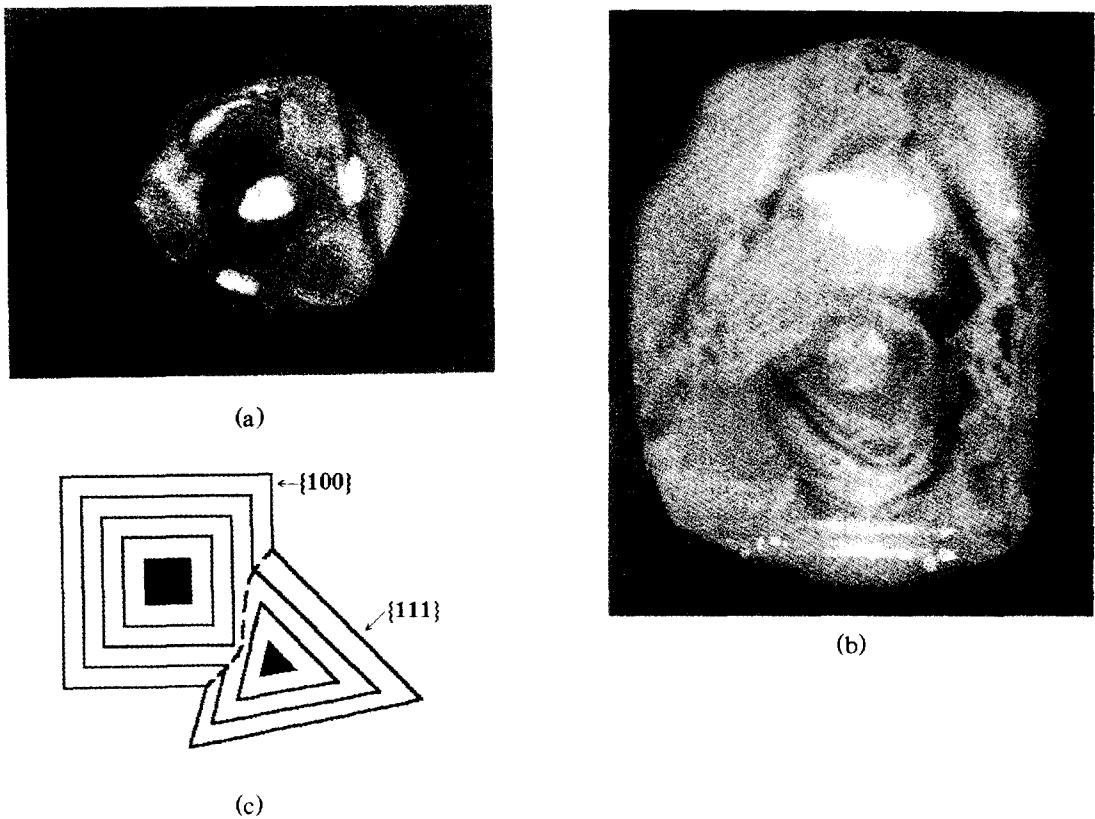
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(a)

(b)

(c)

Fig. 8. Schematic ongrow on the {100} and {111} faces (a). Images of the laser-luminescence of internal diamond crystals structure 9Yakutia), with visible embryocrystals (b, c) or succesive ongrowing layers (c) (Mironov and Antonyuk 1994).

Letnikov believes (1983), the activity of post-magmatic solutions could generate the epitaxial diamond growth on seeds which emerged at substantial depths. Analyzing the equilibrium parameters of gases closed as inclusions in diamonds, Nikolskii (1981) determined their closure temperature at 600~800℃ and the pressure as below 10 MPa. To his mind, it was under these conditions that the epitaxy process took place in nature on the seeds through a liquid-phase.

The technical conditions corresponding to the aforementioned P and T ranges are feasible using state-of-the art autoclave technology. Just as in the piezoelectric quartz synthesis, it is necessary to place in the autoclave seeds in the form of a well-developed, small crystal or a plate cut out

according to the orientation (Skinner 1979). In the natural conditions the seed was usually a well-developed microcrystal on which successive diamond layers grew. Mironov and Antonyuk (1994) demonstrated that in the growth process there could be variations of the temperature and pressure conditions on which the habit of growing diamond depends (Sunagawa 1982; Szymański et al. 1991). Tomographic scanning of the interior of Yakutian diamond crystals, performed using a nitrogen laser, showed there were crystals of the embryo crystal in the central part and distinct sequential growth layers in some crystals (Fig. 8a, b, c).

The research by Bakoń and Szymański (1979, 1980) and Cherian (1980), compared with the results of Akaishi et al. (1991), Kanda et al. (1991)
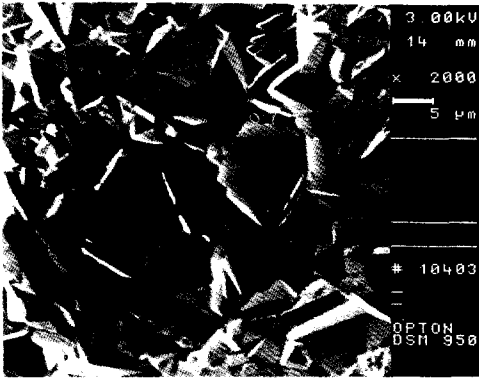
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Fig. 9. Low-pressure/low-temperature hydrothermal epitaxy (LP/LTHE) of diamond on the natural seed crystal with weight 0.222 g(1.11 ct): seed crystal surface coated with overgrowth polycrystalline brush composed of octahedral habit diamond crystals (Szymański 1994b, Szymański et al 1995).
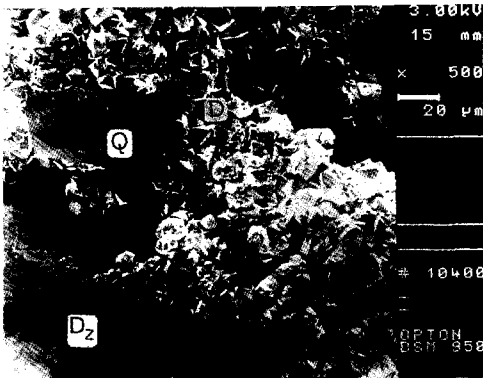

Fig. 10. Low-pressure / low-temperature hydrothermal epitaxy (LP/LTHE) of diamond on the natural seed crystal as on Fig. 9: part of seed crystal surface (Dz) with paragenetic crystallization of quartz (Q) and second-generation of diamond crystallization (D) (Szymański 1994b) (X325).

and Yamaoka et al. (1992), distinctly showed that an alkaline or neutral solution of carbonates, sulfates or hydroxides, possibly with an addition of liquid hydrocarbons (Krasoń et al. 1991), should be applied as the solution for the hydrothermal diamond synthesis. The carbon precursor should be fine-grained diamond, vitreous carbon or
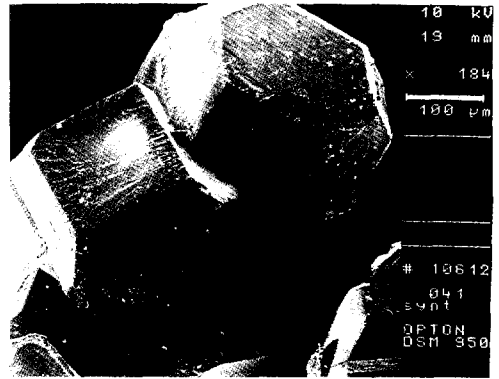

Fig. 11. Low-pressure/low-temperature hydrothermal epitaxy (LP/LTHE) of diamond: heal-up diamond crystals synthetized with high-pressure/high-temperature (HP/HT) process.

emulsion of crude oil and water. The pressure and temperature conditions for the natural hydrogenesis processes were outlined after Wyllie (1980) and the predicted conditions of diamond hydrosynthesis were marked with a framed rectangle (Fig. 1).

EXPERIMENT SUMMARY

The effect of studies conducted for many years on potential genetic data which would indicate the possibility of hydrothermal diamond synthesis was the development and implementation of real research processes (Szymański 1994b, Szymański et al. 1995, Szymański 1996a, b, 1997). The experimental syntheses were performed in an autoclave filled with a purpose-prepared water solution, with the seeds being natural diamonds with weights of 0.22 g and 0.49 g and synthetic diamonds suspended in a metal wire container. The process was conducted for 21 days at a temperature of 400°C under 170 MPa. In Fig. 1 this point is marked by a double rhombus. The process effects included: surface crystallization in the form of a brush of diamond microcrystals with octahedral habit (Fig. 9), paragenetic quartz and second-generation of diamond crystallization in a recess
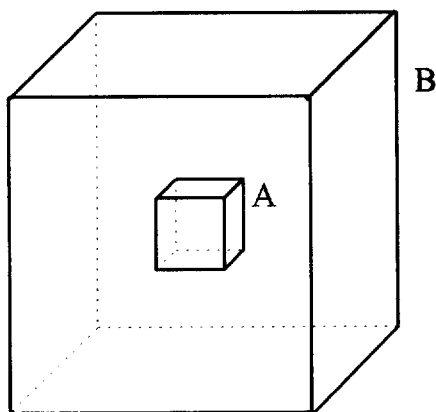
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Fig. 12. Presumable volumetric and weight increase of the natural seed diamond crystal with hexahedral habit, size 4×4×4 mm and starting mass of 1. 125 ct, after 30 days of the optimized hydrothermal process of synthesis. As calculated overgrowth rate 0.5 mm per day was assume.

on the surface of the seed diamond (Fig. 10) and the coupling of synthetic diamonds with their planes (Fig. 11).

The technique of hydrothermal synthesis of single-crystals, which was implemented on a laboratory scale even in the 1930's, was introduced in industrial applications in the 1940's to produce quartz crystals. Positive results were also obtained for berlinite, ruby and gold. The average volume increase was usually 1 mm per day and changed with the crystallographic orientation and the top/down autoclave temperature differences. For diamond this was confirmed by the data given by Yamaoka et al. (1992) (Fig. 4). This increase can be flexibly modelled. Assuming conservatively that the controlled increase level in the optimized process can be 0.5 mm pe day, the potential opportunities offered by the method are shown in Fig. 12. When a natural seed diamond with hexahedral habit, with dimensions of 4×4×4 mm and mass of 1.125 ct, is placed in the autoclave, after 30 days the crystal should reach the dimensions of 34×34×34 mm=39 304 mm³×3.515=138.13 g ×5=about 690 ct of weight.

From the technological point of view, two main problems remain to be solved: the optimization of the composition of the solution and the precursor material. In addition, the real technology will result from a correct choice of three factors: P, T and t; and, additionally, from the top/down autoclave temperature differences. An extremely significant element of the good technology will be the time factor, which in nature does not limit the possibility and efficiency of the crystal growth process. In technology this factor can determine the success of the hydrothermal synthesis of high-quality diamond single-crystals. It is only a synthesis implemented in pressure-temperature autoclaves that permits an "arbitrarily" long process to be performed in conditions reflecting natural colloidal-capillary systems, controlling the composition of solutions and the course of the process in a completely free way, unrestricted by a short process time. The hydrothermal conditions permit this time to be greatly extended compared with the CVD and HP/HT syntheses. In these conditions large single-crystals, slowly cooled after the process and thermally destressed, can be obtained.

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