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Diamond crystallization from an Mg-C system at high pressure high temperature conditions

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Diamond nucleation and growth in the magnesium-carbon system were studied at a pressure of 7 GPa and temperatures in the range of 1500-1900 °C. To explore the effects of kinetics in diamond crystallization processes the duration of experiments was varied from 5 min to 20 h. It was established that the induction period preceding diamond nucleation decreased with increasing temperature from about 17.5 h at 1500 °C to almost zero at 1900 °C, while the rate of diamond growth increased by almost three orders of magnitude, from 10 μm/h (1500 °C) to 8.5 mm/h (1900 °C). Cube was found to be the stable growth form of diamond over the entire range of temperatures used in the study. Based on the data obtained it was suggested that diamond growth in the Mg-C system took place in the kinetically controlled regime. Spectroscopic characterization revealed that the synthesized diamond crystals contained boron and silicon impurities. A specific continuous absorption, giving rise to the abundant brown coloration of the produced crystals, and a band at about 1480 cm⁻¹ found in the Raman spectra were tentatively assigned to defects involving π-bonded carbon atoms.

Introduction

Investigation of diamond crystallization in systems of different composition still holds great interest, since it provides better understanding of the mechanisms of diamond nucleation and growth and broadens our possibilities in producing crystals with specific properties. Most of the studies devoted to diamond nucleation and growth at high pressure high temperature (HPHT) conditions were carried out in the metal-carbon systems, with Fe, Ni, and Co being most frequently used as the catalysts.¹⁻⁶ Among the original but poorly investigated systems of particular interest is the Mg-C system. According to the published data, diamond has been synthesized in this system at pressure of 7.7-8.2 GPa and temperature of 1800-2000 °C with the run duration of 10-30 min.^{7,8} The phase diagram of the Mg-C system has been previously studied at pressures up to 7.7 GPa⁹ and reconsidered recently for high pressures.¹⁰ Kanda¹¹ classifying the catalysts for diamond growth considered Mg as a carbide forming agent belonging to the so-called GE (General Electrics) type catalysts, comprising group VIII elements. In a manner similar to other carbide forming catalysts such as Fe and Mn, magnesium reacts with carbon to produce stable carbides, but promotes diamond formation at higher temperatures where

the carbides decompose. Following this logics Andreev and Kanda¹² attempted at decreasing P-T conditions of diamond growth from the Mg-C system by making use of Mg-Cu alloys. In the experiments at 6 GPa, 1550 °C for 2 h they established diamond growth on seeds and spontaneous nucleation for Cu-rich alloys (less than 10 at. % Mg). For Mg-rich alloys dissolution of the seed diamond crystals was observed, that was explained by the stability of magnesium carbides at the experimental conditions.¹² Possible effects of kinetic factors on nucleation and growth of diamond have not been considered in the previous investigations. Additional interest to the Mg-C system at high P-T parameters has been evoked by the recent reports on successful synthesis of new compounds, such as Mg₂C and Mg₂C₃, with unique structural features and promising properties.^{10,13} Taking into account the fact that diamond crystallization processes in the Mg-C system have been studied insufficiently, while being rather promising for producing nitrogen-free and boron-doped crystals, we conducted experiments at pressures of 6.3 and 7 GPa in the temperature range from 1500 to 1900 °C. To explore the kinetic effects in diamond nucleation and growth processes, which are typical of many unusual systems, including melts of carbonates,¹⁴ sulfur,¹⁵ phosphorus¹⁶ and antimony,¹⁷ duration of experimental runs in the Mg-C system was varied from 5 min to 20 h.

Experimental Section

The experiments on diamond crystallization in the Mg-C system were conducted at pressures of 6.3 and 7 GPa in the temperature range of 1500-1900 °C. The split-sphere high pressure apparatus was used in the study.¹⁸ Most of the

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† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

experiments were performed at 7 GPa using 19×19×22 mm high-pressure cells shaped as a tetragonal prism with a graphite heater 9 mm in diameter and 15.8 mm high. At 6.3 GPa cells with dimensions 21.1×21.1×25.4 mm were used. A PtRh6/PtRh30 thermocouple was used to measure temperature in each experiment. In accordance with the previously published calibrations of the P-T parameters,^{19,20} the accuracy of the pressure and temperature measurement at 7 GPa and 1700 °C was estimated to be ± 0.2 GPa and ± 40 °C. The experimental procedure allows maintaining stable P-T parameters in runs as long as several tens of hours and has been tested in the studies on growing large high-quality diamond crystals.⁶ The starting materials were a graphite rod (99.99% purity), magnesium (Alfa Aesar, 99.9% purity), and cuboctahedral synthetic diamonds (*ca.* 0.5 mm) as the seed crystals. The graphite rod was machined into thick-walled capsules. Pressed Mg cylinders (3.5 mm in diameter and 3.5 mm high) together with the seed crystals were placed inside the capsules. To avoid penetration of the components of the isolating sleeve (a mixture of MgO and CsCl), the capsules were isolated with a 0.1 mm thick molybdenum foil from all sides. The sample assembly is shown in Fig. 1. After the experiments, metallic Mg and the products of its interaction with carbon decomposed rapidly in air, while the resulting phases were easily soluble in water or diluted hydrochloric acid. The degree of the graphite-to-diamond conversion, α , which is defined as $\alpha = M_{\text{Dm}} / (M_{\text{Dm}} + M_{\text{Gr}}) \times 100$, where M_{Dm} is the mass of synthesized diamond and M_{Gr} is the mass of residual graphite,²¹ was determined for each growth run. The produced diamond crystals were studied using optical and scanning electron microscopy. Spectroscopic characterization of diamond crystals was performed by means of infrared (IR) absorption, photoluminescence (PL) and Raman scattering. IR spectra were recorded using a Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer fitted with a Hyperion 2000 microscope. Raman/PL spectra were measured using a Horiba Jobin Yvon LabRAM HR800 spectrometer with the spectral resolution of about 1.0 cm⁻¹. A 523-nm solid state laser and a 325-nm He-Cd laser were used as excitation sources. For the low-temperature measurements a Linkam FTIR600 heating/freezing stage was used.

Results

The results of experiments in the Mg-C system at 6.3 and 7.0 GPa and temperatures ranging from 1500 to 1900 °C are summarized in Table 1. In experiments performed at 1900 °C for 1 h (run 871/7) and 20 min (run 872/7) the graphite capsules were completely transformed to a polycrystalline diamond aggregate. After dissolution, the aggregate was disintegrated into separate fragments and blocks. Single crystal blocks had sizes from 300 μm to 1 mm and showed some elements of faceting, namely, the {100} faces. The color of the diamond blocks varied from colorless to red-brown. In a 5-min run (880/7) diamond synthesis was incomplete and the initial graphite capsule was partly preserved. The degree of the graphite to diamond transformation was approximately 50%.

Table 1. Experimental results

Run No.	P, GPa	T, °C	τ , h	Diamond growth on seeds	Diamond nucleation	α , (%) Gr→Dm transformation
871/7	7.0	1900	1	+	+	100
872/7	7.0	1900	0.33	+	+	100
880/7	7.0	1900	0.08	+	+	50
1312/1	7.0	1800	0.33	+	+	20
1338/3	7.0	1800	0.5	+	+	40
1318/1	7.0	1800	2	+	+	100
1316/1	7.0	1700	0.5	+	-	0
948/1	7.0	1700	1	+	+	<<1
1765/2	7.0	1700	2	+	+	5
1306/3	7.0	1700	10	+	+	45
1301/1	7.0	1600	10	+	-	0
1303/3	7.0	1600	15	+	+	<1
1309/3	7.0	1600	20	+	+	5
1311/1	7.0	1500	15	-	-	0
1310/3	7.0	1500	20	+	+	<<1
1702/2	6.3	1650	20	+	-	0
1706/2	6.3	1500	20	-	-	0

"+" – was observed; "-" – was not observed. α is the degree of the graphite-to-diamond transformation, $\alpha = M_{\text{Dm}} / (M_{\text{Dm}} + M_{\text{Gr}}) \times 100$, where M_{Dm} is the mass of obtained diamond and M_{Gr} is the mass of residual graphite. Dm – diamond, Gr – graphite.

The produced crystals often formed aggregates and twins with sizes varying from 100 μm to 1.2 mm. Diamond morphology was mostly determined by the {100} faces; minor {111} faces were rarely present. Most of the crystals were transparent and colorless, but smoky or pale brown crystals occurred as well. Diamond crystals grew towards both the graphite capsule and the melt. In the former case, the crystals were separated from the graphite by a melt layer 30–40 μm thick. General schemes of diamond crystallization in the Mg-C system are presented in Fig. 1.

At 1800 °C diamond crystallization via both spontaneous nucleation and growth on seeds was established in experiments lasting 20 min (1312/1) and 30 min (1338/3). The degree of the graphite-to-diamond transformation was 20 and

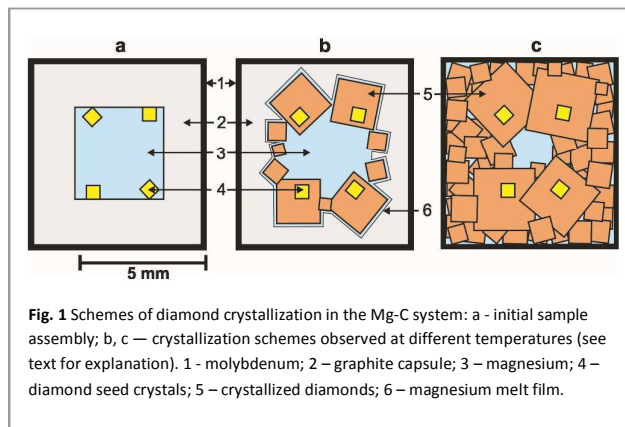


Fig. 1 Schemes of diamond crystallization in the Mg-C system: a - initial sample assembly; b, c – crystallization schemes observed at different temperatures (see text for explanation). 1 - molybdenum; 2 - graphite capsule; 3 - magnesium; 4 - diamond seed crystals; 5 - crystallized diamonds; 6 - magnesium melt film.

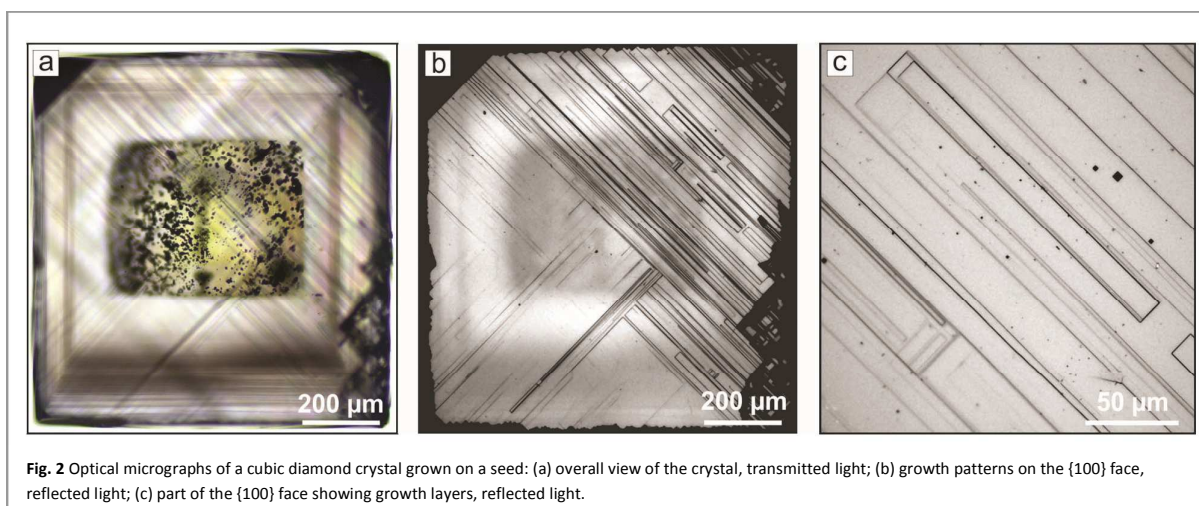


Fig. 2 Optical micrographs of a cubic diamond crystal grown on a seed: (a) overall view of the crystal, transmitted light; (b) growth patterns on the {100} face, reflected light; (c) part of the {100} face showing growth layers, reflected light.

40% in the 20- and 30-min experiments, respectively. Diamond crystals were located at the interface between the melt and graphite capsule. The crystals had cubic morphology showing sometimes slightly developed {111} faces. The size of spontaneously nucleated diamonds varied over a broad range from 100 to 900 μm . Crystals grown on the seed crystals were even larger reaching up to 2 mm in the experiment lasting 30 min. The seed crystals were easily discernible due to their cartellistic yellow color and specific bands of inclusions. The synthesized diamond crystals usually had pale brown coloration, while those of largest sizes appeared dark brown. A distinct zoning along the [100] direction, which appears as the alternation of zones of different colors (Fig. 2a), was frequently observed in the crystals. The {100} faces show rectangular growth layers with height varying from 0.9 to 15 μm , which propagated in the [110] directions (Fig. 2b, c).

The ends of the growth layers were always formed by the {111} microfaces. Octahedral faces on the crystals were mirror smooth and were usually characterized by insignificant development. When run duration was increased to 2 h, the graphite capsule was completely transformed to a diamond aggregate consisting of large overgrowths and twin crystals.

At 1700 $^{\circ}\text{C}$ no spontaneously nucleated diamonds were found in a 30-min run (1316/1). Slight diamond growth on the seed crystals was detected. In the experiment lasting 1 h (948/1), diamond layers grown on the seed crystals were from 100 to 300 μm thick and had red-brown color. A few spontaneously nucleated diamond crystals, 3-5 μm in size, were found. In a 2-h experiment, cubic crystals with sizes varying from 400-500 μm to 2 mm were produced via diamond growth on seeds. Spontaneously nucleated crystals were 20-30 μm in size and had brown color. The degree of the graphite-to-diamond transformation was estimated as approximately 5%. A significant amount of diamond crystals with cubic morphology and sizes varying from 20-30 μm to 200-300 μm were found in the experiment lasting 10 h (1306/3). The maximum size of crystals grown on seeds reached 2.2 mm. Some crystals were cleaved along the {111} planes. Most of the crystals were black. But, inspecting thin sections and cleavages we found them transparent and having red-brown color. The degree of

the graphite-to-diamond transformation was $\sim 45\%$. It should be noted that metastable graphite in the form of lamellar crystals was found in all experiments performed at 1700 $^{\circ}\text{C}$.

At 1600 $^{\circ}\text{C}$, a run duration of 10 h (1301/1) was insufficient for spontaneous diamond nucleation. Minute diamond growth layers were observed on partially dissolved seed crystals. At a run duration of 15 h (1303/3), approximately 30 spontaneous cubic diamond crystals with size varying from 20 to 100 μm were detected. The crystals were mostly of black color; small ones were dark brown. The layers grown on the seed crystals were less than 100 μm thick. Several tens of cubic diamond with size varying from 100 μm up to 1 mm were detected in run 1309/3 lasting 20 h. Large crystals were black, while small ones were brown. The degree of the graphite-to-diamond transformation was estimated at 5%. Lamellar crystals of metastable graphite were found in the central part of the capsule after dissolution.

No spontaneous diamond nucleation occurred at 1500 $^{\circ}\text{C}$ and run duration of 15 h (1311/1). The seed crystals were dissolved to approximately 50%. In the 20-h experiment (1310/3), insignificant growth of black diamond was revealed on one of the seed crystals and tens of spontaneous cubic diamond crystals and their aggregates 10-25 μm in size or, very rarely, up to 50 μm , were detected. Crystals were reddish-brown in color. Insignificant amounts of metastable graphite were present.

At 6.3 GPa 20 h long experiments were conducted at 1650 and 1500 $^{\circ}\text{C}$. No spontaneous diamond crystals were detected at 1650 $^{\circ}\text{C}$ (1702/2). Diamond growth yielding crystals with cubic morphology and 400 μm in size was detected on the seed crystals dissolved by more than 50%. The central part of the capsule contained a large amount of metastable graphite. The interaction between the graphite capsule and the solvent was insignificant at 1500 $^{\circ}\text{C}$ (1706/2). Neither diamond nucleation nor growth on seeds was detected. The seed crystals were preserved; however, they were partially dissolved and appeared as round-shaped crystals with a stepped structure of the faces (Fig. 3f). Fine-grain graphite was detected at the graphite capsule–melt interface.

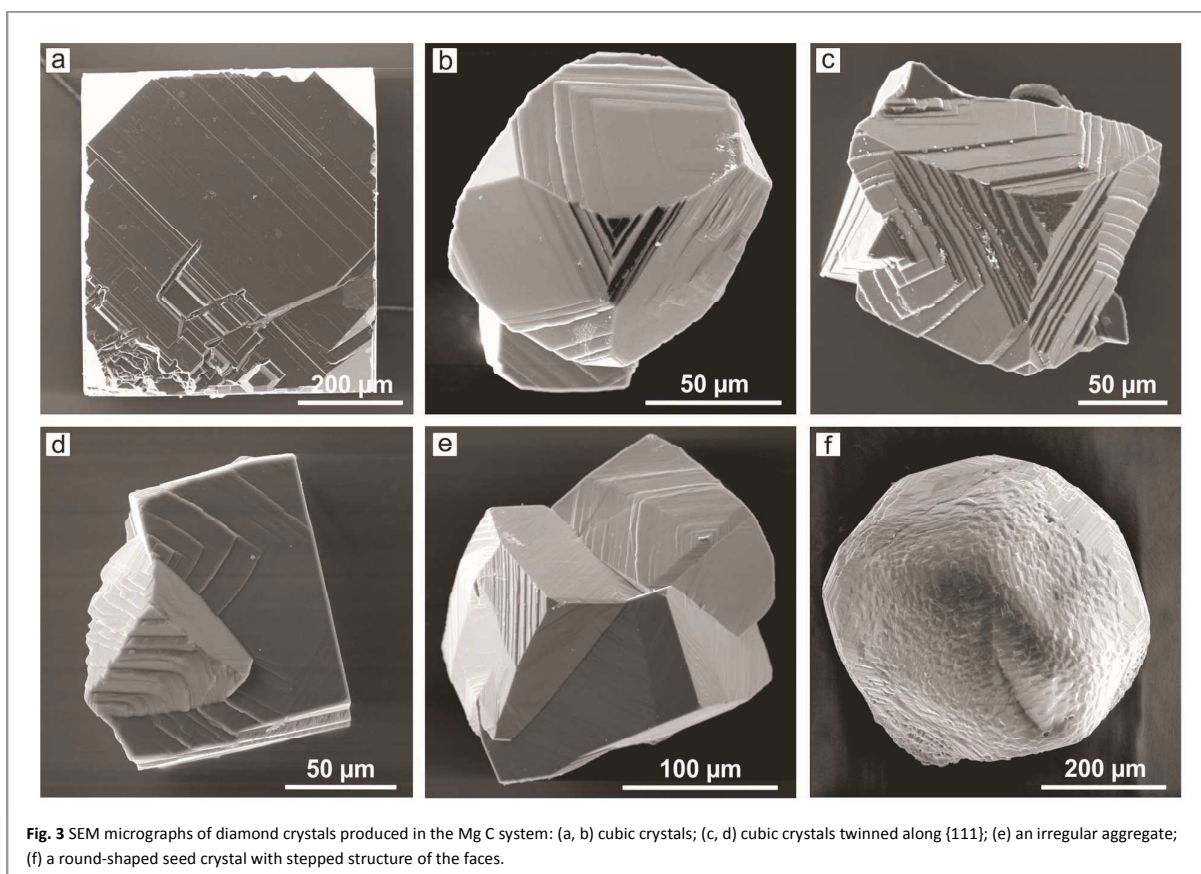


Fig. 3 SEM micrographs of diamond crystals produced in the Mg-C system: (a, b) cubic crystals; (c, d) cubic crystals twinned along $\{111\}$; (e) an irregular aggregate; (f) a round-shaped seed crystal with stepped structure of the faces.

Let us now consider morphological features and internal structure of the synthesized diamond crystal in some greater detail. Over the entire range of P-T parameters, cube is found to be the dominating form of diamond growth in the Mg-C system. The produced diamonds are represented by cubic single crystals (Fig. 3a, b), cubic crystals twinned along $\{111\}$ (Fig. 3c, d), or irregular overgrowths (Fig. 3e). The $\{100\}$ faces exhibit a specific stepped structure. Growth layers are formed at one or several points on the $\{100\}$ faces and propagate in $[110]$ directions forming a clear orthogonal pattern on the face (Fig. 2b, c). Macrosteps formed by the growth layers give rise to a specific rectangular hatching on the $\{100\}$ faces. Spontaneous diamond crystals typically show thick macrolayers in the form of rounded rectangles (Fig. 3b-e). The ends of the growth layer are always formed by the $\{111\}$ microfaces. The polygonal stepped relief of the faces and their convex structure resulted from this arrangement of the layers (Fig. 3b-e). No crystals with depressions on the $\{100\}$ faces or with elements of skeletal growth were detected in the entire series of experiments over the broad range of temperatures and run duration.

Fig. 4 shows a $\{100\}$ section plate prepared from a cubic diamond crystal grown on a seed. The inner part of the plate has intense deep brown color and is characterized by fine zoning along the $[100]$ direction (Fig. 4b). The most intense dark brown color is typical of the boundaries between the $\{100\}$ growth sectors. In the outer portions of the crystal (Fig. 4b, d) it is clearly seen that the most intensely colored zones are associated with the macrolayers

on the $\{100\}$ faces and are confined to the base of the dihedral angle between the $\{100\}$ face containing the macrolayer and the $\{111\}$ end face of the growing macrolayer. The nonsynchronous joining of the growth macrolayers at the edges between adjacent $\{100\}$ faces yields specific “parquet” pattern at the growth sector

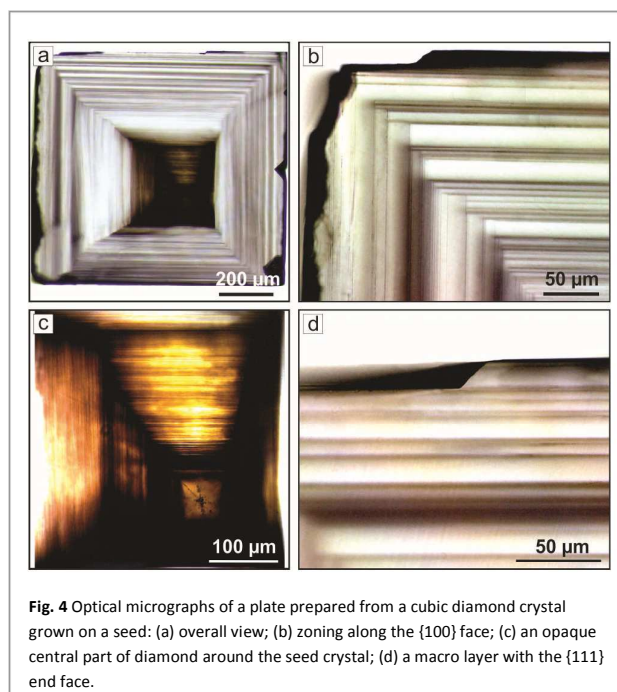


Fig. 4 Optical micrographs of a plate prepared from a cubic diamond crystal grown on a seed: (a) overall view; (b) zoning along the $\{100\}$ face; (c) an opaque central part of diamond around the seed crystal; (d) a macro layer with the $\{111\}$ end face.

boundaries (Fig. 4c).

Along with the unique growth and morphological features, diamonds produced in the Mg-C system also demonstrate remarkable optical characteristics related to their defect and impurity structure. First of all this concerns their specific coloration ranging from colorless to dark brown or black, with all of the colors being sometimes observed in different areas within one crystal. As a general tendency we note that as the crystallization temperature increases both the intensity of the brown coloration and the abundance of brown colored crystals in the run products decreases. Unfortunately, due to relatively small sizes of the produced diamond crystals we were not able to measure absorption spectra in the visible range using conventional spectrophotometers. Nevertheless, below we shall discuss possible origin of the observed coloration and corresponding defects in some more details. Microscopic infrared absorption measurements revealed that the crystallized diamonds typically contain boron impurity in concentrations up to 1 ppm (Fig. 5). The absorption due to uncompensated boron acceptors is generally more intense in the spectra recorded from lightly colored areas and/or crystals than in the spectra taken from brown areas. No absorption features that can be assigned to nitrogen impurities in the single substitutional C-form or in the paired A-form were observed, indicating that the brown color is not due to nitrogen impurities. On the other hand, spectra recorded from brown colored areas, along with the absorption features due to the boron acceptors, show an absorption which steadily increases toward larger wavenumbers (Fig. 5). The strength of this continuous absorption correlates with the intensity of brown coloration. Obviously, it is this continuous absorption which extending to the visible part of the spectrum gives rise to the specific brown or reddish brown coloration of the synthesized diamond crystals.

Another remarkable feature of diamonds synthesized in the Mg-C system concerns their photoluminescence spectra. It is found that irrespective of the synthesis conditions the diamonds produced in this system typically exhibit

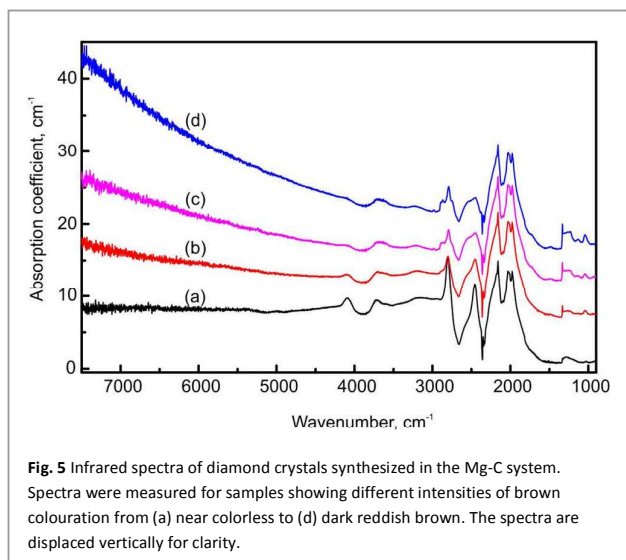


Fig. 5 Infrared spectra of diamond crystals synthesized in the Mg-C system. Spectra were measured for samples showing different intensities of brown colouration from (a) near colorless to (d) dark reddish brown. The spectra are displaced vertically for clarity.

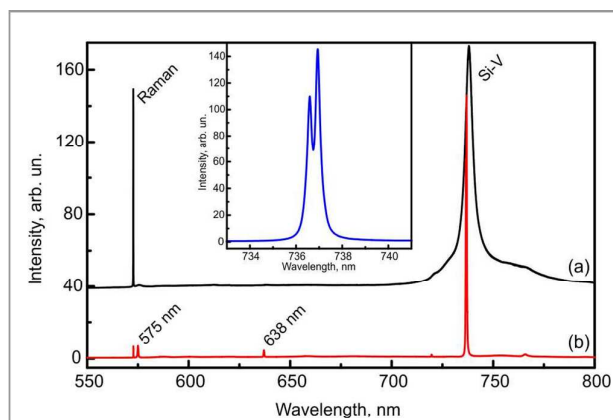


Fig. 6 Typical photoluminescence spectra of diamond crystals synthesized in the Mg-C system. The spectra were measured with the 532-nm excitation at (a) 300 and (b) 80 K. The spectra are displaced vertically for clarity. The inset shows ZPL region the 737-nm PL system at 80 K.

photoluminescence due to the well-known silicon-vacancy (Si-V) centers. The corresponding spectrum comprises a zero-phonon line (ZPL) peaking at about 737 nm at room temperatures and a tail at larger wavelengths due to phonon-assisted transitions (Fig. 6a). In low temperature (about 80 K) spectra the ZPL splits into a doublet, whose components are separated by about 0.3 nm (Fig. 6b).

Occasionally weak features due to the nitrogen-vacancy centers (ZPLs at 575 and 638 nm) are present in the spectra. It is found that the distribution of the Si-V centers within a particular diamond sample is very inhomogeneous, so that it is difficult to assess the effect of the crystallization temperature. For the sample shown in Fig. 4 we found that the 737-nm system tended to be more intense in zones that had darker color, and showed very high intensity as compared to the diamond Raman line in the central very dark zone of the sample. The occurrence of the Si-V centers in diamonds synthesized in the Mg-C system was also noted previously.⁸ It is remarkable that this crystallization system provides very favorable conditions for incorporation of silicon in diamond with formation of optically active Si-V centers, even though Si is present in the initial reagents in trace amounts. This is in contrast with many conventional transition metal solvent-catalysts, for which deliberate doping with Si (5-10%) is necessary to produce diamonds with Si-V centers.^{22,23}

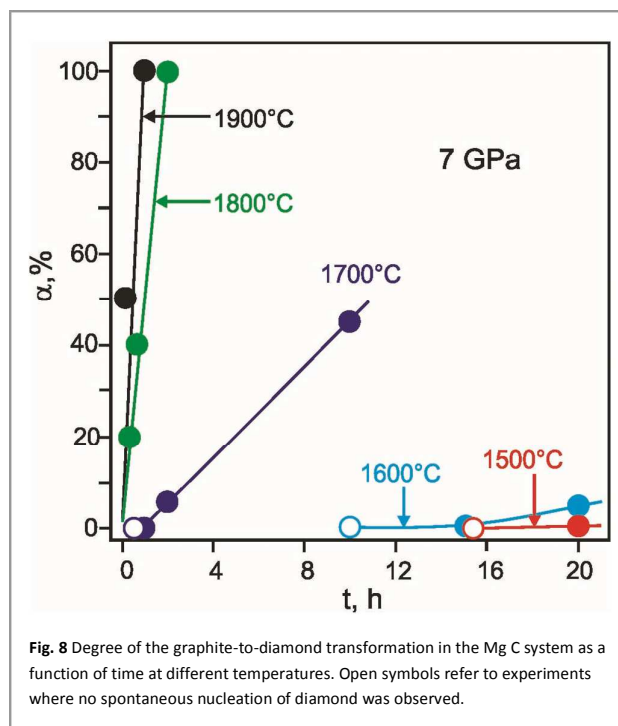
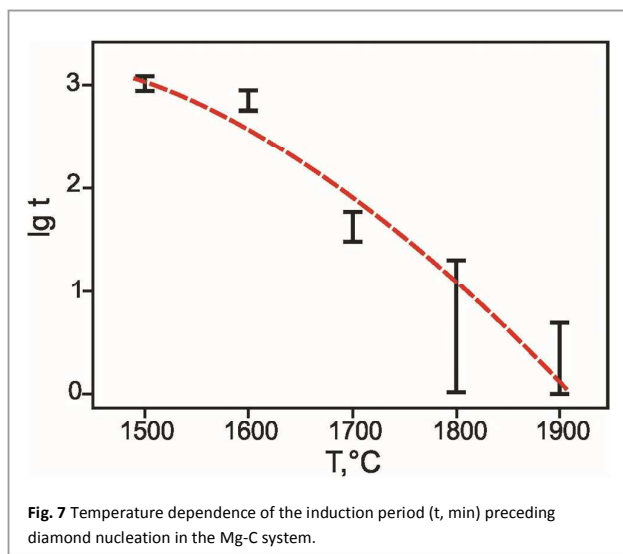
Discussion

Let us discuss first the effect of temperature on diamond nucleation and growth in the Mg-C system with allowance for kinetic effects which were most pronounced as temperature decreased. Our results indicate that there is a certain induction period preceding diamond nucleation in the Mg-C system. Though accurate determination of the induction period duration at different temperatures is complicated, it is possible to estimate the plausible ranges of the duration and its temperature dependence. At 1900 °C the induction period was very short, if it existed at all. Formally, we can estimate it as

being between 0 and 5 min. At 1800 °C the induction period was also insignificant, less than 20 min. It can be easily determined that at 1700 °C it was longer than 30 min but shorter than 1 h. An analysis of the experiments at 1600 °C shows that the duration of the induction period was longer than 10 h but shorter than 15 h. The data obtained at 1500 °C allow us to estimate the duration of the induction period as being in the range from 15 to 20 h. These estimated data are summarized in Fig. 7 as a function of temperature. It can be clearly seen from Fig. 7 that the duration of the induction period, preceding diamond nucleation in the Mg-C systems, drastically increases with decreasing temperature. A similar phenomenon has been found previously for many nonmetallic solvent catalyts.^{14,24,25}

The degree of the graphite-to-diamond transformation is another important characteristic of diamond synthesis that allows quantitative estimation of the effect of the crystallization conditions. Fig. 8 shows the degrees of the graphite-to-diamond transformation as a function of time at different temperatures. First of all, Fig. 8 shows that crystallization temperature is a crucial factor strongly affecting the overall reaction of diamond synthesis. The effect of the kinetic factor becomes evident with decreasing temperature and it is this factor that makes possible diamond synthesis in the Mg-C system at relatively low temperatures (1500 and 1600 °C).

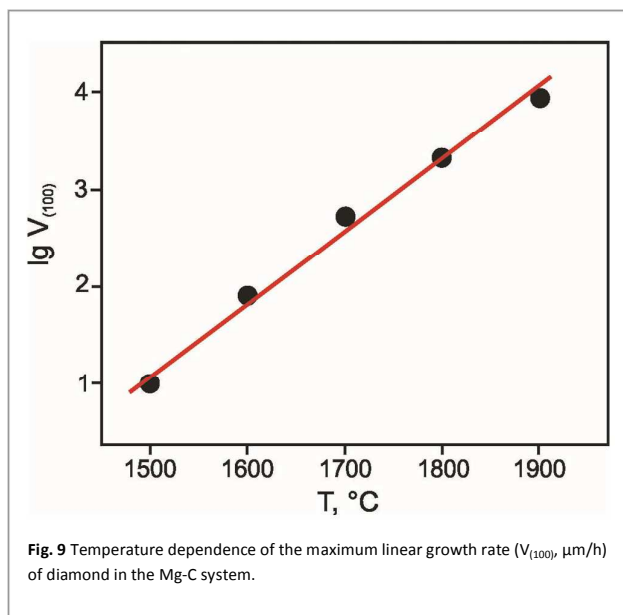
In order to make a more complete characterization of diamond crystallization in the Mg-C, it is reasonable to estimate diamond growth rates at different temperatures. We used the data on crystal size and experimental run duration to estimate the linear growth rates of the {100} faces and took into account the duration of the induction period preceding diamond nucleation at temperatures of 1500 and 1600 °C. Although there could be some uncertainties in determining the onset of diamond spontaneous nucleation and growth on the seed crystals in one experiment, we tried to determine the maximum values of the linear rates for each temperature. The results of the calculations are presented in Fig. 9. It follows



that the linear rate of diamond growth in the Mg-C system increases by more than three orders of magnitude from about 10 $\mu\text{m/h}$ at 1500 °C to as high as 6–8.5 mm/h at 1900 °C.

It is instructive to consider the main features of diamond crystallization in the Mg-C system in comparison with the conventional transition metal catalysts used for synthesis of industrial diamond grit and growth of large single crystals. When diamond crystallizes from carbon solution in the melt of transition metal catalysts, growth layers nucleate near the edges and corners of the growing face and propagate to the face center. With high carbon supersaturation in the melt, growth layers do not cover the entire face and synthesized diamond crystals exhibit depressions in the central part of the faces. In the limiting case, skeletal crystals are formed. In addition, bands of small inclusions extending from the center of the crystal to the corners or edges are characteristic of diamonds synthesized with transition metal catalysts. All these features are indicative of the diffusion-controlled mechanism of diamond growth.^{26–28} In the present study we found that in the Mg-C system growth layers are generated on active points lying on {100} faces of a growing crystal, and a new layer is formed before the previous one reaches the face edge. As a result crystals with flat or convex faces are eventually formed. For the entire set of experiments performed in this study, neither crystals with the elements of skeletal growth, nor specific bands of inclusions tracing the growth of corners and edges of the crystals were observed.

The morphology of diamond crystals in the Mg-C system was determined by the relative development of the {100} and {111} faces. However, the growth rate of the {111} microfaces forming the ends of the growth layer on the {100} faces was significantly higher than the growth rates of the {100} faces. As a result, the shape of the crystal was controlled by the slowly



growing {100} faces, which is typical of the entire temperature range from 1500 to 1900 °C, as opposed to the metal–carbon systems where the morphology changes from cubic to octahedral with increasing crystallization temperature.

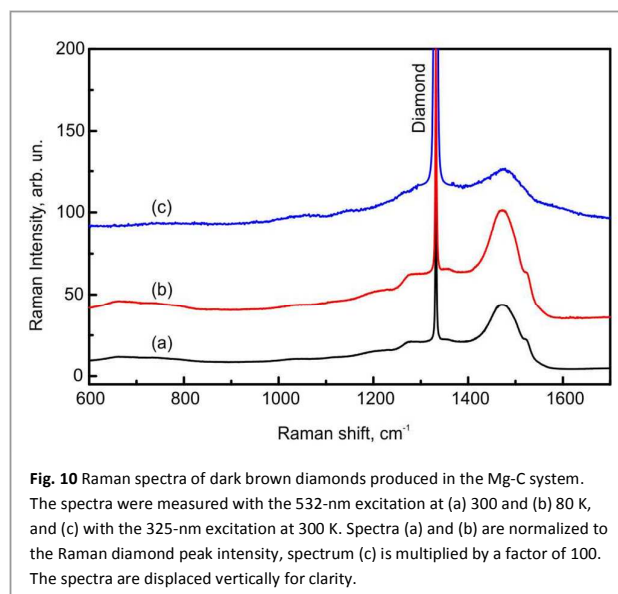
A high number of diamond crystallization centers at the graphite–melt interface and high diamond growth rates are characteristic of diamond synthesis from graphite in the transition metal–carbon systems. The combination of these factors does not allow producing diamond crystals larger than 1 mm in size using the film growth (FG) method. For the Mg-C system we found that the growth rates can be even higher, but the number of crystallization centres is lower. With this combination we were able to synthesize larger diamond crystals via spontaneous nucleation and grow diamond crystals up to 2–3 mm in size on the seed crystals via the film growth method.

The maximum linear rates of diamond growth in the Mg-C system reached 8.5 mm/h, which is approximately 8–10 times higher than those typical for diamond synthesis in the conventional metal-carbon systems by the FG method and incommensurably higher than those of diamond growth by the temperature gradient growth (TGG) method.

All the above considered features indicate that, as opposed to the conventional metal-carbon systems where diamond grows in the diffusion-limited regime, diamond nucleation and growth in the Mg-C system is controlled by the kinetics of embedding of carbon atoms onto the growing surfaces rather than by carbon transport processes.

Finally, we want to consider the question of very specific coloration of diamonds synthesized in the Mg-C system. It is possible that the observed brown coloration and the underlying continuous absorption may have an apparent relation to the problem of brown color of natural plastically deformed diamonds and low quality CVD diamonds, which have been extensively investigated over the last 10–15 years.²⁹ It has been generally accepted now that the featureless

absorption spectrum of brown diamonds is due to multi-vacancy defects whose inner surfaces comprise π -bonded carbon and where there is strong overlap between nearby sp^2 atoms.^{29,30} Providing the concentration of these defects is sufficiently high, one may reasonably expect detecting Raman signatures of π -bonded carbon, which characteristically lie at around 1500 cm^{-1} .³¹ In order to check this we performed Raman measurements for a number of synthesized crystals showing different intensities of brown coloration. For colorless and lightly colored samples only a peak at 1332 cm^{-1} due to the zone-center optical phonon of diamond was found in the Raman spectra. For dark brown samples a number of additional relatively broad bands were detected (Fig. 10). Most intense of them is a band peaking at around 1480 cm^{-1} . The intensity of the 1480 cm^{-1} band, normalized to the diamond Raman peak, correlates with the strength of brown coloration. Since with the 532-nm laser this band lies at around 577 nm and therefore may possibly be related to photoluminescence from the nitrogen-vacancy 575-nm center, additional measurements were performed at a low temperature (80 K) with the 532-nm laser and at room temperature with the 325-nm laser. It is found that the shape of the 1480 cm^{-1} band does not significantly change upon cooling and a band having the same position and similar shape is present in the Raman spectra measured with the UV excitation (Fig. 10). These data allow us to infer that the 1480 cm^{-1} band is due to Raman scattering rather than photoluminescence. Further assignment of this band to a particular vibrational mode and/or defect structure is a formidable task, lying beyond the scope of the present study. However, we can note here that its position is indeed in the frequency range characteristic of π -bonded carbon vibrations. Interestingly, theoretical calculations, which have shown that the featureless continuous absorption of brown diamonds could be attributed to defects in the form a multi-vacancy disk lying on {111} planes, also predicted for these defects a Raman active mode at around 1490 cm^{-1} .³⁰



Another argument supporting our speculation that the brown coloration of diamonds studied in this work may have somewhat similar origin with the coloration of natural brown diamonds comes from the fact that diamonds crystallized in the Mg-C system at 1900 °C have much lighter coloration. As shown in many previous studies on natural brown diamonds, their specific coloration can be significantly altered or completely removed by HPHT treatment at temperatures of about 2000 °C and higher.^{32,33} We may further speculate that the high concentration of the vacancy cluster defects in the studied diamonds can be related to the specificity of diamond crystallization in the Mg-C system, such as growth by thick growth layers with high growth rates. It is intuitive that with the crystal growth proceeding via fast propagation of relatively thick layers, the probability for burying small vacancy clusters would be much higher than in case of propagation of thin (atomically thick) growth layers.

Conclusions

In this study we demonstrate that diamond nucleation and growth in the Mg-C system occurs over a broader range of P-T conditions than was determined previously. Variation of experimental run duration from 5 min to 20 h under pressure of 7.0 GPa allowed us to determine the temperature dependence of the induction period preceding diamond nucleation in the temperature range of 1500-1900 °C. The minimum temperature of diamond nucleation and growth in the Mg-C system is 1500 °C at 7.0 GPa. It is found that the duration of the induction period preceding diamond nucleation strongly depends on temperature and significantly increases as temperature decreases, changing from almost zero at 1900 °C to ~17.5 h at 1500 °C. Diamond growth on the seed crystals is established in the temperature range of 1500-1900 °C at 7.0 GPa and at a lower pressure of 6.3 GPa at 1650 °C. The specific feature of the Mg-C system is that irrespective of P-T conditions the stable growth form of diamond is cube. It is found that the maximum linear rate of diamond growth almost exponentially depends on temperature and varies from 10 μm/h at 1500 °C to 8.5 mm/h at 1900 °C, which is 8-10 times higher than the diamond growth rate in the conventional metal-carbon systems. The combination of the determined temperature dependences of crystal morphology and internal structure, as well as the nucleation and growth kinetics, indicate that diamond growth in the Mg-C system occurs in the kinetically controlled regime. It is found that diamonds crystallized in the Mg-C system exhibit many intriguing characteristics such as the occurrence of deep brown or reddish brown coloration, the presence of boron impurities and silicon-related optical centers, specific Raman spectra, which are not typical for HPHT diamonds produced from many other metal or nonmetallic solvents. All these features are obviously connected with the specificity of diamond crystallization in this system and deserve further detailed investigations.

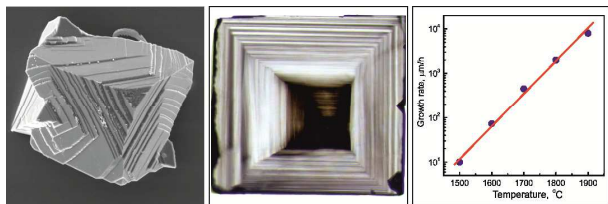
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The effects of temperature and kinetics on diamond crystallization in the Mg-C system at high pressure high temperature conditions are established.