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Effect of temperature and alloy-solvent content on diamond crystallization in Mg-based systems for HPHT method

Defect-impurity composition of diamond single crystals grown in Mg–C and Fe–Mg–C systems depending on growth temperature and magnesium content at pressure 7.7 GPa and temperature 1700–2000 °C was studied. It was established that in Mg–C system an increase of the growth temperature leads to an increase of the amount of uncompensated boron in crystals in ~ 3 times. In Fe–Mg–C system with an increase of the magnesium content in the growth medium up to 70 at % the concentration of boron in the grown crystals increases 1.5–2.6 times. All these features can be explained by the change in the thermodynamic activity of the main impurities in the diamond crystal lattice on crystallization front depending on the composition of the growth system and the growing temperature.

Keywords: high pressure, high temperature, diamond, single crystal growth, Mg-based systems, boron.

INTRODUCTION

The study of the diamond crystallization process in various growth systems is of considerable interest in connection with the possibility of obtaining more complete information about the mechanisms of diamond formation and growth and the expansion of the possibilities for obtaining crystals with given properties. The main growth method of diamond single crystals is growth under high pressure and high temperature conditions [1–5]. As solvent alloys, elements capable of dissolving carbon under conditions of high pressure and temperature and providing the necessary supersaturation in diamond thermodynamic stability region such as Fe, Ni, Co are usually used [5–10]. In recent decades considerable attention has been paid to modeling the processes of natural diamond formation in melts of carbonates, silicates, and sulfides [11–15]. Diamond crystallization in single-component solvents Ge, Cu, Sb, Se, P, Mg which allows obtaining diamonds with unique properties, for example, *n*-type conductivity, new optical centers connected with germanium or copper, is also actively investigated [16–21].

Properties of crystals – their structural perfection, thermal conductivity, electrical conductivity are determined by the presence and distribution of impurities in diamond, primarily nitrogen and boron [22–26]. It is known that the doping growth systems with boron leads to crystallization of type II*b* diamonds with semiconductor properties. Boron forms in the diamond lattice an acceptor state $(Ea = 0.37 \text{ eV})$ to produce *p*-type conductivity. Diamonds containing uncompensated boron acceptors are rare in nature and typically has an uncompensated boron concentrations of $5 \cdot 10^{16} \text{ cm}^{-3}$.

To produce semiconductor diamond at high pressures and temperatures Fe–Al–C or Co–Fe–Ti/Al–C systems with the addition of boron or boron-containing components are usually used [27]. Boron concentrations as high as $> 10^{20}$ cm^{-3} are reported for diamonds grown in these systems [27–29]. Type IIb diamonds have a characteristic infrared absorption consisting of a series of relatively sharp zero-phonon peaks at 2455, 2802 and 2928 cm^{-1}, which are due to bound-hole transitions, a photoionization continuum, starting at around 3000 cm^{-1}, and boron-induced one-phonon absorption band peaking at 1290 cm^{-1} [27].

In recent years attention has been paid to diamond crystallization in magnesium-based systems [20, 30–33]. Resent studies shown a number of unique features of diamonds grown in Mg-based systems such as high growth rate and semiconductor properties. Linear growth rate of diamonds grown in Mg–C system is 0.6–0.8 mm/h and weight rate is 24–36 mg/h, which exceeds the growth rates of diamond single crystals in systems using transition metals in 8–10 times [20]. It also was established that with increasing temperature from 1500 to 1900 °C, diamond growth rate increased by almost three orders of magnitude, from 10 to 8.5 mm/h, respectively [31].

EXPERIMENT

Experiments on diamond crystallization were carried out in high-pressure equipment of the "toroid" type in Mg-based systems (Mg–C, Fe–Mg–C) at 7.7 GPa and 1700–2100 °C. Graphite GSM1, high-purity Mg and Fe with a fraction of 30–40 μm were used in the experiments. Graphite and metals were mixed, and then mixed powder was pre-pressed into a disk. The Mg additives used in the experiments in Fe–Mg–C system were 30, 50 and 70 wt %. The growing process was carried out by the spontaneous crystallization method. The duration of the experiments was 10–40 min. The pressure in the growth cell was determined from the load characteristics constructed using fixed points of the electrical resistance of Bi and Ta [34]. A PtRh30/PtRh6 thermocouple was used to measure temperature. The accuracy values of the pressure and temperature measurement were ±(0.2–0.4) GPa and ±(40–60) °C, respectively. The produced diamonds were studied using optical and scanning electron microscopy. Spectroscopic characterization of crystals was performed by means of infrared (IR) absorption. IR spectra were recorded using a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer fitted with a Nicolet Continuμm microscope.

RESULTS AND DISCUSSIONS

All of the studied diamonds grown in Mg–C and Fe–Mg–C systems show the typical IR absorption bands arising from the electronic and phonon states related to uncompensated B in FTIR absorption measurements, including peaks at 2455, 2802 cm^{-1} (Fig. 1). The concentration of uncompensated B (B_0) was estimated by the method developed by [26, 35] using equitation: $B_0 = 5,53 \cdot 10^{-4} \cdot I_{2802}$, where B_0, ppm; I_{2802} – integrated area measured under the 2802 cm^{-1} B peak, cm^{-2}. Another method [36] uses the peak height of peak at 2800 cm^{-1}. Both methods yielded similar results within the given errors [24].

In Mg–C system crystals with a size of 50 μm–1 mm were obtained. The results of the experiments in Mg–C system are summarized in Table 1. The characteristic absorption bands for uncompensated boron impurity, described above, were observed in the IR spectra of all diamond crystals grown in the Mg–C system. Rises from 1.9 to 3.5 ppm of uncompensated boron concentration in colorless crystals of cubic habit was observed. An increase of growth temperature leads to an increase

of uncompensated boron impurity concentration in crystals from 1.9 to 6.4 ppm (see Table 1); the crystals acquire a noticeable blue hue. For blue crystals, the concentration of uncompensated boron impurity rises to 3.6–6.4 ppm.
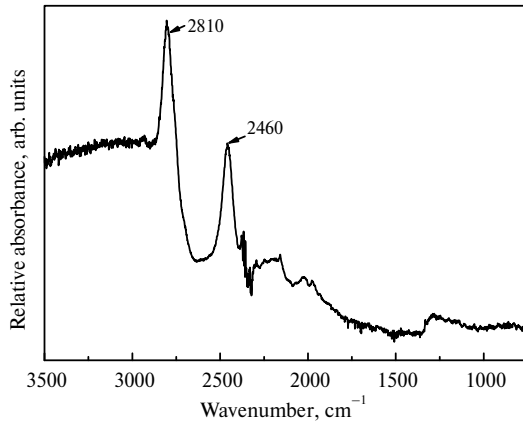

Fig. 1. Typical FTIR absorption spectrum of diamond single crystal grown in Mg–C system (see table 1, run 3).

Table 1. Experimental results of diamond growth in Mg–C system

Runs	Color	T, °C	B_0, ppm
1	colorless	1770	1.9
2	colorless	1829	2.8
3	colorless	1829	3.5
4	colorless	1829	3.1
5	light blue	1900	4.1
6	light blue	1900	3.6
7	blue	2000	4.99
8	blue	2000	6.4

The experiments on the growth of diamond crystals in the Mg–C system showed that during spontaneous crystallization, an increase in the growth temperature leads to an increase in the diffusion rate of boron atoms at the crystallization front and, consequently, an increase in the amount of boron impurity in the grown crystals; an increase in the growing temperature by 200 °C leads to an increase in the amount of boron in crystals in ~ 3 times (Fig. 2) and the color changes; the crystals are colorless at 1700–1829 °C and turn light blue at 1900 °C and blue at 2000 °C.

In Fe–Mg–C system diamond single crystals with a size from 200 μm to 1 mm were obtained. The results of the experiments in Fe–Mg–C system are summarized in Table 2. In the area of manifestation of natural lattice vibrations, a system of absorption bands is observed associated with uncompensated boron with characteristic peaks at 2460, 2810 cm^{-1}. Depending on the magnesium content in the growth system, a change in the concentration of boron impurities in the grown crystals is observed (Table 2). The minimum boron concentration is observed in crystals grown in the growth system with 30 at % Mg. With an increase of the magnesium content in the growth medium up to 70 at % the concentration of boron

in the grown crystals increases 1.5–2.6 times. A further increase in the magnesium content of the growth system to 100 % leads to an increase of the boron concentration in 1.5–4 times.
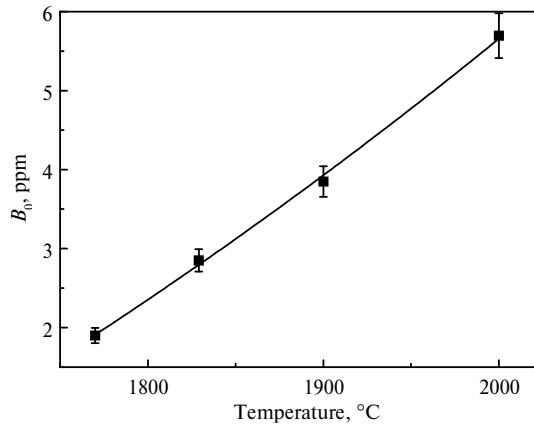

Fig. 2. Dependence of uncompensated boron impurity concentration on the growth temperature in diamond crystals obtained in Mg–C system.

Table 2. Experimental results of diamond growth in Fe–Mg–C system

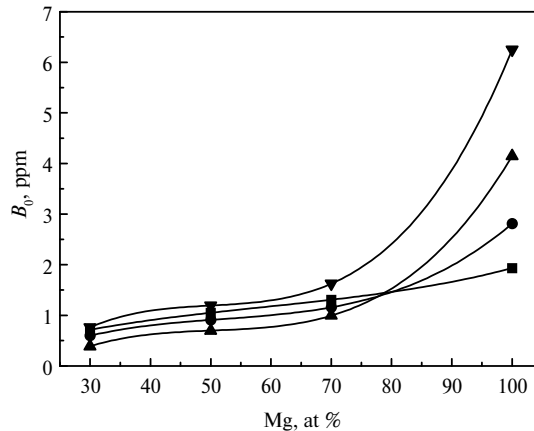| Mg, at %	B_0, ppm, at T, °C			
	1700	1800	1900	2000
30	0.72	0.60	0.39	0.76
50	1.05	0.91	0.70	1.19
70	1.31	1.16	0.99	1.63
100	1.93	2.81	4.15	6.25

Fig. 3. Dependence of uncompensated boron impurity concentration on the Mg content in the Fe–Mg–C system at T = 1700 (■), 1800 (●), 1900 (▲), 2000 (▼) °C.

It should be noted that in all experiments carried out in the Mg–C and Fe–Mg–C growth systems exactly the same graphite was used as the carbon source in all experiments, which contains about $(1–4) \cdot 10^{-5}$ wt % of boron.

All these features of the change in the defect-impurity composition of diamond grown in Mg–C and Fe–Mg–C systems can be explained by the change in the thermodynamic activity of the main impurities of carbon substitution in the crystal lattice of diamond, nitrogen and boron, depending on the composition of the growth system and the growing temperature. The main feature of the change in thermodynamic activity is that boron, which enters as a small amount in the carbon source ($< 10^{-5}$ wt %) enters the crystal in significant quantities due to the increase in its activity at the crystallization front.

CONCLUSIONS

In Mg-based systems type II*b* diamonds crystallize without boron doping by using the graphite source with a trace amount of boron ($\sim 10^{-5}$ wt %).

In Mg–C system an increase in the growing temperature by 200 °C leads to an increase in the amount of boron in crystals in ~ 3 times.

The concentration of uncompensated boron in crystals grown in Fe–Mg–C system with an increase in the magnesium content from 30 to 70 at % increases in ~ 1.5–2.6 times.

Досліджено дефектно-домішковий склад монокристалів алмазу, отриманих в ростових системах Mg–C та Fe–Mg–C в залежності від температури вирощування й вмісту магнію при тиску 7,7 ГПа і температурі 1700–2000 °C. Встановлено, що в системі Mg–C підвищення температури вирощування приводить до зростання кількості нескомпенсованого бору в кристалах в ~ 3 рази. В системі Fe–Mg–C з підвищенням вмісту магнію в ростовому середовищі до 70 % (ат.) концентрація бору в вирощених кристалах зростає в 1,5–2,6 рази. Усі ці особливості зміни дефектно-домішкового складу алмазу можна пояснити зміною термодинамічної активності основних домішок заміщення вуглецю в кристалічній гратці алмазу, азоту й бору, залежно від складу ростової системи і температури вирощування.

Ключові слова*: високий тиск, висока температура, алмаз, ріст монокристалів, системи на основі Mg, бор.*

Исследован дефектно-примесный состав монокристаллов алмаза, выращенных в ростовых системах Mg–C и Fe–Mg–C в зависимости от температуры выращивания и содержания магния при давлении 7,7 ГПа и температуре 1700–2000 °C. Установлено, что в системе Mg–C повышение температуры выращивания приводит к увеличению количества нескомпенсированного бора в кристаллах в ~ 3 раза. В системе Fe–Mg–C с повышением содержания магния в ростовой среде до 70 % (ат.) концентрация бора в кристаллах возрастает в 1,5–2,6 раза. Все эти особенности изменения дефектно-примесного состава алмаза можно объяснить изменением термодинамической активности основных примесей замещения углерода в кристаллической решетке алмаза, азота и бора, в зависимости от состава ростовой системы и температуры выращивания.

Ключевые слова*: высокое давление, высокая температура, алмаз, рост монокристаллов, системы на основе Mg, бор.*

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