

Formation of mixed types of diamonds in the Fe–Co–Mg–C growth system at HTHP-crystallization

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This paper presents the results of a study of diamond single crystals of defect-impurity composition grown in a temperature gradient at high pressures and temperatures (HTHP-crystallization of diamond) in a Fe–Co–C solution with an addition of Mg depending on the amount of Mg, the content of nitrogen changes in various sectors of crystals growth, which causes a mixed type of crystals. The peculiarities of changes in the defect-impurity composition of the grown diamond single crystals were studied using IR spectroscopy and optical microscopy for concentration limits of 1.8–5.7 at. % of Mg content.

Keywords: diamond, single crystal, crystal growth, temperature gradient method, nitrogen and boron impurities, high pressures and temperatures.

Утворення змішаних типів алмазів у ростовій системі Fe–Co–Mg–C при HTHP-кристалізації. *Т.В.Коваленко, В.В.Лисаковський, С.О.Івахненко, В.В.Стрельчук, О.О.Заневський, А.С.Ніколенко*

Представлено результати дослідження дефектно-домішкового складу монокристалів алмазу, вирощених методом температурного градієнта при високих тисках і температурах (HTHP-кристалізація алмазу) в розчин-розплавних системах Fe–Co–C при легуванні їх Mg. В залежності від кількості Mg змінюється вміст азоту в різних секторах росту кристалів, що обумовлює отримання змішаного типу кристалів. Особливості зміни дефектно-домішкового складу вирощених монокристалів алмазу вивчено із застосуванням ІЧ-спектроскопії і оптичної мікроскопії для концентраційних меж з 1,8–5,7 ат. % вмісту Mg.





Представлены результаты исследования дефектно-примесного состава монокристаллов алмаза, выращенных методом температурного градиента при высоких давлениях и температурах (HTHP-кристаллизация алмаза) у раствор-расплавных системах Fe–Co–C при легировании их Mg. В зависимости от количества Mg изменяется содержание азота в различных секторах роста кристаллов, что обуславливает получение смешанного типа кристаллов. Особенности изменения дефектно-примесного состава выращенных монокристаллов алмаза изучены с применением ИК-спектроскопии и оптической микроскопии для концентрационных пределов 1,8–5,7 ат. % содержания Mg.

1. Introduction

Diamond single crystals obtained by solution-melt crystallization at high pressures

and temperatures (HTHP diamond single crystals), depending on the growing conditions, can have a nitrogen and boron impurities in a fairly wide content range from

Table. Experimentally determined concentration intervals of diamond formation of types Ib, Ib + IIa and Ib + IIb and mass growth rates of crystals depending on the Mg content in the solvent based on Fe — 40 at. % Co; $p = 6.3$ GPa

Sample No	Mg content in the solvent, at. %	Temperature range, °C	Crystal type	Mass growth rate, mg / h	Nitrogen content, N(x) ppm	Boron content, ppm	Weight, carat	Crystal habit	Crystal photo
1	1.80	1500 – 1560	Ib	6.1 – 7.0	30 – 40	–	2.12	Cuboctahedron	
2	2.20	1520 – 1600	Ib+IIa	6.8 – 7.4	5 – 10	–	8.14	-/-	
3	3.50	1560 – 1650	Ib + IIb	8.1 – 9.5	5 – 25	5 – 15	3.28	-/-	
4	4.50	1650 – 1750	Ib	10.3 – 13.5	30 – 35	–	3.93	Octahedron	

10^{16} to 10^{21} cm⁻³. When using solvents based on Fe–Co and growth systems doped with Ti, Zr, Al and B, it is now possible to obtain structurally perfect diamond single crystals of types Ib, IIa and IIb and sizes up to 10 mm and more [1–3]. However, the narrow temperature range and low crystallization rates cause instability of the growth process; therefore, it is necessary to study the possibility of changing the composition of solvents by introducing new components. In this sense, the addition of Mg to the growth system was promising; this made it possible to significantly increase the growth rate of crystals while maintaining their quality [4].

The aim of this work was to study the effect of Mg in the content from 1.8 to 5.7 at. % doped into the Fe–Co–C growth system on the growth rate and defect-impurity composition of the diamond during its HTHP crystallization.

2. Experimental

To grow structurally perfect diamond single crystals in the region of thermodynamic stability, the temperature gradient method was used [5, 6]. A high-pressure apparatus was used, which made it possible to load growth cells up to 7 GPa and 1800°C using a six-punch cubic press. The growth volume in which the crystals were grown on seeds was 19 cm³; the duration of the growing cycles was 150–200 h.

To grow diamond single crystals by the temperature gradient method, a solvent

alloy Fe55–Co45 at. % prepared by vacuum induction melting was used; the required amount of magnesium was introduced into the growth volume by adding magnesium powder (in the appropriate weight) with a particle size of 50–40 µm.

3. Results and discussion

Results of experiments on growing structurally perfect single crystals of diamond at pressures of 6.3–6.5 GPa and temperatures of 1500–1750°C using solvents based on Fe–Co and varying the magnesium content in the range of 1.8–5.7 at. %, are given in Table.

In the studied range of concentrations of magnesium additives in the Fe–Co solvent, a cuboctahedral or octahedral habit was observed during crystal growth; the degree of development of octahedron faces for all used solvent compositions increased with increasing temperature. But even at the highest temperatures, 1750°C, the area of the cube faces was at least 7–10 % relative to the total surface of the crystal. The formation of rhombododecahedron and tetragontrioctahedron faces was absent in all growth experiments. As can be seen from Table, an increase in temperature within 1500–1750°C, when using magnesium as an alloying addition to the composition of carbon solvent alloys based on Fe–Co, leads to an increase in the mass growth rate by ~ 2 times. If we compare the values of the rate in the studied growth systems with the commonly used crystallization media Fe–Ni,

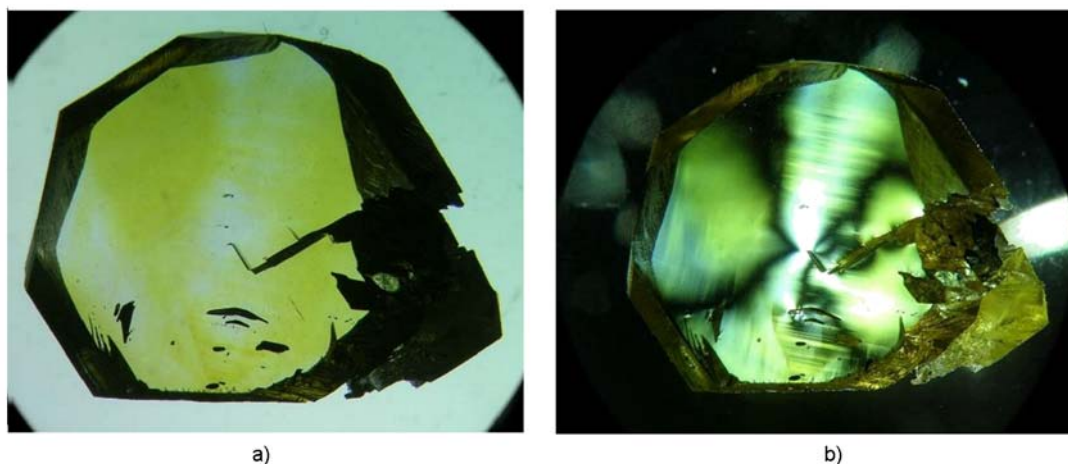


Fig. 1. A plate of a diamond single crystal grown in the Fe–Co–Mg–C growth system, with a Mg content of 2.90 at. %, with orientation in the $\langle 111 \rangle$ direction; optical microscope magnification, $\times 8$, plate thickness 0.3 mm: a) — image in transmitted light, b) — image in polarized light.

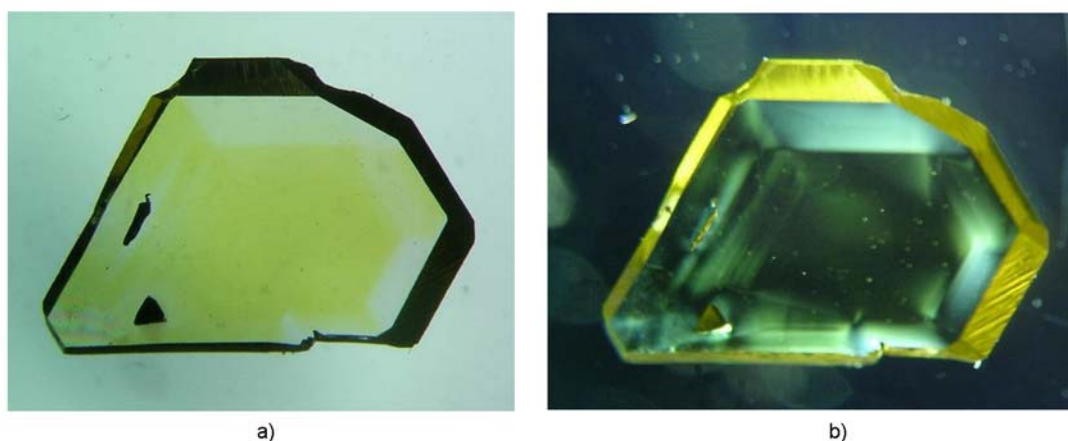


Fig. 2. A plate of a single diamond crystal grown in the Fe–Co–Mg–C growth system, with a Mg content of 1.80 at. %, with orientation in the $\langle 110 \rangle$ direction, optical microscope magnification, $\times 8$, plate thickness 0.3 mm: a) — image in transmitted light, b) — image in polarized light.

Fe–Ni–Co and Fe–Al, then they increase even more, by 3–3.5 times.

For crystals obtained with the magnesium content in the range of 1.80–2.20 at. %, the formation of type Ib crystals was observed. The amount of nitrogen, calculated from the ratio of the peaks at 1345 and 1135 cm^{-1} , recorded in the one-background region of the IR spectra, was 30–40 ppm. With increasing the magnesium content higher than 2.20 at.% (2.20–3.50 at.%), a decrease in the intensity of these peaks and a decrease in the level of nitrogen in crystals to 5–10 ppm are observed for both growing sectors. In this case, the growth sectors of the octahedron faces are yellow, which is characteristic of crystals with single paramagnetic nitrogen

atoms in the substitutional position (C-defects) [7], Figs. 1 and 2. The growth sectors of the cube are observed as colorless; this feature is inherent in type IIa diamonds (the nitrogen amount is less than 10^{18} cm^{-3}), for which there is no IR absorption in the one-background region [7]. Yellow and colorless growth sectors are observed in transmitted light on plane-parallel plates cut from the obtained crystals with $\langle 111 \rangle$ and $\langle 110 \rangle$ orientations. The images in polarized light show that at the boundaries of the $\{111\}$ and $\{100\}$ growth sectors of the grown crystals of the cuboctahedral habit (Table, item 2), there are rather significant contact mechanical stresses.

The results of IR spectroscopy and optical microscopy on the crystallization of dia-

mond in solvents with a magnesium content of 2.20–3.50 at.% make it possible to conclude that the type of crystal, Table, item 2, should be classified as a mixed type Ib + IIa; in this case, the octahedral growth sector is of type Ib, and the cubic one is of type IIa; the determined nitrogen content of 5–10 ppm for the crystal as a whole is relevant only to the octahedral growth sectors. When alloying the Fe–Co solvent alloy with magnesium in the range of 3.50–4.60 at.% in the IR absorption spectra, in addition to the characteristic peaks associated with nitrogen impurities (1345, 1135 cm⁻¹), a system of bands associated with single boron atoms is observed: 2460 and 2810 cm⁻¹, of which the latter is more intense; while the color growth sectors {111} and {100} with magnification of ×8 of the optical microscope practically does not change in the corresponding concentration range of magnesium content in the alloy-solvent, Table, item 3. An estimate of the magnitude and ratio of the lines (1345, 1135 cm⁻¹) and (2460, 2810 cm⁻¹) allows us to conclude that the amount of nitrogen in the octahedron sectors is 5–25 ppm, the amount of boron in the cube sectors is 5–15 ppm; such crystals should be referred to as mixed type Ib + IIb.

The appearance of boron as a substitutional impurity in diamond crystals when they are grown using solvents based on Fe–Co doped with magnesium in an amount of 3.50–4.50 at.% is not an unexpected result. Earlier we found [8] that when using almost all natural graphites, even when using samples with a minimum amount of boron in them at the level of 10⁻⁵–10⁻⁶ at. %, the grown crystals can contain, depending on the temperature level, a significant amount of boron, up to 10 ppm. It is logical to assume that in our case the use of a solvent with a magnesium content of up to 5.7 at. %, the effect of an increase in the thermodynamic activity of carbon substitution with boron is observed in comparison with the substitution of nitrogen for carbon in the crystal lattice of diamond. It is noteworthy that a change in the concentration of magnesium as a component of the solvent, with an increase in its amount in the cube growth sector, first leads to a decrease in

the nitrogen content, and then causes the prevalence of boron in the crystal structure compared to nitrogen; however, after the amount of magnesium reaches 4.50 at. % and more, the activity of nitrogen impurity reaches the initial level.

4. Conclusion

Thus, the experiments have shown that with a magnesium content of 2.20–4.50 at.% in a carbon solvent based on Fe–Co, at high pressures of 6.3–6.5 GPa and temperatures of 1650–1750°C, the formation of two mixed types of diamond single crystals is possible: Ib + IIa (at lower temperatures) and Ib + IIb (at higher temperatures). This result can be explained by the competing thermodynamic activity of nitrogen and boron impurities with carbon, as well as with each other at the diamond crystallization front. An increase in the mass rates of crystal growth by a factor of 2 or more in solvents containing magnesium within certain limits is due to an increase in the amount of carbon transfer by surface and volume diffusion at high temperatures.

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