ISSN 2409-9066. Sci. innov. 2015, 11(1): 45—48 doi: http://dx.doi.org/10.15407/scine11.01.045

Novikov, M.V., Lisakovskiy, V.V., Zanevskiy, O.A., and Ivakhnenko, S.A.
V.N. Bakul Institute for Superhard Materials, NAS of Ukraine, Kyiv

INNOVATIVE ATTRACTIVENESS OF STRUCTURALLY PERFECT DIAMOND SINGLE CRYSTALS IN THE VIEW OF THEIR PURPOSEFUL USE IN THE CUTTING-EDGE TECHNIQUES OF THE 21ST CENTURY

The research carried out at the Institute for Superhard Materials have made it possible to determine regularities of carbon phase transformations and transfer in metal solvents and to create methods for growing large-size structurally perfect diamond single crystals. The results of research underlay a basis for a diamond production technology to be used in electronics, manufacture of laser equipment and drilling tools, and in precision machining. The use of large 6-punch high pressure equipment has allowed the researchers to develop a much more effective technique for growing diamond single crystals.

Keywords: diamond, single crystal, defects, additives, growing methods, high pressure, and high temperature.

In several past decades, the study of physicochemical and structural aspects of phase transformations in carbon materials allowed the researchers to achieve important results in the field of superhard materials, primarily, to develop technologies for growing diamonds. Today, there are two advanced technological solutions for growing structurally perfect diamond single crystals:

1) at high pressure and temperature (HTHP method) in the area of thermodynamic stability;

2) by deposition of carbon from methane (CVD method) in metastable conditions.

Using these methods one can get diamond crystals with controlled defect-impurity composition having a size of 10 mm. They have properties, at least, as good as those of the natural crystals. However, the use of the second method is limited because it is very problematic to keep the equilibrium conditions of diamond formation process during the reaction $CH_4 \leftrightarrow C_{diamond} + 4H$, as a result of which, at a certain stage of growth, carbon graphite deposits on the diamond surface thereby complicating the further process. Therefore, today, the CVD diamond growing method allow the researchers to obtain structurally perfect diamond films and layers having a thickness of a few millimeters, however, to get bulk samples is a serious problem to address which a long time is required.

The HTHP method for growing diamonds, as opposed to the CVD method, is used in the area of thermodynamic stability of diamond. The main types of high pressure apparatuses (HPA) used for studying the crystallization of diamond and for growing the crystals are showed in Fig. 1 (see color inset).

For a long while, the team of authors were studying the growth of diamond single crystals using «anvil with hollow» TS40 HPA (the hollow has a spherical shape) developed at the Institute of Superhard materials (ISM) of the NAS of Ukraine. This apparatus ensures stable growth conditions with possible duration of diamond growing cycle of up to 500 hours [1]. Its design makes it possible to enter thermocouples and electric contacts in the reaction zone for *in-situ* monitoring of crystallization parameters. An advantage of the «toroid» type HPA as compared with other types is a simpler assembly of growth cells, a faster load of containers, and a wider range of pressure variation.

The HTHP method research conducted at the ISM of NAS of Ukraine has made it possible to identify patterns of carbon transfer and phase transitions in solvents, to substantiate techniques for computer simulation and calculation of temperature distribution in growth volume, to establish configuration of thermal fields for creating required temperature gradients, as well as to develop methods of precision control of temperature and pressure for single crystal growth. Based on these results the researchers have developed methods for growing large diamond single crystals having a perfect structure (Ib, IIa and IIb types).

Growing diamond single crystals with a perfect structure and controlled composition of admixtures by HTHP technique is interesting from the scientific standpoint and allows the researchers to define a set of important functional properties, including the color of crystals. From scientific point of view, the influence of oversaturation with carbon, temperature, and pressure on the kinetics of growing diamond crystals of seeds from carbon solutions is a very relevant issue [2, 3]. These diamond crystals obtained under controlled P-T parameters and composition of the growth medium are applied to electronics, laser technology, precision machining, and manufacture of drilling tools. They surpass the natural crystals by many characteristics, especially, due to the fact that in the process of mass production it is possible to keep stable the impurity composition and, consequently, thermal conductivity, electrical conductivity, and required habit shape.

The research conducted at the ISM of the NAS of Ukraine has made it possible to study the basic laws governing the process of growing perfect crystals of similar structure and to create equipment and methods to ensure their production in required amount. The main technical requirement for this is to create a high pressure apparatus and diamond growth cells.

The experience of operating the TS40 HPA of «toroid» type has showed that for growing single diamond crystals of seeds it is advisable to use the Strong-Wentorf method of temperature gradient [4], which involves the placement of the carbon source and the seed crystal in carbon solvent keeping a temperature difference between them of ~50 K ($T_{sourse} > T_{seed}$). The carbon solvents are Fe-Ni-Co-based alloys with dopes of Cu, Sn, Ti, Zr, and Al; the diamond is growing at a temperature of 1300–1700 °C depending on the composition of the growth system. The growth is realized as carbon recrystallization from the source to the seed crystal. This is a melt crystallization of diamond. To obtain large single crystals having a perfect structure the process should be stable, i.e. it is necessary to keep temperature constant and to ensure required distribution of axial and radial gradients of temperature, carbon concentration, and their ratio [5, 6].

The developed methods for crystal growth have allowed the authors to obtain large perfectly structured single crystals of Ib, IIa (Figs. 2, 3, see the color inset) and IIb types (Fig. 4, see the color inset).

In addition to the «toroid» HPA, there are *Belt* and *Bars* HTHP apparatuses widely used for growing diamond single crystals (see Fig. 1). However, in recent years, there has been reported a considerable interest in the 6-punch devices having a reaction volume of up to 1 dm^3 and more. The devices are made in China. These devices have an unmatchable performance for spontaneous crystallization as compared with other HPA. This has enabled China to bring the annual production of diamond grinding powders and their polycrystalline derivatives to 12 billion carats. However, for growing large perfect diamond single crystals it is necessary to design a new HPA container, as well as to develop methods and algorithms for controlling the growing process. An attractive solution of this problem is to use a much larger

ISSN 2409-9066. Sci. innov. 2015, 11(1)

reaction volume to facilitate the large-scale industrial production of diamond crystals.

CS-VII manufactured by Hualin (PRC) was chosen as experimental model of 6-punch press. Its diameter and plunger capacity are 560 mm and 25 MN, respectively (Fig. 5, see the color inset). The presses of this type have proven themselves to be effective for the production of diamond grinding powders and have highly reliable hydraulic components and mechanisms, good rigidity, and attractive stability of carbide compressing elements (punches) $(5 \div 10) \cdot 10^3$ load cycles.

A general view of the production area equipped with *CS-VII* presses is given in Fig. 6 (see the color inset). This press was purchased under the contract and used to develop the growth cells for growing single crystals of Ib, IIa, and IIb types on seeds by the temperature gradient technique.

The use of basic technical guidelines developed specifically for the «toroid» devices has helped to configure the heating system and to calculate the temperature distribution and the magnitude of required temperature gradients for *CS-VII* HPA container (Fig. 7, see the color inset).

Having optimized the size of the growth cell and the parameters of crystal growth, the researchers developed algorithms for growing structurally perfect diamond single crystals of different types with significantly increased output during one cycle of growing (Fig. 8, see the color inset).

It should be noted that while implementing the project on the use of *CS-VII* 6-punch press for growing diamond single crystals on seeds by the temperature gradient technique, the authors have developed insulation materials and electric heaters, as well as growing techniques that make it possible to create a technology for large-scale commercial production of such products. Today, there are 6-punch HPAs for spontaneous crystallization and production of diamond grinding powders with a volume of growth cell that exceeds 2.5–5 times that of *CS-VII* device. They are the *CS-XII* and *CS-XIII* presses with a plunger diameter of up to 1 m. These devices can produce 100 carats of perfect diamond single crystals and more during one growing cycle. The organization of manufacture of diamond single crystals using new 6-punch HPAs with a capital investment of about USD 10–20 million will bring annually, at least, 10 thousand carats of perfect diamond crystals for different applications. The investment attractiveness of this project is based on a payback period of 2–3 years.

REFERENCES

1. Ivakhnenko, S.A. (1998). Regularities of Directed growth of Diamond Single Crystals in the Area of Thermodynamic Stability. Eng. Sci. Doctor's Theses. Kyiv (in Russian).
2. Ivakhnenko, S.A. and Novikov, N.V.: Growing Large Diamond Crystals in the Area of Thermodynamic Stability. In: Superhard Materials. Production and Application. In Novikov, N.V. (Ed.), 1, 179–199 (2003) (in Russian).
3. Novikov, N.V. and Ivakhnenko, S.A.: Growing and Thermobaric Processing of Diamond Single Crystals Under Extra High Pressure with Controlled Composition of Admixtures. *Physical and Technical Problems of Modern Material Science*, 2, 33–53 (2013) (in Ukrainian).
4. Strong, H.M. and Wentorf, R.H.: The Growth of Large Diamond Crystals. *J. Naturwissenschften,* 59, 1, 1–7 (1972).
5. Ivakhnenko, S.A. and Budiak, A.A.: On Carbon Mass Transfer Model for Growing Diamond Single Crystals on Seeds. *Superhard Materials,* 4, 11–17 (1990) (in Russian).
6. Ivakhnenko, S.A., Novikov, N.V., and Katsay, M.Y.: Kinetics of Diamond Crystals Growth at High Static Pressure. *New Diamond Science and Technology,* 71–90 (1991).

М.В. Новіков, В.В. Лисаковський,
О.О. Заневський, С.О. Івахненко

Інститут надтвердих матеріалів
ім. В.М. Бакуля НАН України, Київ

ІННОВАЦІЙНА ПРИВАБЛИВІСТЬ СТРУКТУРНО ДОСКОНАЛИХ МОНОКРИСТАЛІВ АЛМАЗУ ДЛЯ ЇХ ЦІЛЕСПРЯМОВАНОГО ВИКОРИСТАННЯ В НОВІТНІХ ТЕХНОЛОГІЯХ 21 СТОРІЧЧЯ

Наукові дослідження, виконані в Інституті надтвердих матеріалів, дозволили визначити закономірності фазових перетворень та переносу вуглецю в металевих розчинниках і створити методи вирощування великорозмірних структурно досконалих монокристалів алмазу. Отримані результати склали основу технології виробництва алмазної продукції для використання в електроніці, лазерній техніці, прецизійній механічній обробці матеріалів та в буровому інструменті. Застосування 6-пуансонної техніки високих тисків великого об'єму дало можливість ство-

рити технологію вирощування монокристалів алмазу із значно підвищеною продуктивністю виробництва.-

Ключові слова: Алмаз, монокристал, дефекти, домішки, методи вирощування, високі тиски та температури.

Н.В. Новиков, В.В. Лысаковский,
О.А. Заневский, С.А. Ивахненко

Институт сверхтвердых материалов
им. В.Н. Бакуля НАН Украины, Киев

ИННОВАЦИОННАЯ ПРИВЛЕКАТЕЛЬНОСТЬ ПРОИЗВОДСТВА СТРУКТУРНО СОВЕРШЕННЫХ МОНОКРИСТАЛЛОВ АЛМАЗА ДЛЯ ИХ ЦЕЛЕНАПРАВЛЕННОГО ИСПОЛЬЗОВАНИЯ В НОВЕЙШИХ ТЕХНОЛОГИЯХ 21 ВЕКА

Научные исследования, выполненные в Институте сверхтвердых материалов, позволили определить закономерности фазовых превращений и переноса углерода в металлических растворителях и создать методы выращивания крупноразмерных структурно совершенных монокристаллов алмаза. Полученные результаты создали основу технологии производства алмазной продукции для использования в электронике, лазерной технике, прецизионной механической обработке материалов и в буровом инструменте. Применение 6-пуансонной техники высоких давлений большого объема позволило разработать технологию выращивания монокристаллов алмаза с более высокой производительностью производства.

Ключевые слова: алмаз, монокристалл, дефекты, добавки, методы выращивания, высокие давления и температуры.

Received 18.11.14