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A. G. Dutov[1], V. A. Komar[1], V. B. Shipilo[1], N. V. Shipilo[1],
I. I. Azarko[2], M. V. Frontasieva, S. S. Pavlov

INFLUENCE OF SYNTHESIS CONDITIONS AND THE NEUTRONS OF FISSION SPECTRUM ON PHYSICAL PROPERTIES OF FINE CRYSTALLINE DIAMONDS

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[1]Institute of Solid State and Semiconductor Physics of NASB, Minsk, Belarus
[2]Belarusian State University, Minsk

INTRODUCTION

The problem of finding optimal techniques to improve the structure of synthetic diamond crystals may be solved by way of comprehensive consideration of the processes of modifying the synthesis conditions and subsequent irradiation of fission spectrum by the neutrons.

Owing to the active influence of primary radiation defects on the microlevel, neutron irradiation can effectively form macroscopic properties of diamond crystals. Earlier a correlation was discovered between the change in degree of strength of synthetic diamond crystals and the concentration of electrically active defects in them after irradiation by small fluences of reactor neutrons [1]. Also, a supposition was put forward about the dependence of the change in a set of crystal properties on their containing of incidental admixtures, in particular, of aluminum.

Subsequently, based on scientific and practical interest, this investigation was continued at the synthesis of fine crystalline diamond powders in wider time intervals, and for high-energy processing the fission spectrum neutrons of pulsed reactor were used, which are more energy-hard in comparison with the neutrons of the steady state reactor.

EXPERIMENTAL PROCEDURE

Diamond crystals were obtained by the method of spontaneous synthesis at pressure P = 5.5 GPa and at temperature T = 1620 K in the Mn-Ni system with 0.15 % of copper added. The source of carbon was high purity graphite. The time of synthesis varied in the interval of 15–300 s with a pace Δt = 10 s, i.e., each experiment lasted for $(15 + n\ \Delta t)$ s, where n =1, 2, ..., 30. In the spontaneous process of synthesis during alternating periods of growth and dissolving of crystals, fine crystalline diamonds with sizes of granules from 315/250 to < 40 μm were forming. Extraction of diamonds and their sorting were performed in the way similar to the procedures described in the paper [2].

Irradiation of samples was conducted at the fast pulsed reactor IBR-2, FLNP JINR, Dubna, in the proportion of flux density of fast neutrons (≥ 1.0 MeV) to thermal neutrons equal to 3.34. In comparison with the experiments carried out at the steady state reactor WWR-C, for which this correlation was $2.10 \cdot 10^{-3}$ [1], the neutron spectrum was more hard. It should be noted that mean values of the neutron flux density in the steady state reactor exceed the appropriate values for the IBR-2 reactor [3], but the latter is characterized by a considerably higher peak power. Nevertheless, it is not so high, that the interactions between shifted atoms or between shifted atoms and disordered regions in the cascades generated by different neutrons appeared to be possible in crystals. This is caused by a very long neutron path in a diamond before a collision. The path is so long that only 1-5 successive interactions may occur in the crystals with size

up to 400 μm in the time interval 10^{-10}–10^{-11} s. Heating of the samples in the reactor channel did not exceed 30–40°C.

The contents of paramagnetic centers and concentration of admixtures (Ni, Mn, Al) were determined in the same samples before and after irradiation by neutrons by the method of EPR-spectroscopy, by the roentgen fluorescent analysis, as well as by the epithermal neutron activation analysis at the IBR-2 reactor in Dubna [4].

RESULTS AND DISCUSSION

As shown in the paper [1], along with the lattice point atoms of nitrogen, paramagnetic nickel is also a very sensitive indicator of the condition of diamond crystalline lattice. With an increase of the time of synthesis and the crystal sizes in synthetic diamond samples a gradual decrease of paramagnetic centers of lattice point nickel is observed, which is accompanied by a decrease of width of the EPR line. In Fig. 1 the dependence of lattice point nickel concentration on the crystal granule size before and after irradiation is presented for three times of synthesis.

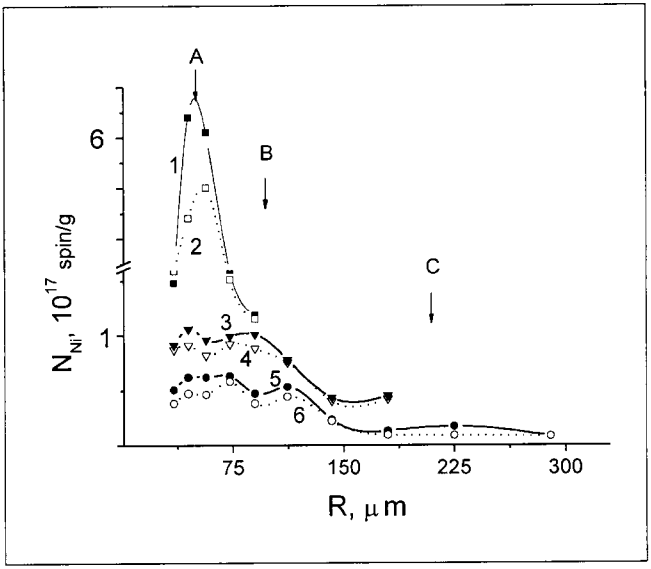

Fig. 1. Dependence of the Ni^- concentration on the size of crystals:
1, *2* – t_{syn} = 20 s; *3*, *4* – t_{syn} = 90 s; *5*, *6* – t_{syn} = 220 s
before and after irradiation by neutrons, respectively

Basic features of the paramagnetic nickel behavior: a) decrease of the Ni^- concentration as a result of irradiation; b) presence of maximum; c) possible increase of the Ni^- concentration after irradiation (reverse distributions).

In the report [5] a supposition was put forward about a mass generation of the diamond phase clusters during martensite transformations and about their participation in the growth of large (of micron range) crystals. If we take into account that the surface of clusters is highly developed, then the adsorption of nickel atoms and growth of crystals with their participation in accordance with tangential mechanism in conditions of small supersaturations will lead to the incorporation of nickel admixture into the crystalline lattice points. During the alternating periods of growth of crystals and their dissolving in the process of long synthesis, concentrations of lattice point nickel and other admixtures decrease asymptotically but at certain moments, due to the intensification of crystal growth, after the stage of dissolving they may increase, simultaneously, maxima B and C are formed (Fig. 1).

It is also possible that during the periods of growth and dissolving, as well as during irradiation in superficial layers of crystals, forming of vacancies occurs and, to a smaller extent, of its own interstitial atoms, which may replace or displace lattice point and interstitial atoms of admixtures. In this case a change of the synthesis time proves to be analogous in its influence to a certain dose of irradiation of the crystals.

Thus, during the process of growth-dissolving the displacement of atoms including the admixed ones is possible deep into the crystals parallel to the surface as well as incorporation into the lattice points by unaccented way. Whereas irradiation by fast neutral particles, which interact weakly with the nuclei of elements is an extended process, which may lead not only to the decrease of concentration of admixed lattice point atoms due to the displacements but also to a change of distributions along the crystals with different history of growth (time of synthesis, number of growth-dissolving cycles, size of blocks, etc.) owing to the displacements of nonlattice point atoms (the number of displacements usually exceeds considerably the number of replacements).

Maximum A in Fig. 1 is probably connected with the loss of crystals of a very small size ($R < 35$ μm) during extraction and sorting.

Diminution of difference in concentration of nickel centers due to the irradiation for the crystals less than 40 μm, in comparison with the larger ones, is possible because of the influence of the dimensional effect, when the block diameter in crystal is comparable to the diameter of the displaced atom cascade resulting from the hit of a fast neutron.

In this case the replacements on the boundaries of blocks will be lost, which, in contrast to the displacements, concentrate on the periphery of the cascade [6], i.e., the size of a cascade may be discrete.

As follows from Fig. 1, in fine-granular ($R < 40$ μm) crystals the number of displaced nickel atoms is almost two times less than in crystals with the size of granules 250/200 μm, which were grown for 220 s of synthesis and, consequently, have undergone numerous growth-dissolving cycles.

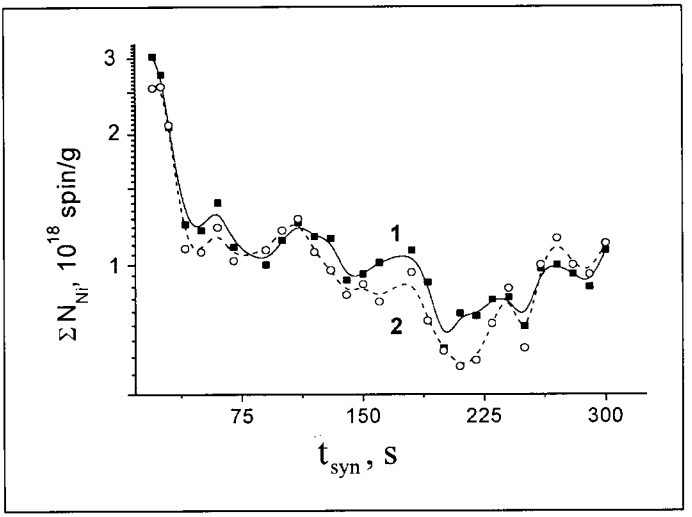

Fig. 2. Dependence of the integral Ni^- concentration on the time of synthesis for diamond crystals with granularity from < 40 to 315 μm: 1, 2 – before and after irradiation by neutrons

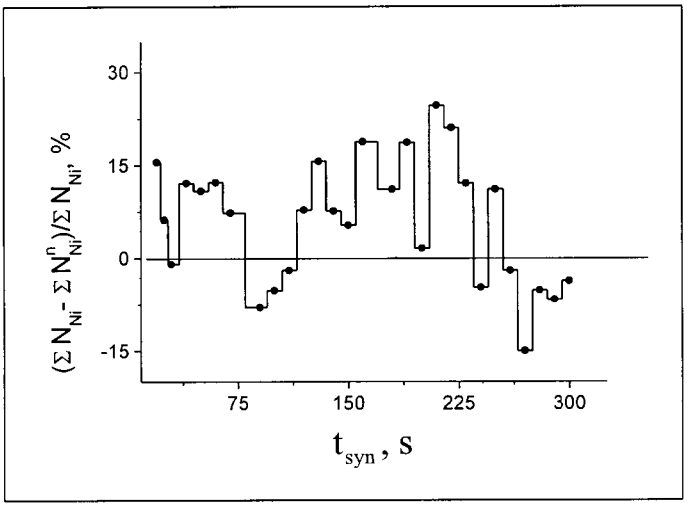

Fig. 3. Dependence of difference of the Ni integral concentrations (before and after irradiation) on the synthesis time of crystals

As seen from Fig. 2, after the completion of initial phase of synthesis ($t_{syn} \geq 50$ s), when the growth-dissolving stages occur, the concentration of paramagnetic nickel begins to vary near a decreasing mean value. In Fig. 3 on the curve of the dependence of difference of the Ni^- integral concentrations on the synthesis time (before and after irradiation) one can single out two regions where the concentration of lattice point nickel after irradiation exceeds the initial values.

If we assume that the concentration of nickel atoms, captured by dislocations or interblock boundaries of diamond lattice in the process of periodical rearrangement of the crystal macrostructure, starts to exceed the concentration of admixtures in lattice points then, it follows from this, that during irradiation nonparamagnetic nickel may transit additionally into lattice point position. Higher density of neutron flow in the pulse also contributes to this.

Statistical processing of the obtained data concerning aluminum concentrations, paramagnetic centers (PC) P1 and PP-defects, as well as of concentration ratios $K = C_{Mn}/C_{Ni}$ for atoms of manganese and nickel, captured incoherently by joint borders of crystal and characterizing correlations between tangential and normal rates of crystal growth more distinctly than in the paper [1], showed the dependence of the Al N precipitate forming on the conditions of crystal growth.

The initial values of K are defined by the composition of charge, and in the process of synthesis their composition may alter by an order.

The growth of absolute values of concentrations of the captured admixtures of manganese and nickel with an increase of crystal sizes is of degree nature. However, the relation C_{Mn}/C_{Ni} usually diminishes to a certain constant value with an increase of crystal size as well as with synthesis time. This ultimate relation may give evidence of the establishment in the system of maximum supersaturation, at which the rate of normal growth may be either higher than the rate of tangential expansion or equal to it.

Figure 4 shows the dependence of the change of the PC P1 relative concentration, resulting from neutron irradiation, on the contents of aluminum admixtures in the crystals grown in the time interval 30-300 s. Stoichiometric correlation $C_{Mn}/C_{Ni} = 1.50$ prescribed initially by the composition of charge [5] is observed.

Crystals with such values of K in all the experiments have the largest size of granules. They have undergone the greatest number of growth-dissolving cycles during which a part of aluminum atoms forms the Al N precipitates and along with the atoms of nitrogen is removed from crystals. (The Al concentration in crystals of the given series of synthesis decreases by a factor of 3-11 with an increase of granule size and the concentration of nitrogen admixture decreases by a factor of 2-3). The rest aluminum atoms are distributed in the diamond lattice more evenly (a usual effect during the refinement of crystal) and, therefore, with greater probability they react with the nitrogen atoms displaced from lattice points. The displacement is carried out by their own interstitial atoms from the encounter cascade of fast neutron.

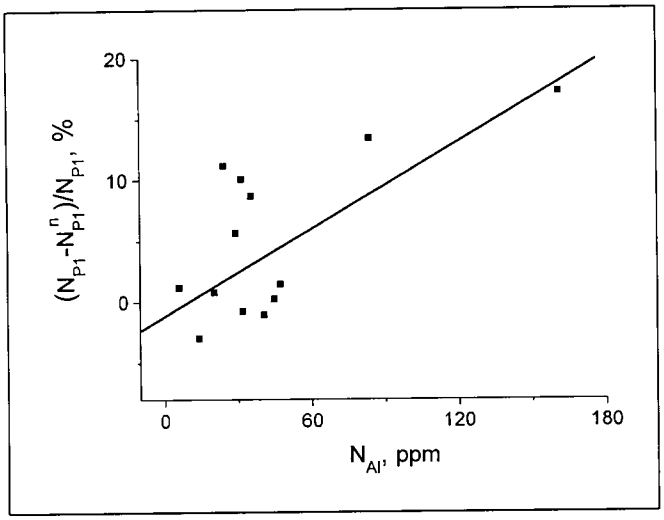

Fig. 4. Dependence of relative change in concentration of lattice point nitrogen (PC P1) after neutron irradiation on the contents of aluminum admixture in diamond crystals

The correlation coefficient lowers to 0.39 for the crystals with maximum values of the manganese-nickel quantity ratio (K = 6.1–8.3). As a rule, these crystals are of the smallest size with a maximum concentration of aluminum admixture. Also, the latter is distributed in crystals extremely unevenly, the spread of concentration values in various batches exceeds 200 %. In the initial moments of synthesis (t < 100 s), when metallic environment of growing crystal does not have exactly usual structure, crystals of the largest size may have $K < 1.50$, which points to the displacement of a part of manganese atoms in melt or to the growth of supersaturation of such crystals. Certainly, in such crystals the distribution of accidental aluminum admixture is unequal and, consequently, the correlation coefficient is low.

In Fig. 5 the relation between changes in concentration of PP and P1 defects for crystals with R < 40 μm is shown. As seen from the figure, the dependence is linear and is described by equation:

$$\Delta N_{PP} / N_{PP} = a + b(\Delta N_{P1} / N_{P1}), \qquad (1)$$

with α=0.895 (probability of the given accidental arrangement of points $p=3.7\cdot10^{-9}$). Here $\Delta N_{PP} = N_{PP} - N_{PP}^{(n)}$; $\Delta N_{P1} = N_{P1} - N_{P1}^{(n)}$ – change of concentrations of PP- and P1-centers resulting from irradiation, respectively. This dependence shows, that the PP defects are, probably, electron states formed due to deformations of diamond lattice around a lattice point atom of nitrogen. And these deformations spread at a distance

equal to ~4 constants of lattice and affect about 100 neighboring atoms. And it is precisely by a factor of 100 that the PP-defect concentration usually exceeds the P1-concentration. Other parameters of paramagnetic centers PP and P1, for example, the width of the line, also change synchronously at irradiation [1].

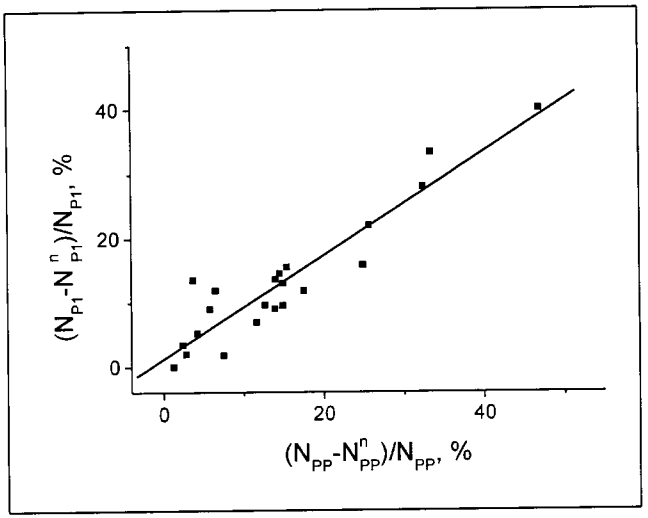

Fig. 5. Relation between the changes of relative concentrations of the PP and P1 defects as a result of neutron irradiation of the crystals with R < 40 μm

For the crystals with R > 40 μm *b* coefficients in the equation (1), and also correlation coefficients decrease quadratically concurrently with the growth of crystal size (Fig. 6). Here α=0.949 (for the smoothed ones by FFT).

The authors believe, these data show that, since the crystals of large size grow with higher rate than that, at which the rates of normal growth are comparable or surpass the tangential one, then in these crystals the portion of matter with less perfect crystalline lattice should also be higher. This is also confirmed by the conclusions of the work [7] concerning a fast increase of the capture of melt by incoherently joint borders. In such lattice the distortions enlarge, hence, a second source of PP-defects occurs and the value of their concentration, now with smaller probability, correlates with concentration of P1-centers. Thus, in large crystals the internal surface, which restricts the regions of perfect crystalline structure, increases and the coefficient *b* starts to decrease quadratically together with the size of crystal beginning with R=50/40 μm.

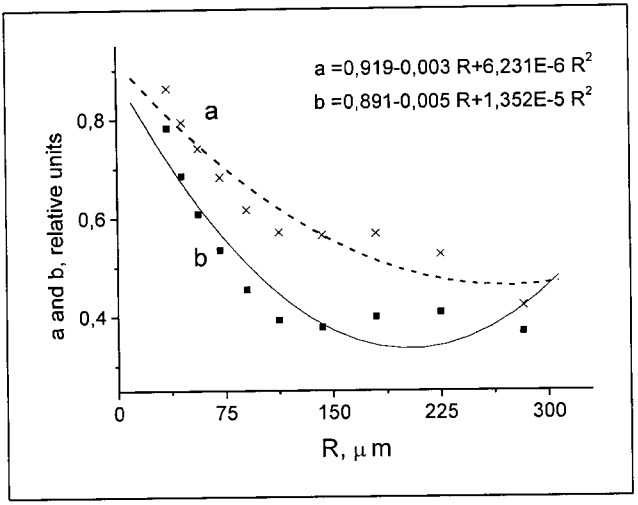

Fig. 6. Change of values of *b* coefficient from the relation (1) and the correlation coefficient depending on the size of crystals

Direct correlation with $a = 0.61$ was discovered between the relative changes in concentration of PP-defects resulting from neutron irradiation and the contents of aluminum for the crystals with $K \leq 1.5$. Such correlation gives evidence of the second mechanism of the PP-defects formation characterized by *a* coefficient in the equation (1).

At the same time, the value of *a* coefficient from (1) showing the proportion of PP-defects, which are formed without the lattice point nitrogen participation, generally, increases with the augmentation of crystal sizes having maximum at R ~100 and ~250 μm (in the given experiment $a \sim b$ by the order of magnitude for the crystals with R<40 μm). In much the same way as silicon [8], these maxima (as well as the dimensional effect, see above) may be a consequence of the cascade development from primarily knocked-on carbon atoms with average energy, which changes discretely with the energy of neutrons of fission spectrum.

The results of Fig. 6 are also confirmed by the data obtained in the experiments with synthetic diamond crystals grown at various temperatures, at the same time $T_3 > T_2 > T_1$ (see the table).

Here the supersaturating growth of solution-melt is defined by increase of temperature, as a result of which a normal component of crystal growth rate [7] augments and the coefficient of linear correlation in the equation (2) decreases:

$$N_{PP} = a + b \cdot N_{PI}. \qquad (2)$$

Dependence of the correlation coefficient α, values *a* and *b* in the expression (2) on the temperature and size of crystals

Crystal sizes and temperature	$a, 10^{19}$ spin/g	*b*	α	Probability of random distribution, P
<40 μm				
T_1	1.9164	0.0503	0.9276	0.0009
T_2	1.3096	0.0455	0.8057	0.0158
T_3	1.0144	0.0509	0.5373	0.1697
80/63 μm				
T_1	1.6903	0.0459	0.6111	0.1075
T_2	1.2119	0.0158	0.1151	0.7860
T_3	0.6101	0.0541	0.1289	0.7609
315/250 μm				
T_1	0.9639	0.0416	0.4758	0.2805
T_2	0.3791	0.0389	0.2605	0.5726
T_3	0.1467	0.0732	0.5516	0.1993

CONCLUSION

As the conducted investigations showed, the character of behavior of admixtures, such as nickel, aluminum, nitrogen and other elements, which are constantly present in crystals, their interaction with structural defects created, among other things, by neutron irradiation reflect accurately enough the processes occurring inside the reaction cell at spontaneous synthesis of diamond crystals and change of mechanism of crystal growth.

The influence of neutrons of fission spectrum on artificial diamonds is fairly strong and at defined doses is determined by the technology of crystal synthesis.

A similar nature of phenomena was detected taking place under the action of time and dimensional factors in the process of synthesis, as well as under the influence of neutron irradiation, in particular, a change of concentration of paramagnetic nickel in crystals.

It was shown that the change in concentration of PP-defects is related to the change in concentration of lattice point nitrogen defects.

The obtained results make it possible not only to better understand the processes occurring in the course of spontaneous synthesis but also be used to obtain larger and more perfect crystals.

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Влияние условий синтеза и нейтронов спектра деления
на физические свойства мелкокристаллических алмазов

В работе исследовалось влияние условий синтеза микрокристаллических порошков алмаза и облучения нейтронами спектра деления на процессы образования собственных и примесных дефектов. Установлено немонотонное изменение концентрации парамагнитных никельсодержащих дефектов в зависимости как от времени синтеза, так и от воздействия нейтронов. Показано, что поведение примесей в кристаллах связано с процессами, протекающими при их синтезе, и выявлено сходство изменений концентраций парамагнитного никеля под воздействием различных (временных, размерных и радиационных) факторов. Установлено также, что изменение концентрации PP-дефектов связано с изменением концентрации дефектов узельного азота. Полученные результаты могут быть использованы для определения условий спонтанной кристаллизации алмазов в замкнутой системе при высоких давлениях и температурах.

Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка ОИЯИ.

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Dutov A. G. et al. D14-2003-220
Influence of Synthesis Conditions and the Neutrons
of Fission Spectrum on Physical Properties
of Fine Crystalline Diamonds

The influence of synthesis conditions of fine crystalline diamond powder and of fission spectrum irradiation by the neutrons on the processes of formation of natural and admixed defects was investigated. Nonmonotonous change of concentration of paramagnetic nickel-containing defects was determined depending both on the time of synthesis and on the neutron influence. It was shown that the behaviour of admixtures in crystals is connected with the processes occurring during their synthesis, and the similarity of changes in concentrations of paramagnetic nickel under the influence of various (time, size and radiation) factors was detected. It was also determined that a change in concentration of PP-defetcs is connected with a change in concentration of defects of lattice point nitrogen. The obtained results may be used to determine the conditions of spontaneous diamond crystallization in a closed system at high pressures and temperatures.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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141980, г. Дубна, Московская обл., ул. Жолио-Кюри, 6.
E-mail: publish@pds.jinr.ru
www.jinr.ru/publish/