Irradiation of diamonds with 14 MeV neutrons

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Abstract

The results of natural diamonds irradiation with 14.1 MeV fast neutrons, produced during the operation of a neutron separator used for dry enrichment of kimberlite ore by the tagged neutron method, are discussed.

Key words: diamonds irradiation, fast neutrons, tagged neutron method, dry enrichment of kimberlite, portable neutron generator

1. Introduction

At present, the use of the tagged neutron method (TNM) to detect diamonds hidden in kimberlite ore, without destroying it, is an object of intensive studies [1-3].

The essence of the TNM is the irradiation of kimberlite ore with 14.1 MeV fast neutrons which are generated in a binary nuclear reaction

$$d + {}^{3}H \rightarrow {}^{4}He + n. \qquad (1)$$

In this reaction, the neutron and the α-particle (^{4}He nucleus) scatter almost in opposite directions. Therefore, by detecting the α-particle accompanying the neutron, we can determine the direction of neutron emission. This procedure is called neutron tagging. Tagged neutrons, getting into the object of investigation, induce inelastic scattering reactions

$$n+A \rightarrow n'+A^*,\ A^* \rightarrow \gamma+A, \qquad (2)$$

as a result of which the nucleus is deexcited by the emission of gamma quanta with the energy spectrum characteristic of each chemical element. Registration of the characteristic γ- radiation is carried out by γ-detectors in coincidences with a signal from the α-detector. The alpha detector is made in the form of a matrix, each element of which is responsible for a separate tagged neutron beam. As a result, the whole area of inspection (for example, a tray with a rock) is divided into separate cells (voxels), in which the elemental composition is determined. This is an important difference between the TNM and the well-known methods of neutron activation analysis – it does not simply determine the energy spectrum in the entire inspection area, but differentiates this information by specific elements within the inspection area.

An experimental demonstration of the TNM ability to detect diamonds in kimberlite was performed in [2]. Irradiation of 33 samples of kimberlite with linear dimensions of 15-20 cm and a mass of 1-2 kg detected the presence of a local excessive carbon concentration in one of the samples. Subsequent examination of this sample revealed the presence of two heterogeneous diamond inclusions in it, with a diameter of up to 7 mm, consisting of small particles with a size of 1 to 2 mm.

At present, with the support of the Skolkovo Foundation, work to create a TNM-based neutron separator is underway. The prototype facility was tested at the Lomonosov mine of PJSC Severalmaz (Arkhangelsk) [3]. The tests demonstrated the possibility of detecting diamonds in pieces of ore, the size of which is 10 times the size of the diamond.

In a neutron separator, the irradiation time of one portion of the ore is from 4 to 10 seconds. An important question arises: does irradiation with fast neutrons during this time lead to a change in the properties of the diamond, which may be considered as an attempt to refine the diamond. To study the effect of neutron radiation in the TNM separator, a collection of diamonds was selected from the current production of diamonds from the Mir, Aikhal and Udachnaya pipes of the JSC ALROSA, which was irradiated with beams of 14.1 MeV neutrons. Optical-spectroscopic studies of the crystals

were performed at the Geo-Scientific Research Enterprise, JSC "ALROSA" before and after the irradiation. During the irradiation of the samples the induced radiation activity was also monitored.

2. Equipment and methodology

Irradiation of diamond crystals was performed by a portable neutron generator ING-27 with a built-in 9-pixel alpha detector. The portable neutron generator ING-27 manufactured by the Research Institute of Automatics named after N.L. Dukhov creates 14.1 MeV neutrons. Its overall dimensions are 260x140x279 mm. Weight is 7.5 kg. The neutrons are tagged by a silicon alpha detector consisting of 9 cells measuring 10x10 mm, which are joined into a 3x3 matrix. The intensity of the neutron beam was $I = 3.2 \times 10^7\ s^{-1}$.

To control the radiation activity, a wide-range dosimeter DRG-01T1 was used.

2.1 Visual mineralogical description of crystals

The mineralogical description of each crystal of the collection before the irradiation was performed using the Leica Wild M420 binocular. To excite the photoluminescence (PL) when characterizing the luminescence color an AIL-3 laser (λ=337 nm) was used. The crystals were photographed using a Leica M205 binocular microscope with a highly sensitive digital camera Leica DFC 495.

Investigation of the crystal properties before the irradiation included a morphological characteristic and a description of its physiographic features: aggregate state, integrity, the type of the chip, fracturing, surface sculptures, inclusions, color, visual evaluation of the photoluminescence color, presence of ferrogination, pigmentation spots. The morphological characteristics includes the definition of the diamond's variety according to Yu.L.Orlov's classification and information on the morphological type of the crystal from the system of mineralogical description of diamonds used in JSC ALROSA.

The visual study of the crystals after irradiation was aimed at identifying the presence of radiation exposure signs, namely, the detection of induced blue-green, yellow-brown hues in the color, changes in crystal transparency, and the detection of radiation patches around mineral inclusions in diamonds.

2.2 IR spectroscopy

Spectroscopic studies of diamonds before and after neutron irradiation were carried out on a VERTEX 70 FT-IR spectrometer (Bruker) in combination with a Hyperion 2000 IR microscope. The

measuring range: 400-5500 cm^{-1}. Images of integral spectra (from the whole volume of the crystal) were taken. The spectra were normalized by absorption in the two-phonon region [4,5].

As a result of irradiation, vacancies and interstitial atoms can appear in the diamond lattice, and it is difficult to distinguish a vacancy from an interstice by optical transitions in the diamond. Such defects in the lattice of a natural diamond are accompanied by the appearance of a dipole moment and IR absorption bands of 1332, 1190, 1065 and 1010 cm^{-1}, irrespective of the nitrogen concentration [6]. Presumably, absorption bands at 1550 and 1525 cm^{-1} also refer to the interstitial carbon. It should be noted, however, that vacancies and interstitial atoms in a diamond can also appear as a result of plastic deformation arising during the growth of crystals or during the post-growth period in mantle conditions. Absorption band systems in the 4060-6200 cm^{-1} region ("amber" centers) are often observed in the IR absorption spectra of natural diamonds with traces of plastic deformation and in the PL spectra at 490.7 nm [4].

As a result of irradiation, there can be also formed both nitrogen-vacancy defects (3H, H3, H4, 575 nm, 637 nm, etc.) and interstitial nitrogen, whose concentration is estimated from the absorption band at 1450 cm^{-1}. About 98% of natural diamonds have significant concentrations of nitrogen, which determines many of the diamonds' physical properties [7-8]. To date, several dozen different nitrogen and related centers are known in the diamond. The main defects are usually C-, A-, B1- and B2-centers, which have characteristic IR absorption spectra [9]. It was found that the C-center is a single substitutional nitrogen atom in the diamond lattice, the A-center consists of two nitrogen atoms in adjacent lattice sites [10]. The B1-center is an aggregate of four nitrogen atoms and a vacancy, and B2 (platelets) are plate-like separations of interstitial carbon atoms by {100} containing an admixture of unstructured nitrogen [11]. In the IR region, the C-center produces a system of absorption bands of 1130, 1332 and 1344 cm^{-1}; the A centers have a system of bands of 480, 1100, 1215, and 1282 cm^{-1} in the one-phonon region of the IR absorption spectra; the B center determines the system of absorption bands of 1010, 1100, 1175 and 1332 cm^{-1}. The content of B2 defects is determined from the absorption coefficient of the band in the 1358-1380 cm^{-1} range. Under the influence of radiation there can form vacancies, which then form nitrogen-vacancy defects with the C-, A- and B1-centers.

In analyzing the features of the IR absorption spectra of diamonds before and after the irradiation with 14.1 MeV fast tagged neutrons, the focus is made on identifying the bands responsible for the appearance of new vacancy, nitrogen-vacancy defects and "amber" centers.

2.3 Study of photoluminescence spectra

The photoluminescence spectra of diamond crystals were photographed before and after irradiation by an InVia Raman scattering microscope (Renishaw, UK). All the spectra were taken at the temperature of liquid nitrogen (T = 77 K). The excitation source is the laser of a Raman microscope, λ - 325 nm, with a power of 20 mW. A reflective holographic grating of 2400 lines / mm was used, the measured spectral range at an excitation radiation of 325 nm was 326 ÷ 740 nm. Thorlabs 15x UV lens, numerical aperture - 0.32, working distance - 8.5 mm was used. The radiation receiver is a Peltier-cooled CCD-matrix of 1024 × 256, the pixel size - 26 μm, the spectral resolution is not worse than 0.5 cm^{-1} in the visible range (using the appropriate combinations of light sources, lenses and gratings), reproducibility is not worse than 0.1 cm^{-1}. All the photoluminescence spectra taken have diamond Raman lines of the first (339.7 nm) and second (355.8 nm) order, as well as their diffraction repetitions. In addition, on some spectra there are high narrow (0.05 nm) parasitic peaks due to the triggering of a matrix CCD receiver in the event of accidental exposure to cosmic rays.

For each crystal, the photoluminescence spectra are photographed at several points on the surface. This approach was realized because of the well-known phenomenon of the inhomogeneous distribution of photoluminescence centers in the volume of natural crystals. A real diamond crystal is inhomogeneous, with a zonal, zonal-sectorial distribution of structural, impurity, optically active centers in the volume. This fact is rarely taken into account directly, and many studies remain unclear on the influence of the effects of various types of hard radiation on the optical-spectroscopic properties of diamonds as well as on the fact that the measurements are performed in the same local regions.

At the comparative analysis of the photoluminescence spectra of diamonds before and after neutron irradiation, the presence, intensity, reproducibility of the bands were studied and possible methodological reasons for the observed changes were rechecked. The main attention is focused on the identification of photoluminescence bands, known from catalogs and publications, that appear after artificial irradiation of diamonds, as well as on the analysis of the intensity of the bands known and widespread in natural diamonds and associated with nitrogen-vacancy optically active centers.

It should be noted that at present we are unaware of the data on the nature of possible radiation damage in a diamond crystal caused by monoenergetic 14.1 MeV fast neutrons. In work [6], the effect of reactor epithermal neutrons (0.5 ÷ 3 MeV) on carbon atoms in diamond was studied. It was shown that such neutrons can generate, so-called displacement wedges - partially amorphized regions containing up to 10^4 atoms. The inner part of these wedges (or clusters) is rich with vacancies, and the outer part - with interstitial carbon atoms. It can be assumed that as a result of irradiation with 14.1 MeV neutrons, a tree of clusters can arise, similar to a chain reaction, since at a collision the energy of

the knocked-out carbon atom can reach 2 MeV. In this case, in some regions of the crystal, the local concentration of defects in a volume of the order of several dozens of cubic microns can reach the values necessary for their manifestation in the PL spectrum, despite the low values of the integrated neutron flux density of $\approx 10^7$ neutrons $\times$ cm^{-2} as compared to the surface density of the square grid nodes of 3.14×10^{11} cm^{-2}, corresponding to a concentration of 1 ppm in a diamond lattice equal to 1.76×10^{17} cm^{-3}.

In measurements of the IR absorption in a diamond, the concentration of absorbing centers is averaged along the path of the measuring beam through the entire crystal, and as a result, the contribution to the absorption of the emerging radiation centers will be proportional to their average concentration in the volume of the crystal, i.e. it may be subtle. In this connection the IR spectroscopy was supplemented by highly sensitive micro-spectroscopy of photoluminescence at the liquid nitrogen temperature.

3. Mineralogical characteristics of diamonds.

The collection for the experiment on neutron irradiation of diamonds comprised crystals from the current production of Mir, Aikhal and Udachnaya pipes. The collection volume is 90 crystals of which 52 crystals are from Mir pipe and by 19 diamonds from Aikhal and Udachnaya pipes. The crystals of the selected deposits are significantly different in morphology, physical properties. The general view of diamonds is shiown by Figs. 3.1-3.3.

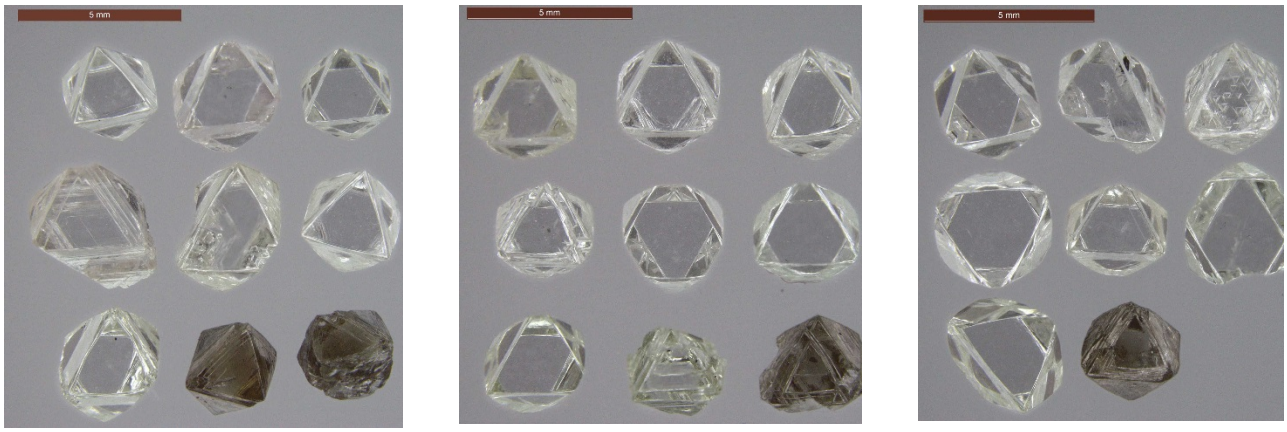

Fig. 3.1 Diamonds from the Mir pipe.

Fig. 3.2 Diamonds from the Aikhal pipe.

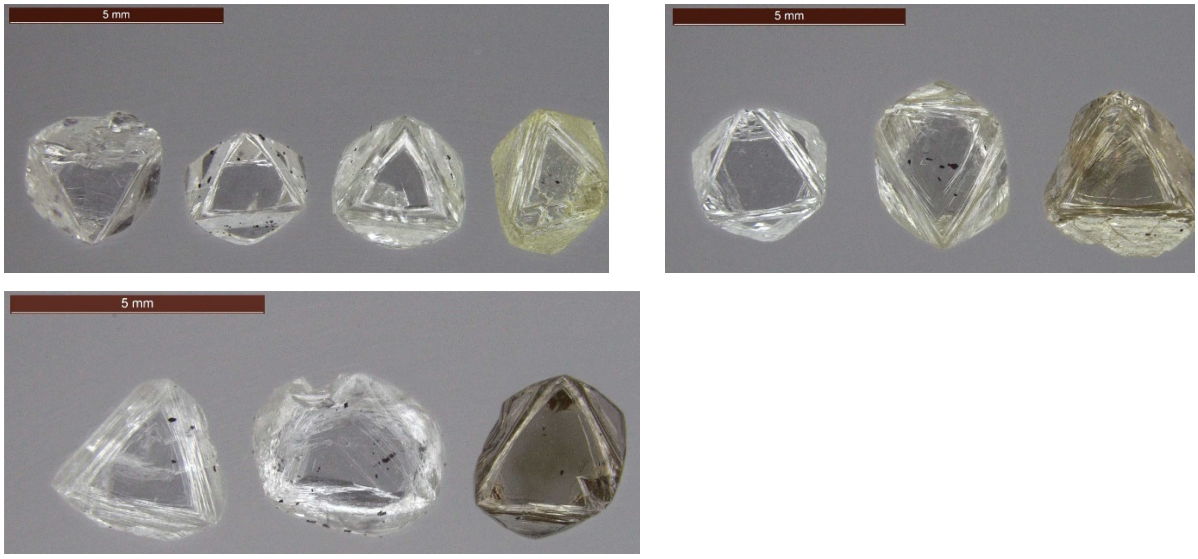

Fig 3.3 Diamonds from the Udachnaya pipe.

To carry out the irradiation experiment, well preserved crystals were chosen. Diamond samplings from each deposit contained no more than 2-4 crystals with an estimated loss of the initial volume of

more than 30%. On the chips of the damaged crystals, natural protomagmatic surfaces, as well as chip surfaces of mechanical and obviously technogenic nature, have been observed.

4. Measurements

The 90 pcs. collection of diamonds was divided into 6 batches of 15 crystals. In each batch there were diamonds from the Mir, Udachnaya and Aikhal pipes. All the 6 batches were irradiated as a single assembly, from which, after a certain time, they were removed batch by batch. The irradiation time of a batch varied from 4 sec to 32 min. When a neutron separator operates, the time of irradiation of a tray with kimberlite is from 4 to 10 seconds.

Samples of diamonds were set at a distance of 43 cm from the target of the neutron generator. The neutron beam intensity during irradiation was $I = 3.2\times10^{7}\ s^{-1}$.

Table 4.1 sums up the irradiation conditions and presents the fluence and radiation dose received by each batch of diamonds.

Table 4.1 Irradiation conditions for diamonds.

Parameter	Batch number					
	1	2	3	4	5	6
Number of crystals	17	15	14	14	15	15
Exposure time	4 sec	2 min	4 min	8 min	16 min	32 min
The integral neutron flux density (fluence) during the exposure time, neutron/cm^2	5.51×10^{3}	1.65×10^{5}	3.31×10^{5}	6.61×10^{5}	1.32×10^{6}	2.64×10^{6}
Integral energy density of irradiation during the exposure, eV/ cm^2	7.75×10^{10}	2.32×10^{12}	4.64×10^{13}	9.29×10^{12}	1.86×10^{13}	3.71×10^{13}
The number of crystals with changes in color, coloring and other visual properties.	0	0	0	0	0	0
Number of crystals with changes in the IR absorption spectra after irradiation	0	0	0	0	0	0
Number of crystals with	0	0	1	1	2	3

changes in PL spectra after irradiation						

5. Discussion of results and conclusions

As one can see from the results given in Table 4.1, the density of the integral flux (fluence) of neutrons during the exposure time varied from F= 5.51×10^{3} cm^{-2} to F= 2.64×10^{6} cm^{-2}. Accordingly, the integral energy density during the irradiation time did not exceed E= 3.71×10^{13} eV cm^{-2}. At the actual operation of the neutron separator, the irradiation time does not exceed 10 sec, so the diamond can not receive an energy density greater than E=2×10^{11} eV cm^{-2}. In other measurements, it was found that the energy density threshold for changes in diamond was ~10^{16} eV cm^{-2} [6].

As a result of optical-spectroscopic studies, the following conclusions were made:

1. The color, transparency, photoluminescence color and intensity of the crystals in the collection before and after neutron irradiation for all exposure durations have no visually noticeable signs of change.

2. Comparison of the diamonds IR absorption spectra before and after neutron irradiation for all exposure durations did not reveal the appearance and transformation of intrinsic and impurity defects in the structure of diamonds, including radiation defects in diamonds from the Mir, Aikhal and Udachnaya pipes with various concentrations of nitrogen impurity concentration. "Amber"-centers are present only in crystals of brown color, their intensity of absorption after irradiation does not change.

3. For the overwhelming majority of diamonds there have not been established any changes in the spectral characteristics of photoluminescence. However, in the photoluminescence spectra of 7 crystals out of 90 after irradiation with fast neutrons, low-intensity lines of 526.3 and 536 nm, which were absent before irradiation, were revealed, and a shift of the structureless band with a maximum at 530 nm was registered, an increase in the luminescence intensity of the bands of H3 centers and NV centers (637 nm) relative to the intensity of the zero-phonon line of the N3-center was observed. The number of crystals in different categories of radiation doses in which changes in the photoluminescence spectra have been recorded are presented in the bottom line of Table 4.1.

It is important to note that in crystals irradiated for less than 2 min, no changes in the photoluminescence spectra were recorded.

Measurements of the induced radiation activity by the DRG-01T dosimeter showed that when the radiation background in the laboratory was 12 μR / h, the dose rate of the collection before irradiation

was 13 μR / h, and after irradiation - 12 μR / h. That is, within the accuracy of the measurements, no induced activity after irradiation of the diamond collection for 32 minutes was detected.

Thus, it can be concluded that irradiation with fast neutrons with integral radiation energy densities of less than 2.32×10^{12} eV / cm² cause no changes in either the visual properties of diamonds, the IR absorption spectra, or the photoluminescence spectra. This means that the use of fast neutron separators for enrichment of kimberlite ore does not affect the properties of the found diamonds.

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