Application of repetitive high power (high voltage) nanosecond electromagnetic pulses to improve technological properties of diamond-bearing kimberlites

I Zh Bunin, N E Anashkina and M V Ryazantseva
N.V. Mel’nikov Institute of Comprehensive Exploitation of Mineral Resources of the Russian Academy of Science, IPKON RAN, 4 Kryukovsky Tupik, Moscow, 111020, Russia

E-mail: bunin_i@mail.ru

Abstract. In this paper we used Fourier transform infrared spectroscopy (FTIR), analytical electron microscopy, microhardness measurements and other methods to study changes in the morphological, structural defects, hydrophobicity, mechanical and technological properties of rock constituents of kimberlite igneous rocks and crystals of natural diamonds exposed to nonthermal action of the repetitive nanosecond electromagnetic pulses. The destruction of secondary mineral surface films, their removal from the diamond surfaces, the growth of crystal hydrophobicity, and an increase in the number of $\mathbf{B}_2$ defects were observed after 30-50 seconds of electrical pulse treatment. The obtained result indicates possibility of applying pulsed energy effects to intensify the diamond flotation and to advance efficiency of the weakening of kimberlite rock constituents without damaging the precious crystals and ensuring their preservation by the subsequent grinding of refractory ores.

1. Introduction
In the mineral processing of diamond-bearing refractory kimberlites from Russia deposits, the damage of diamond crystals ranges from 25% to 75%, and the loss of mass of valuable crystals is 12% [1]. The process of self-grinding of kimberlites (in wet autogeneous grinding mills) is the main source of diamond crystals damage, and leads to integrity violation up to ~30% of crystals [1]. The efficiency of processing (beneficiation) of diamond-bearing ores can be improved by developing and introducing new (non-mechanical) energy-saving methods aimed at increasing the quality of concentrates via kimberlite softening, the selective identification and withdrawal of diamond crystals in milling ores, and finding new distinctions and enhancing the contrast between the chemical surface state, electrical, hydrophobic and luminescent properties of diamonds and kimberlite rock constituents [1].

The application of high-power microwaves (carrier frequency is 2.45 GHz, radiation power is 600 W) caused effective heating and selective disintegration of diamond-bearing kimberlite ores [2].

In [3] we defined the parameters of nonthermal action of high-power nanosecond electromagnetic pulses (HPEMP) on the gold-(silver, PGM)-bearing refractory ores to improve the efficiency of the disintegration of mineral complexes and to enhance the valuable components in the mineral processing. The experiments with nanosecond electromagnetic pulse treatment of natural and artificial media made use of so-called nonthermal action [3]. The energy of a single pulse (~0.1 J), and the energy of a series of pulses, were insufficient to raise the temperature of macrospecimen [3, 4].
In this paper, we studied the nonthermal effect of nanosecond high power (high-voltage) electromagnetic pulses on the chemical surface state, structural, mechanical, hydrophobic and flotation properties of diamond crystals and the main kimberlite rock constituents (calcite, olivine, and serpentine). For this purpose, we used Fourier transform infrared spectroscopy (FTIR), analytical electron microscopy, microhardness Vickers method, and other methods.

2. Experimental

2.1. Minerals

We used in our experiments the mineral samples of kimberlite rock constituents, namely, calcite (CaCO$_3$; Mohs hardness 3), serpentine (lizardite – Mg$_3$SiO$_5$(OH)$_4$, antigorite – (Mg, Fe)$_3$Si$_2$O$_5$(OH)$_4$; Mohs hardness equal to 2.5-4), and olivine (Mg, Fe)$_2$(SiO$_4$; Mohs hardness 7). The sample size for measuring the microhardness was 10×10×4.5 mm in size. For conducting spectroscopic studies, we used powdered mineral samples with 100+63 µm in size.

To study the effect of pulse treatment on the structural and chemical properties of diamonds, we used the naturally occurring diamonds Bulkur River deposit (Russia, Yakutia). The diamonds were ~2 +1 mm in size.

2.2. Research Technique

Mineral samples were treated with nanosecond electromagnetic pulses using the laboratory generator equipment (IPKON RAS, Moscow, and NPP Phon, Ryazan). The pulse duration was 10 ns; steep-front impulse was 1–3 ns; the pulse the voltage amplitude in the active electrode was ~25 kV; the electric field strength was ~5×10$^6$–1×10$^7$ V m$^{-1}$; the pulse repetition rate was 100 Hz; the pulse energy was 0.1 J, and the range of time variation in electropulse impact $t_{treat}$=10–150 s per dose of electromagnetic pulse radiation. To increase efficiency of the electromagnetic pulse effect, we moistened the samples of kimberlite minerals with distilled water (solid to liquid ratio S:L of 5:1) prior to electromagnetic pulse treatment.

Nonthermal action of HPEMP did not produce microdamages in diamonds, since the breakdown voltage of an electric field is about 10$^9$ V m$^{-1}$ for diamonds, two orders of magnitude higher than the strength of electric field in the interelectrode space of the pulse generator.

FTIR on a Nicolet-380 (microlighting special attachment, Karl Zeiss) and IRAffinity-1 (IR-spectrometer, DRS-8000 diffuse-reflection attachment, Shimadzu) spectrometers were used to analyze the chemical composition and structural defects of diamond crystals. The IR-spectra of mineral samples in the spectral range from 400 to 4000 cm$^{-1}$; the resolution of the spectrum measurement was 4 cm$^{-1}$. The surface defects structure and qualitative chemical surface composition of minerals were studied via analytical scanning electron microscopy on a LEO 1420VP (EDX Oxford INCA Energy 350 raster electron microscope), and a low vacuum electron microscope JEOL JSM-6610LV.

A contact device (designer, V.A. Glembotskii) was used to assess diamond surface wettability. Diamond crystals were considered hydrophobic if they stuck to the bubble in a less than 50-ms period of contact; they were hydrophilic if they did not stick in a period longer than 5 s. If a diamond stuck to a bubble in periods of contact ranging from 50 ms to 5 s, it was classified as a crystal of mixed type.

The contact angle of the wetting ($\Theta$) of calcite, olivine and serpentine thin section surfaces before and after HPEMP treatment was determined using the sessile drop approach with a optical microscope, equipped with a Moticam 2300 digital camera with software to input and process images (Motic Image Plus 2.0 ML). A drop of distilled water with a diameter of no more than 2–3 mm was placed on each sample’s surface and held under standard conditions for 40 s until the drop profile was determined. The angles of wetting were estimated using the ImageJ analysis program with special DropSnake and LB-ADSA plug-ins [5]. We studied flotation ability of natural diamond crystals using foamless flotation in Hallimond’s tube.
The microhardness of kimberlite rock constituents minerals in the initial state and after electromagnetic pulse irradiation was determined using the Vickers approach (HV, MPa) according to GOST-2999-75 (ISO 6507-1:2005) with a PMT-3M microhardness tester at an loading times of 10-15 s. The indenter load on polished mineral surface was 50, 100, and 200 g for calcite, kimberlite rock mass, and olivine – serpentine specimens respectively.

3. Results and Discussions

3.1. Effect of nanosecond electromagnetic pulses on structural defects and chemical (phase) composition of diamonds

Considerable changes in the natural diamond IR-spectra were observed after HPEMP treatment of diamonds with iron oxide mineral films, strongly adhesive clayish mineral coatings, and other impurities on their surfaces (figure 1a,b). As a result of impulse action, diamond crystals were purified from secondary mineral phases and impurities containing hydroxyl and hydrocarbon groups. For example, the IR-spectrum of one crystal showed a sharp drop in the intensity of the spectral lines at 2918, 2849, and around 3400 cm\(^{-1}\) after \(t_{\text{treat}} \geq 50\) s. This usually indicates the presence of hydrocarbon impurities and H\(_2\)O.

![Figure 1](image-url)

**Figure 1.** (a, b) Diamond crystal coated with a hydrophilic film of a secondary mineral phase (white); (c) fragment of the mineral phase (possibly biotite), removed from the diamond surface when exposed to nanosecond pulses within 30 seconds \((t_{\text{treat}}=30\) s\)), and (d) the X-ray spectra from this fragment.

Scale bars, (a) 500 \(\mu\)m, (b) 10 \(\mu\)m, and (c) 200 \(\mu\)m, SEM – EDX.

According to our SEM – EDX data, the separation of secondary mineral phase fragments from 40 to 100-200 \(\mu\)m in size from a natural diamond’s surface was observed during its HPEMP treatment \((t_{\text{treat}} \geq 30\) s\)); these were presumably calcium sulphate and iron oxides (hydroxides) (figure 1c,d). These
results testify to the effectiveness of nanosecond HPEMP nonthermal action, as a result of which the diamond’s surface was cleansed of mineral impurities without any notable damage to the crystal’s surface.

As a result of the analysis of wettability data (contact Glembotskii device), we have established an increase in the hydrophobic properties of diamonds under the electromagnetic pulse treatment of $t_{\text{treat}} \leq 50$ s. The number of hydrophilic diamonds decreased from 45% to 23%, and the number of crystals with mixed properties increased at $t_{\text{treat}} \leq 150$ s.

Analysis of the results of flotation experiments (foamless flotation conditions in the Hallimond tube) showed that flotation activity (recovery) of diamonds increased from 47% (without HPEMP treatment) to 56% after short-term ($t_{\text{treat}} \leq 10-30$ s) pulse pretreatment of the crystals (figure 2a). Under these conditions, the number of hydrophobic floated crystals increased, and the number of hydrophilic non-floated crystals decreased. Thus, the application of short-term actions of nanosecond electromagnetic pulses can prove to be an effective method for directed modification of the chemical surface composition, structure and technological properties of natural diamonds.

![Graphs and Images](image1.png)

**Figure 2.** (a) Effect of electromagnetic impulse treatment ($N_{\text{imp}}$ – number of pulses) on floatability of diamond crystals and (b, c, d) contact angle ($\Theta^\circ$) of (b) serpentine, (c) olivine, and (d) calcite.

It should be noted that, as a result of preliminary electromagnetic pulse treatment of diamonds, the flotation activity of the crystals increased from 47% to ~60% with a maximum ($\varepsilon_{\text{max}}=61\%$) at $t_{\text{treat}}=150$ s. At the same time, the action of nanosecond electromagnetic pulses caused a decrease in the hydrophobic properties of the surface of rock-forming minerals. Electrical pulse treatment from 10 s to
As a result of analysis of the FTIR-spectra ( Nicolet-380 spectrometer) of diamonds, it was found the nitrogen impurity in B form (lines 1010 cm\(^{-1}\) and 1175 cm\(^{-1}\)) and A form (480 cm\(^{-1}\) and 1282 cm\(^{-1}\)). We also found the presence of \(B2\) – defects (so-called, platelets [6, 7]) in the crystal structure of diamonds (distinct line in the IR-spectrum 1365-1375 cm\(^{-1}\)).

Analysis of FTIR (Nicolet-380) results showed that the nonthermal action of nanosecond HPEMP resulted in a notable systematic increase in the line intensity around 1365 cm\(^{-1}\), indicating there was an increase in the number (content) of lamellar \(B2\) defects represented by inter-node carbon atoms [6, 7]. At the same time, we did not observe the destruction or global rearrangement of the diamond crystal structure; i.e., there was almost no change in either the concentration or distribution of nitrogen centers (%N(B)). Platelets are microshift defects in a layered octahedron diamond, with their formation being due to nitrogen \(B\)-centers inside the crystal. The action of nanosecond HPEMP can presumably generate new \(B2\)-centres inside diamonds of the medium-nitrogen crystal group, mostly in those with layered octahedron internal structures and elevated shares of nitrogen \(B\) defects. The results of measuring the microhardness of diamonds [8] shown, that an increase in the number of \(B2\)-defects substantially increases the dispersive strength of diamond crystals.

3.2 Effect of nanosecond electromagnetic pulses on microhardness of kimberlite rock constituents

In [9, 10], we established the following mechanism for changing the structural state of the surface of the main rock-forming minerals of kimberlites under the action of nanosecond electromagnetic pulses. Serpentine for example, pulse actions during 10 s reduced fraction of trivalent silicon Si\(^{3+}\) and raised the atomic concentration of quadrivalent silicon Si\(^{4+}\). Increasing the duration of pulse action to 100 s reduced the atomic concentration of silicon Si\(^{4+}\) and the surface atomic concentration of oxygen bound in the state Si–O–Mg. These results indicate breaking of the bonds between the layers of magnesium–oxygen octahedrons and silicon tetrahedrons, resulting in disorder in the surface structure due to the octahedral layer escaping from its initial bound state. The main processes of selective disintegration of calcite are the opening of intercrystalline boundaries, the propagation of cracks along the cleavage surfaces, and the formation of microcrystal fragments upon extending the pulse action to \(t_{\text{treat}} \geq 50\) s.

The maximum relative decrease in calcite microhardness (\(\Delta H\)) to 66% (from 790 MPa down to 265 MPa) was observed as a result of the HPEMP action for 100-150 s. There was a significant decrease in the microhardness of the calcite samples (by 45%) for the first 10–30 s of electric pulse treatment. The olivine microhardness decreased monotonically from 4250 MPa (HV of the olivine in the initial state) to 1560 MPa after HPEMP treatment as the time of pulse treatment was increased to \(\sim 150\) s; the maximum \(\Delta H\) was \(\sim 63\%\). The serpentine microhardness decreased from 430 MPa (HV of serpentine in the initial state) to 260 MPa after HPEMP treatment for 50-150 s. The maximum relative change in the microhardness was \(\sim 40\%\). The microhardness of kimberlite rock mass decreased from 360 (in the initial state) to 200 MPa (\(t_{\text{treat}} \leq 150\) s); the relative reduction in HV was \(\sim 44\%\).

3.3 Practical applicability of HPEMP for improving the technological process of diamond ores

Based on the features of current mining and processing technology for kimberlite ore used in Russia, we can suppose that impulse energy impact can be applied for treating tails of processing operations aimed at re-grinding (circulation) with grain size less than 5 mm.

Our experimental results show the effectiveness of the short-term electromagnetic pulses action to improve the technology properties of natural diamonds and rock-forming minerals of Kimberlites. In this case, we can expect implementation of the following positive effects due to preliminary electromagnetic impulse treatment of diamond-bearing ores: (i) intensification of kimberlite rock disintegration before the operation of tails regrinding, increasing the selectivity of mineral clusters opening and the preservation of diamonds in autogenous grinding mills; (ii) directed modification of the surface structure, chemical composition of surface layers and flotation properties of naturally hydrophilic diamond crystals to intensify the efficiency of valuable components extraction from the
tails of enrichment operation (circulation), as well as the controlled change in mechanical properties of kimberlite minerals (calcite, olivine, serpentine). To realize the effect of diamonds flotation properties directed change, it is rational to use the HPEMP method for processing concentrates before operations of sticky separation and flotation.

4. Conclusion
The high-voltage nanosecond pulses cause the directed surface chemical transformation in the functional cover of diamond, namely, the secondary mineral phase (hydrophilic thin films) breaks down and remove from the diamond surface. Additional defects of type $B_2$ in the crystal lattice of natural diamonds are formed; this effect may cause dispersion hardening of diamond crystals. Improvement in the hydrophobic properties and flotation ability of diamonds was observed at impulse treatment time equal to $t_{\text{treat}} \leq 50$ s. The action of nanosecond high-power pulses causes formation of the microdamages type electrical breakdown canales in the kimberlite rock constituents (calcite, olivine, and serpentine). As a result of impulse treatment, the decrease in microhardness of rock-forming minerals was from 40 to 70%. The obtained experimental result indicates possibility of applying pulsed energy effects to intensify the diamond flotation and to advance efficiency of the weakening of kimberlite rock constituents without damaging the precious crystals and ensuring their preservation by the subsequent grinding of refractory ores.

Acknowledgments
Work supported in part by the President of the Russian Federation under contract number NSh–7608.2016.5 (academician V.A. Chanturiya’s scientific school).

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