Influence of High-Voltage Electromagnetic Pulses on Technological Properties of Diamond Crystals and Kimberlite Rock-Forming Minerals

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Abstract

For optimization of diamond processing technology the influence of nanosecond high voltage pulses on mechanical and technological properties of diamond crystals and kimberlite rock-forming minerals (calcite, olivine, serpentine) was investigated. Using methods of Fourier Transform Infrared Spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), microscopy and mikrohardness measurement the changes of structural, physic-chemical surface properties, and microhardness of minerals as the result of impacts, was studied. Non-thermal impacts caused a decrease of kimberlite rock-forming minerals microhardness in general to 40–66% as the result of surface microstructure destruction which is caused by formation of micro cracks, traces of surface breakdown and other defects. At the same time, the pulse energy impact on natural diamonds led to formation of B2 type crystal lattice microsift defects, elevated concentration of which increases the hardness properties of crystals. The obtained result indicates possibility of applying pulsed energy effects to improve the softening efficiency of diamond-bearing kimberlites rock-forming minerals without damaging the diamond crystals and ensuring their preservation by the subsequent grinding of ores. The effect of increasing the natural diamonds flotation activity by 14% (from 47% to 61%) was experimentally established as a result of processing diamond crystals with nanosecond pulses (~ 10–50 sec), which indicates the principal possibility of using pulsed energy impacts to intensify the diamond flotation during processing diamond-bearing kimberlites.

Keywords: kimberlite, diamonds, high-voltage nanosecond pulses, hydrophobicity, micro-hardness, floatability

Introduction

The current technology for mining and processing diamonds from primary deposits in Russia damages the diamond crystals at a rate of 25–75%, leading to an average weight loss of 12% (Chanturiya et.al., 2015; Chanturiya, Goryachev, 2008). Diamonds are usually damaged during the autogeneous grinding of kimberlites (in mills of wet autogeneous grinding), and up to 29% of all diamonds disintegrate (Chanturiya et.al., 2015; Chanturiya, Goryachev, 2008). Therefore, in processing of diamond-bearing kimberlites the actual problem of prime importance is development of new effective processes feasible to provide a higher grade concentrates due to softening of kimberlite, to preserve diamond crystal safety in autogenous ore grinding circuits, and to enhance difference of hydrophobic, lipophobic, luminescent properties of diamonds and rock minerals (Chanturiya et.al., 1999, 2017).

This work presents new experimental data on changes in the structure, chemical composition of surface atoms, hydrophobicity, and microhardness of rock_forming minerals in Yakut kimberlites and synthetic and natural technical diamonds as a result of nonthermal action produced by nanosecond high voltage pulses (high_power electromagnetic pulses, or HPEMPs) (Bunin et.al., 2001; Mesyats, 2004; Cherepenin, 2006). Our aim was to assess the efficiency of using HPEMPs in the enrichment of diamond-bearing ores.

Materials and research technique

We used samples of AS-120 synthetic diamonds with particle sizes of (–50 + 40) μm, along with crystals of natural technical diamonds (–2 + 1) mm in size from the Triassic placer of the Bulkur site in the Nizhne Lenski region (the northeastern part of the Siberian platform; from the collection of Yu.M. Sibirtsev; VANPO Aerogeologia) (Anashkina, Khachatryan, 2015) and samples of milled rock-forming minerals with particle sizes of -100 + 63 μm, polished sections 1 × 1 × 0.45 cm in size. Samples of synthetic diamonds and milled minerals (olivine, serpentine, calcite) were subjected to nanosecond high-voltage video pulses (τ (of pulse front), ~1–5 ns; τ (pulse duration), ~50 ns; U (pulse amplitude), ~25 kV; E ~ 10^7 V m^{-1}; pulse repetition frequency, 100 Hz, pulse energy, ~0.1 J; duration t_{treat} of electric pulse treatment, 10–150 s; HPEMP number N_{pulse} ~ (1–15) × 10^3) under standard ambient conditions with no ohmic contact between synthetic diamond particles and our source of high voltage to allow the development of nanosecond pulse atmospheric pressure dielectric barrier discharges (Raizer, 2009). The electric pulse treatment of some technical diamond crystals and polished sections of minerals allowed contact between individual crystals and the grounded electrode of the pulse generator, which in some cases induced a spark (Raizer, 2009) between the mineral's surface and the active electrode (anode) of the pulse generator.

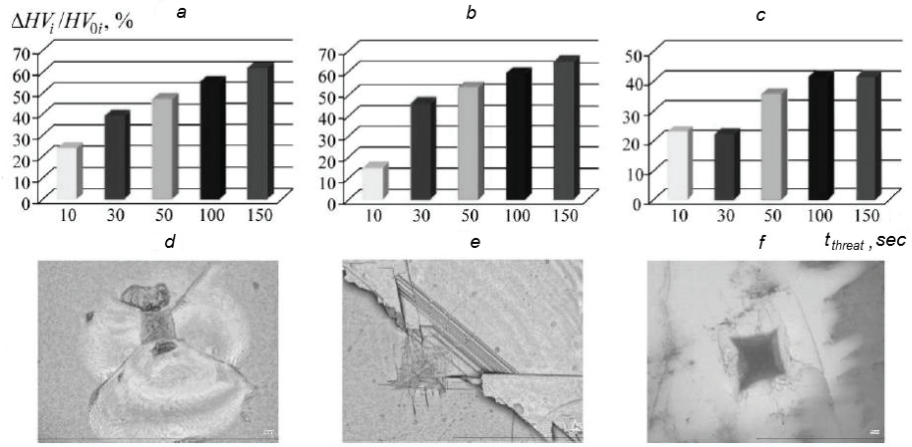

Fig. 1. The relative change in microhardness ($\Delta HV_i/HV_{0i}$%) of olivine (a), calcite (b), serpentine (c) versus time (t_{oep}) of processing; indenter morphology (Vickers diamond pyramid) on the surface of minerals (d) – (f); LCSM, width of scanning window ~100 um

Rys. 1. Względna zmiana mikrotwardości (HHV_i/HV_{0i}%) oliwinu (a), kalcytu (b), serpentynitu (c) w funkcji czasu (t_{oep}) przeróbki; morfologia (piramida diamentowa Vickersa) powierzchni minerałów (d) – (f); LCSM, szerokość okna skanowania ~100 um

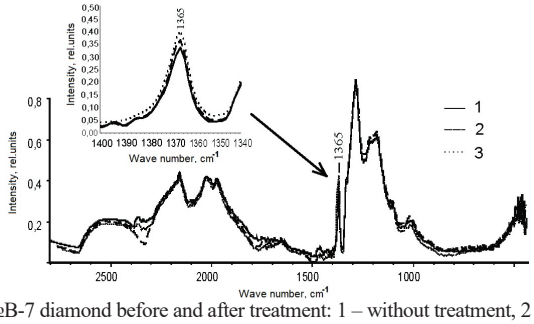

Fig. 2. Spectrum of №B-7 diamond before and after treatment: 1 – without treatment, 2 – 50 sec, 3 – 150 sec

Rys. 2. Widmo diamentu №B-7 przed i po poddaniu impulsów: 1 – bez impulsów, 2 – 50 sekund, 3 – 150 sekund

To analyze the surface phase composition of mineral particles, we used X-ray photoelectron spectroscopy (XPS on a Kratos Axis Ultra DLD spectrometer with a source of monochromatic AlKα radiation). The procedures for our XPS studies of the mineral surface were described in detail in (Minenko, Bogachev, 1999; Chanturiya et.al., 2013). FTIR on a Nicolet-380 spectrometer with a Karl Zeiss microlighting attachment (wave number, 400–4000 cm^{-1}) was used to analyze the phase composition and structural impurities (defects) of natural technical diamonds. The morphological and structural chemical properties of the diamond surfaces were studied by means of analytical electronic microscopy (SEM–XEDS, on a LEO 1420 scanning electron microscope; EDX, on an Oxford INCA Energy 350 scanning electron microscope and a JEOL JSM-6610LV low vacuum microscope); optical microscopy (OM, on an Olympus SZ61 Greenough stereo microscope); and laser scanning confocal microscopy (LSCM, on a KEYENCE VK-9700 microscope). Floatability of natural diamonds of various classification types before and after electromagnetic pulse processing were studied by flotation without reagents in distilled water in Hollimond's tube.

The microhardness of the rock_forming minerals in the initial state and after the mineral polished sections were treated with HPEMPs was calculated using the Vickers method (HV, MPa) using a PMT-3M microhardness meter equipped with an FOM-2 photoelectric ocular microscope. The Vickers microhardness was found using the formula: HV = $(0.189\ P / d^2) \cdot 10^6$, where P is the normal load applied to the diamond point (H), and d is the arithmetic mean for the lengths of both diagonals of the indentation (μm).

Results and discussion

Effect of HPEMP-irradiation on microhardness of kimberlite rock-forming mineral and durability properties of diamonds. Hardness is not a physical constant; it is a complex characteristic depending on elastic (elastic-plastic) properties, brittleness (resistance to fracturing), microstructure of surface material layer, and test procedure. Nevertheless, hardness is "one of properties determined by general laws of a chemical bond in a substance" and variations in it are "conditioned by alteration of inter-atom bond forces, ion polarization and distance between lattice sites" (Shafeev, 1973).

Figure 1 presents the relationships (histograms) between relative variations in microhardness of minerals under HPEMP-irradiation versus the pulsed treatment time: $\Delta HV_i / HV_{0i}$;%, where HV_{0i} is the microhardness of its specimen in initial state; HV_i is the microhardness of its specimen after electric pulse treatment, and indenter morphology (Vickers diamond pyramid) on the surface of minerals.

The experimental data obtained in the present research work show the softening of rock-forming mineral-dielectrics under high-voltage nanosecond electromagnetic pulse irradiation. Non-thermal impacts caused a decrease of kimberlite rock-forming minerals microhardness in general to 40–66% as the result of surface microstructure destruction which is

Tab. 1. Effect of hight voltage impacts on phase composition of synthetic diamonds surface according to XPS, at. %
Tab. 1. Wpływ wysokich napięć na skład fazowy powierzchni syntetycznych diamentów według XPS, przy. %

HPEMP number, 10^3	C 1*s*				O 1*s*			
	–C ($-sp^2$)	C–C ($-sp^3$)	C = O, C = O, O–C–O	–Me	O–Me, $O_{adsorbed}$	HO–Me, C = O	O–C	C–O–C, $H_2O_{adsorbed}$
0	12,5	73,2	12,7	1,5	5,5	32,1	52,8	9,6
3	12,0	73,6	13,4	1,1	5,3	32,2	51,0	11,3
5	12,6	73,5	13,0	1,1	5,3	35,3	51,4	8,1
15	12,7	72,7	13,2	1,3	5,1	36,4	51,9	6,7

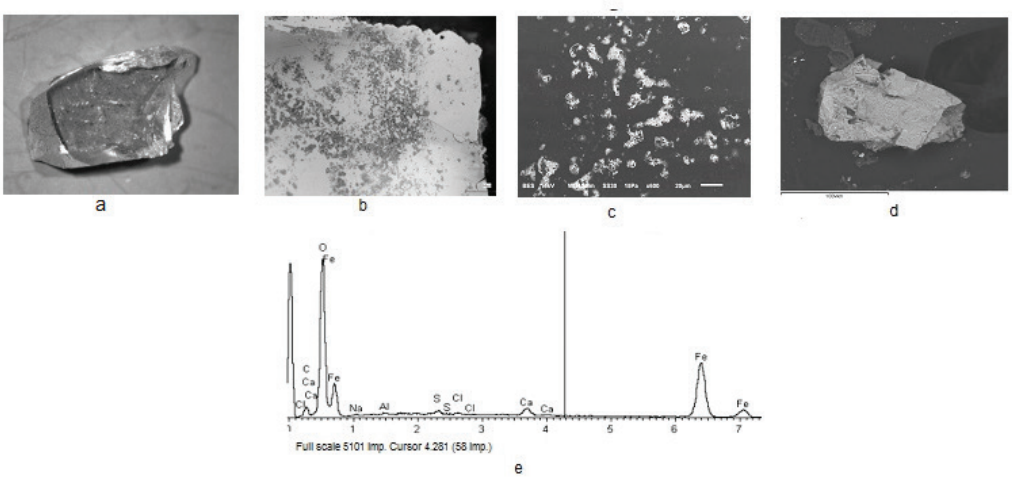

Fig. 3. General view of diamond crystal (a, b - optical microscopy), an enlarged district of its surface, (c) and a fragment of the hydrophilic mineral phases (d), separated from the diamond surface as a result of impulse treatment, t_{proc} ~30 s (SEM-EPMA); X-ray spectrum of the surface mineral film fragment (e)

Rys. 3. Widok ogólny kryształu diamentu (a, b – mikroskop optyczny), powiększonego obszaru jego powierzchni (c) i fragmentu hydrofilowych faz mineralnych (d), oddzielonych od powierzchni diamentu w wyniku impulsu leczenie, t_{proc} ~30 s (SEM-EPMA); Widmo rentgenowskie powierzchniowego fragmentu filmu mineralnego (e)

caused by formation of micro cracks, traces of surface breakdown and other defects. The experimental data on microhardness variations for rock-forming minerals correspond to the results of our spectroscopic investigations (Bunin et.al., 2015).

A gradual process of selective disintegration of the mineral was the main mechanism behind the dissipation of energy in a high-voltage pulse electric field: the opening (loosening) of intercrystalline boundaries, the formation and propagation of cracks along the cleavage surfaces, and the formation of microcrystal fragments upon extending the pulse action to $t_{treat} \geq 50$ s.

Note that the experiments with nanosecond electromagnetic pulse treatment of natural and artificial media made use of so-called nonthermal action, since the energy of a single pulse (~0.1 J), and even the energy of a pulse train, were insufficient to raise the experiments, nonthermal HPEMP treatment did not produce microflaws in diamonds (this was monitored by means of microscopy diagnostics), since the breakdown voltage of an electric field is about 10^9 V m^{-1} for diamonds (Cherepenin, 2006), two orders of magnitude higher than the strength of field electric component E in the interelectrode space of the pulse generator.

Analysis of our IRFS results showed that the nonthermal action of nanosecond HPEMP resulted in a notable systematic increase in the absorption coefficient of the line around 1365 cm^{-1} (Fig. 2), indicating there was an increase in the concentration of lamellar B2 defects (platelets) represented by internode carbon atoms (Evans et.al., 1995). At the same time, no deep structural reorganization of the diamond crystals was observed; i.e., there was almost no change in either the concentration or distribution of nitrogen centers. Increased numbers of B2 defects after HPEMP treatment were registered only in seven of fifteen samples from our assortment of natural diamonds. All of these crystals characteristically belonged to a group of medium-nitrogen specimens with elevated degrees of nitrogen aggregation %N(B).

The observed changes in the IR spectra of natural diamonds do not contradict our current understanding of the nature of B2 platelet defects (Evans et.al., 1995; Sobolev, 1978), according to which the content of platelets grows in crystals as the concentration of B form nitrogen rises (Sobolev, 1978). However, B centers in crystals can exist independently, and are not necessarily accompanied by platelets. According to (Khachatryan, 2009), platelets are common in diamonds with layered octahedron internal structures and are virtually never found in crystals with fibrous internal structures. Platelets can consequently be defined as 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 centers inside diamonds of the medium-nitrogen crystal group, mostly in those with layered octahedron revealed the presence of nitrogen in both the A (lines 480 and 1282 cm^{-1}) and B forms (lines 1010 and 1175 cm^{-1}), B2 defects (the line around 1365–1375 cm^{-1}), and structural admixtures of hy-

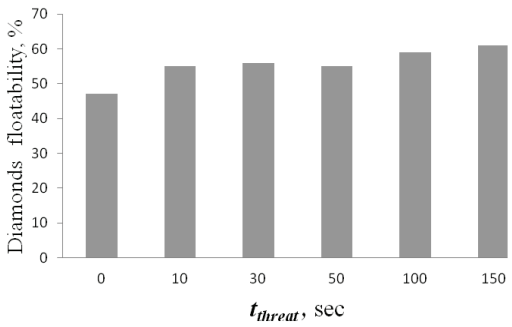

Fig. 4. Effect of impulse impact (t_{threat}) on floatability of diamond crystals
Rys. 4. Wpływ uderzenia impulsowego (t_{threa}) na flotowalność kryształów diamentu

drogen apparent in the form of narrow peaks at 1405 and 3107 cm^{-1}.

Microhardness analysis of diamond crystals, that undergone deformation under natural conditions (Naletov et.al., 1979), showed, that centers of group B increase the dispersion durability of natural diamonds 1,75 times compared to the initial state.

In this way, the experimental results proved applicability of the pulsed energy effect to stimulate softening of rock-forming minerals of diamond-bearing kimberlites and to preserve the wholeness (integrity) of diamond crystals in ore-grinding circuits due to reduced time of kimberlite rock processing in autogenous mills.

Influence of impulse energy effects on surface phase composition, and flotation properties of diamonds. Analysis of XPS data (Tab. 1) showed that structural chemical transformations of the surface layers of synthetic diamonds caused by HPEMP treatment were mainly associated with the altered chemical state of oxygen atoms. In the O spectrum of the 1s level, there was a 3,2–4,3% increase in the proportion (at %) of the peak with E_{bond} = 530,9 eV, due the oxygen from hydroxyl groups bound to the surface metal atoms (admixed during diamond synthesis), or to the oxygen from surface carbonyl groups as part of C=O.

In general, the nonthermal action produced by the high-voltage nanosecond pulses altered the functional cover of the diamond crystal surface via hydroxylation and/or the formation of carbonyl groups due to the oxidation of the surface layer of mineral particles when they interacted with the active products of the radiolytic decomposition of the water–air medium.

Analytical Electron Microscopy.

According to our SEM–XEDS data (Fig. 3), the separation of secondary mineral phase fragments 40 to 100 μm in size from a natural diamond's surface was observed during its HPEMP treatment (t_{treat} ≥30 s); these were presumably calcium sulfate and iron oxides (hydroxides). This fact indicates the effectiveness of non-thermal impact of high-voltage nanosecond pulses, as a result of which the surface cleared from mineral impurities.

IR-spectroscopy.

Considerable changes in the natural diamond IR-spectra were observed after the electric pulse treatment of crystals with iron oxide mineral films, strongly adhesive clayish mineral coatings, and other impurities on their surfaces. Samples with phase impurities containing hydrocarbon and OH-groups lost them after HPEMP treatment. 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_{treat} ≥50 s. This usually indicates the presence of hydrocarbon impurities and H_2O. This testifies 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.

The influence of HPEMP on floatation activity of diamonds surface.

As a result of the experiments, a nonlinear dependence of diamond floatability on electromagnetic impulse time with a maximum at 150 s has been established (Figure 4). In general, the content of floated crystals increased by 14% (from 47% to 61%). A significant increase in flotation activity of diamonds established for small "doses" of electromagnetic impact (≤ 30 c) (Figure 4).

The results of the experiment showed that the maximum content of hydrophobic floatable diamonds was achieved for preliminary pulse treatment in ~ 30 s. The content of hydrophilic non-flotatable diamonds decreased significantly after processing of HPEMP for ~ 10–30 s, which indicates the advisability of applying short-time regimes of treatment for the directed change in the structural-chemical state of the surface, the physical-chemical and flotation properties of diamond crystals.

Conclusion

As a result of experimental studies about influence of high-voltage nanosecond pulses on kimberlite rock-forming minerals, natural and synthetic diamonds, the following new information was obtained:

1. The effect of multidirectional change in mechanical properties (microhardness) of rock-forming minerals of kimberlite (olivine, serpentine, calcite) and diamond crystals under conditions of nanosecond HPEMP was established. It consists in surface layer softening of rock minerals and reduce of their microhardness as a whole by 40–60% due to the formation of structural defects and the simultaneous increase in B2-defects (platelets) concentration in the crystal structure of diamonds, which, presumably, causes an increase in the strength properties of diamond crystals. The obtained result

indicates the possibility of applying of pulsed energy impact to improve the softening efficiency of rock-forming minerals of diamond-bearing kimberlites without damaging diamond crystals and ensuring their preservation by the subsequent grinding of ores.

2. It was found that increase of diamonds floatability as a result of HPEMP treatment associated with detachment and partial destruction of mineral films on the crystal surface, which indicates the advisability of applying high-voltage nanosecond pulses for destroying and removing hydrophilic mineral micro- and nanophases from the surface of diamond crystals. A prolonged energy effect leads to oxidation of crystals surface (confirmed by the XPS method for synthetic diamonds).

3. The effect of natural diamonds flotation activity increasing by 14% (from 47% to 61%) was experimentally established as a result of processing diamond crystals with nanosecond HPEMP, which indicates the principal possibility of applying pulsed energy impact to intensify the diamond flotation process during diamond-bearing kimberlites processing.

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Wpływ wysokonapięciowych impulsów elektromagnetycznych na właściwości technologiczne kryształów diamentu i minerałów tworzących skały Kimberlite

W celu optymalizacji technologii przeróbki diamentów zbadano wpływ impulsów wysokiego napięcia nanosekundowego na właściwości mechaniczne i technologiczne kryształów diamentu i minerałów tworzących skały kimberlitowe (kalcyt, oliwin, serpentynit). Przy pomocy metod spektroskopii w podczerwieni z transformacją Fouriera (FTIR), rentgenowskiej spektroskopii fotoelektronowej (XPS), mikroskopii i pomiaru mikrotwardości badano zmiany strukturalnych, fizykochemicznych właściwości powierzchni oraz mikrotwardości minerałów w wyniku uderzeń. Uderzenia nietermiczne spowodowały zmniejszenie mikrotwardości minerałów tworzących skały kimberlitowe ogólnie do 40–66% w wyniku zniszczenia mikrostruktury powierzchni, spowodowanego powstawaniem mikropęknięć, śladów rozpadu powierzchni i innych wad.

Jednocześnie wpływ energii impulsu na naturalne diamenty doprowadził do powstania defektów mikroprzesunięcia sieci krystalicznej typu B2, których podwyższone stężenie zwiększa właściwości twardości kryształów. Uzyskany wynik wskazuje na możliwość zastosowania efektów pulsacji energii w celu poprawy wydajności zmiękczania zawierających diamenty minerałów tworzących skały jak kimberlity, bez uszkadzania kryształów diamentu i zapewnienia ich zachowania w czasie późniejszego mielenia rudy. Efekt zwiększenia naturalnej aktywności flotacyjnej diamentów o 14% (z 47 do 61%) ustalono eksperymentalnie w wyniku przetwarzania kryształów diamentu za pomocą impulsów nanosekundowych (~ 10–50 sekund), co wskazuje na główną możliwość wykorzystania energii pulsacyjnej. Impulsy wpływają na intensyfikację flotacji diamentów podczas przetwarzania kimberlitów zawierających diamenty.

Słowa kluczowe: kimberlit, diamenty, impulsy nanosekundowe wysokiego napięcia, hydrofobowość, mikrotwardość, flotowalność