The Mechanism of Formation of Finely Dispersed Minerals on the Surface of Diamonds and the Application of Electrolysis Products of Water Systems for their Destruction

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Abstract

The composition of the surface of natural diamonds in interaction with kimberlite minerals and the aqueous phase in the deposit and enriched ore is studied. The sequence and conditions for the formation of minerals on the surface of crystals under conditions of processing of kimberlites have been determined. Confirmed the mechanism of hydrophilization of diamonds comprising crystallization of hydroxides and oxides of iron as a mandatory initial stage. A method of destruction or subsequent dissolution of minerals aggregates by the impact of electrolysis products of aqueous systems has been proposed, which allows to restore the hydrophobicity of diamonds. The use of electrochemically treated water in the froth separation cycle with high diamond recovery made it possible to increase their recovery in the factory's concentrate by 8.8%.

Keywords: kimberlite, diamond, mineral impurities crystallization, hydrophobic, hydrophilic, enrichment, electrochemically treatment

Introduction

The high content of altered minerals in kimberlite ores leads to the formation of hydrophilic films on the surface of the crystals, which reduce the degree of hydrophobicity of diamonds and increase their losses in the processes of greased and froth separation to 20–30% (Kurenkov, 1957, Chanturiya et al., 2005). This fact makes the of the identification of the objective of justification and selection of the method for restoring the hydrophobic properties of diamonds before the separation processes of their recovery presently topical.

Earlier studies have defined that a promising way to solve the problem of reducing the intensity of formation of mineral impurities on the surface of diamonds and increasing the enrichment of kimberlites is achieved through the use of physical and physicochemical methods of impacting on the solid and liquid phase of the pulp (Dvoichenkova, 2011; Chanturiya et al., 2016). An important task of the research that determines the achievement of the goal is to study and substantiate the mechanism of formation of minerals on the surface of diamond crystals. The theory of step crystallization was chosen as a working hypothesis for the mechanism of hydrophilization (Matusevich, 1968).

Research methods and objects

To study the mechanism and regularities of the process of buildup of surface formations on diamonds, diamond crystals from kimberlite ore derivatives are taken as the objects of research. Three types of natural diamond crystals recovered from kimberlite ore were used in the experiments:

- natural-hydrophobic crystals, which do not contain mineral formations on the surface;
- natural-hydrophobic crystals with an insignificant amount of mineral formations on the surface;
- natural-hydrophilic crystals, which surface is covered with dense mineral formations.

As a liquid phase, the mineralized circulating process water of the mineral separation plant and the products of its electrolysis in a bladderless vessel has been used.

Impurities on diamond surfaces are studied by using methods of optical microscopy, Auger and X-ray spectroscopy, infrared spectroscopy, UV-VIS spectroscopy and micro-X-ray spectroscopy. The chemical composition of mineral admixtures is determined by using a JXA-8800R microanalyzer.

The hydrophobicity of the diamond surface was determined by the measurements of the three-phase wetting angle. The flotation activity of diamonds was determined in laboratory conditions by the methods of froth separation at the facilities of the YAKUTNIPROALMAZ Institute. Industrial tests were carried out per the scheme of froth separation of diamond-containing raw materials at the beneficiation plant of the Mirny MPD. The experiments were performed in the laboratories of the Research Institute of Comprehensive Exploitation of Mineral Resources under the Russian Academy

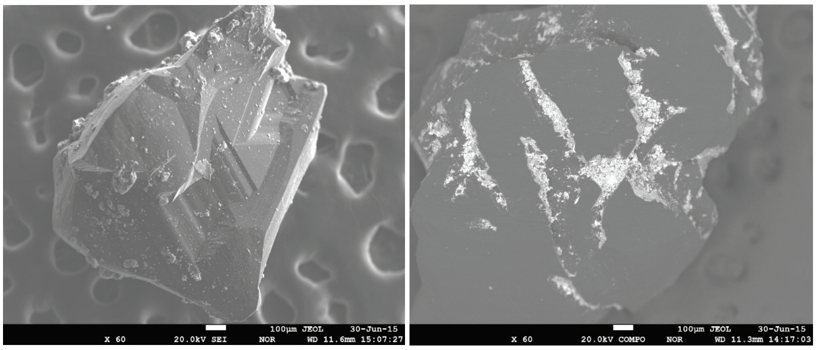

Fig. 1. The outer appearance of mineral impurities on the surface of diamonds

Rys. 1. Wygląd zewnętrzny zanieczyszczeń mineralnych na powierzchni diamentów

of Science, YAKUTNIPROALMAZ Institute and the Scientific Research and Geological Exploration Enterprise of ALROSA company.

At the first stage of the research, the composition of impurities on the surface of diamonds and the regularities of the processes of their formation were studied under the conditions of processing of refractory kimberlites. At the second stage of the experimental research, approbation of the application of electrolysis products of mineralized water was performed to remove mineral formations from the surface of diamonds under laboratory and industrial conditions. The results were mathematically processed and the corresponding graphical dependencies were built.

Experimental work findings and their discussion

An analysis of the mineral and phase composition of the surface of diamond crystals recovered from diamond-bearing kimberlite derived products made it possible to find on the diamonds the presence of mineral impurities in the form of finely dispersed clay minerals and a film-insular type of their attachment on crystals (Fig. 1).

According to the nature of the distribution in Fig. 2 x-ray maps of iron (a) and oxygen (b), respectively, it is possible to diagnose goethite or hematite, and the intensity of the distribution of calcium (b), sulfur (g) and oxygen (b) is diagnosed with gypsum ($CaSO_4 \times 2H_2O$).

Analysis of the composition and preferential location of surface mineral formations on the defects of diamond crystals gave grounds for the analysis of the processes of their hypergenic and technogenic hydrophilization to use the hypothesis of the formation and attachment of hypergenic secondary minerals and salt-like substances on diamond surfaces with a broken crystal structure most prone to epitaxial growth (Ryznar, 1944, Telkes, 1952). Analysis of the distribution of surface mineral formations on diamonds made it possible to adopt the crystallization process in the conditions of oversaturation as the most probable mechanism of their formation (Turnbull and Vonnegut, 1952).

In the case under consideration, the diamond surface serves as a matrix forming the phase of the crystallizing salt. The value of the variable of the crystallographic discrepancy is used as the criterion for the surface activity (substrate) (Volmer, 1939).

$$\delta = |a_{sf} - a_{cr}| / a_{cr}$$

where: a_{sf} – the parameter of the crystal lattice of the substrate;

a_{cr} – the parameter of the crystal lattice of the crystallizing substance.

The formation and growth of crystal nuclei occurs when the parameters of these crystal lattices differ by no more than 20% (δ = 0.2) (Turnbull and Vonnegut, 1952). For example, the results of the micro-X-ray spectral analysis showed that serpentine and calcite are the main rock-forming minerals in kimberlite samples of the Mir pipe. Other primary and secondary aluminosilicate and carbonate minerals, as well as hydroxides and iron oxides, saltlike minerals are widespread (Table 1). Goethite is the mostly presented on the diamond surface among other minerals prone to crystallization.

According to the proposed mechanism for the formation of minerals on the surface of diamond crystals under the conditions considered, a primary change of the natural surface of a diamond can occur as a result of hypergenic processes and lead to the formation of films of metal hydroxides. For example, FeO (OH) (mineral of goethite), has the degree of lattice discrepancy with respect to a diamond is 0.15. Further, according to the crystallographic non-conformity of the goethite lattice with the diamond lattice (δ (c) is 0.15), this mineral can crystallize on the diamond crystal surface and be a substrate for the crystallization of other diagnosed minerals.

In accordance with the data on the crystallographic relationships of the lattices of the minerals considered given in the table and the hypothesis of the formation of mineral impurities, the minerals on the diamond surface are crystallized in the following sequence: diamond – goethite – hematite – phlogopite, halite, gypsum.

The electron image of mineral admixtures on the surface of the diamond recovered from the "Mir" mining kimberlites shown in Fig. 3 graphically is indicative of the joint attachment of hypergenic and saltlike minerals (phlogopite, gypsum and halite) on the film of iron minerals (goethite).

Using mathematical data processing, a proportional dependence of the decrease in the hydrophobicity of diamonds was obtained with an increase in the total impurity content on their surface (Figure 3).

At the second stage of the research, approbation of the application of electrolysis products of mineralized water was performed to remove hydrophylic mineral formations from the surface of diamonds. In previous studies we have shown

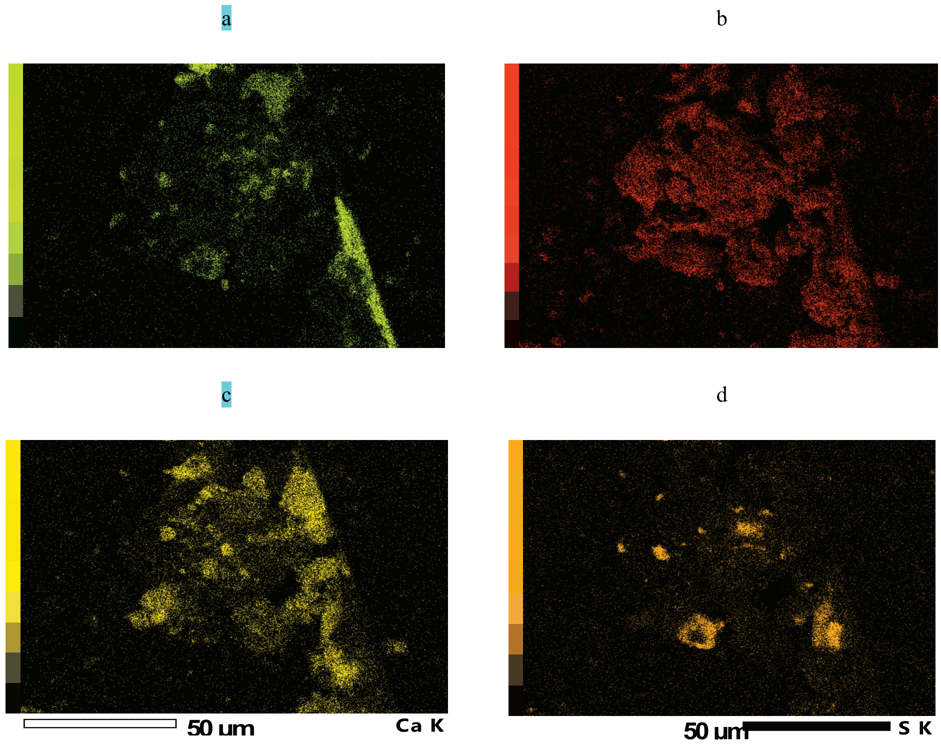

Fig. 2. X-ray maps of distribution of chemical elements: iron (a), oxygen (b); calcium (c); sulfur(d)
Rys. 2. Mapy rentgenowskie rozkładu pierwiastków chemicznych: żelazo (a), tlen (b); wapń (c); siarka (d)

Tab. 1. Mineral formations diagnosed on the surface of diamonds
Tab. 1. Formacje mineralne rozpoznane na powierzchni diamentów

Mineral, formula	Lattice parameter a, A^0			Crystallogr. discrepancy with the diamond			Crystallogr. discrepancy with the goethite			Crystallogr. discrepancy with the hematite		
	a	b	c	δ(a)	δ(b)	δ(c)	δ(a)	δ(b)	δ(c)	δ(a)	δ(b)	δ(c)
Diamond, C	3.57	3.57	3.57	0	0	0	0.28	1.78	0,15	0.41	-	2.85
Гётит, FeO×OH	4.59	9.94	3.02	0.28	1.78	0.15	0	0	0	0.10	-	3.55
Hematite, Fe_2O_3	5.03	-	13.7	0.41	-	2.85	0.10	-	3.55	0	0	0
Phlogopite, $K_2(Mg, Fe)_6[Si_6Al_2O_{20}]$ (OH, F)$_4$	5.3	9.2	10.3	0.48	1.58	1.88	0.15	0.07	2.41	0.05	-	0.10
Halite, NaCl	5.64	-	-	0.58	-	-	0.23	-	-	0.12	-	-
Gypsum, $CaSO_4×2H_2O$	5.68	15.2	6.29	0.58	3.25	0.76	0.24	0.53	1.08	0.13	-	0.54

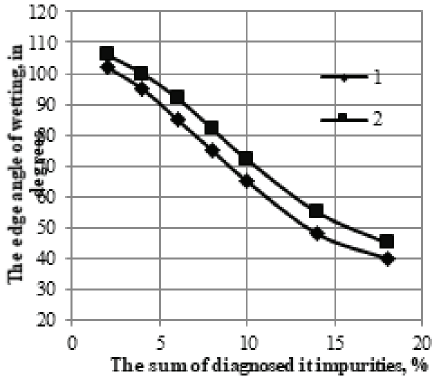

Fig. 3. Dependence of the edge angle of wetting of the diamond surface mine "Mir" (1)
and "Internationalnaya" (2) on the mass fraction of the sum of diagnosed it impurities Si, Ca, Mg, Fe

Rys. 3. Zależność kąta zwilżania dla minerałów z kopalni diamentu „Mir" (1)
i „Internationalnaya" (2) od zawartości zanieczyszczeń Si, Ca, Mg, Fe

Tab. 2. Change in the diamond surface composition and parameters after treatment with water electrolysis products

Tab. 2. Zmiana składu powierzchni diamentu i parametrów po obróbce produktami elektrolizy wodnej

Object of measurement	*the edge angle of wetting in degree*	The concentration on the surface,%					Relation of Σ Si, Fe, Mg of C concentration, %	Film area, %
		C (diamond)	Si	Fe	Mg	O		
hydrophilic diamonds before treatment	33.3	63.5	3.3	4.25	4.5	35.1	19	73
diamonds after treatment	99.8	80.1	1.4	0.7	2.3	15	5.4	19.9

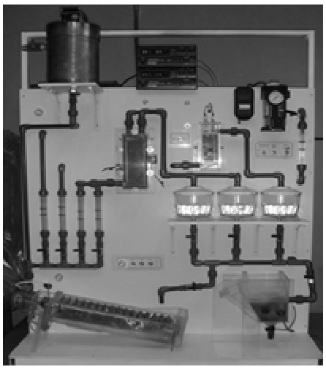

Fig. 4. Laboratory stand for research of the electrochemical conditioning of the water systems in the process of foam separation

Rys. 4. Stanowisko laboratoryjne do badań elektrochemicznego kondycjonowania roztworów wodnych w procesie flotacji pianowej

the possibility of using water electrolysis products for desorption of surface films from a diamond (Chanturiya et al, 2005).

Natural diamonds with a hydrophilic surface were used in the present experiments. Table 2 presents the average results taking into account previous studies.

It was experimentally determined that the crystal surface (group II) washed by the water electrolysis products is characterized by a low content of impurity elements (<5%) and an oxygen content of less than 15%. In this case, the area of the serpentine film armoring a clean surface is not more than 22%; and the amount of diamond carbon reaches 80%. On the initial hydrophilic crystals (group I) covered with mineral impurities, the values of analogous parameters characterizing the impurity film are 2–3 times higher.

Analysis of the absorption spectra of luminescent radiation by the surface of diamond crystals coated with mineral impurities (hydrophilic) and treated with products of electrolysis aqueous systems (hydrophobic) made it possible to determine that:

- the hydrophilic surface of diamonds is characterized by higher values of the absorption coefficient,
- a decrease in the values of the absorption coefficient after the treatment of crystals by electrolysis products of aqueous systems indicates the removal of mineral impurities from their surface.

The obtained results were used in experiments to enhance the efficiency of the process of froth separation of diamond-containing raw materials. To restore the floatability of diamonds, the technology of non-diffracting electrochemical conditioning of the circulating water of the foam separation cycle and the sticky separation cycle was used.

Laboratory tests were carried out on a special stand, which includes an electrolyzer, a foam separation unit and control devices (Fig. 4).

During the experiment, the parameters of electrochemical water treatment varied and optimal conditions were selected. Selected optimal parameters were tested in the course of the technological process at the concentrator plant at the Mirny MPD.

In electrochemical processing was achieved by changing the ionic composition of the water. Concentrations of calcium and magnesium ions decreased, pH decreased. Under these conditions, it was possible to increase the hydrophobicity of diamonds. Another positive effect was a significant increase in the concentration of dissolved gases contributing to the foam separation process.

The use of electrolysis products of aqueous systems in the laboratory experiment conditions made it possible to restore the hydrophobic properties of diamond crystals and increase their yield to the froth separation concentrate from 19.5% to 66.7%, and in the industrial approbation condition to increase the recovery of diamond in the factory's 8.8%.

Conclusions

The mechanism of the formation of mineral impurities on the surface of diamond crystals is represented by the process of crystallization under conditions of saturation of the aqueous phase by crystallizing elements (ions), when the surface of the diamond serves as a matrix forming the phase of the crystallizing salt. The value of the crystallographic disparity between the parameters of the crystal lattice of the substrate (diamond) and the crystallizing substance is used as a criterion for the activity of the surface (substrate).

The decrease of hydrophobicity of diamonds is proportional to the increase of the total content of impurities on their surfaces. The use of electrochemically treated water in the cycle of froth separation of kimberlite ores during the recovery of diamonds into a 98–99% concentrate increases their recovery in the factory averagely by 8.8%.

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Mechanizm tworzenia drobno rozproszonych minerałów na powierzchni diamentów i zastosowanie produktów elektrolizy systemów wodnych do ich zniszczenia

Zbadano skład powierzchni naturalnych diamentów w interakcji z minerałami kimberlitowymi i fazą wodną w złożu i wzbogaconej rudzie. Określono kolejność i warunki tworzenia minerałów na powierzchni kryształów w warunkach przetwarzania kimberlitów. Potwierdzono mechanizm hydrofilizacji diamentów obejmujący krystalizację wodorotlenków i tlenków żelaza jako stały etap początkowy. Zaproponowano sposób niszczenia lub późniejszego rozpuszczania agregatów minerałów przez wpływ produktów elektrolizy układów wodnych, co pozwala przywrócić hydrofobowość diamentów. Zastosowanie elektrochemicznie uzdatnionej wody w procesie separacji piany z wysokim odzyskiem diamentu umożliwiło zwiększenie odzysku w koncentracie o 8,8%.

Słowa kluczowe: kimberlit, diament, krystalizacja zanieczyszczeń mineralnych, hydrofobowe, hydrofilowe, wzbogacanie, obróbka elektrochemiczna