The Formation of Crystalline Mineral Covers on the Surface of Diamonds and Their Destruction with the Use of Electrochemically Treated Water Products

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Abstract. The composition of the surface of natural diamonds in interaction with minerals and the aqueous phase in the kimberlite deposit and processed ore are studied. The sequence and conditions for the formation of hydrophilic minerals on the surface of diamond crystals under conditions of processing of kimberlites have been determined. Confirmed the mechanism of hydrophilization of diamonds surface comprising formation of hydroxides and oxides of iron as a mandatory initial stage of crystallization. A method of restore the hydropobicity of diamonds by the impact of electrolysis products of aqueous systems has been proposed, which allows to destruction or subsequent dissolution of minerals aggregate. The use of treated water in the process of froth separation it possible to increase diamonds recovery in the processing plant concentrate by 8.8%.

1. Introduction

The intensive hypergene processes in kimberlite lead to the formation of hydrophilic cover on crystal surfaces, which reduces hydrophobicity of diamonds and increase their losses in the processes of sticky and foam separation [1,2]. The most common types of these surface formations are crystalline minerals and thin films. These formations are hydrophilic and worsen the interaction of diamonds with collectors and air bubbles. This fact makes topical the issues of identification of the hydrophilization mechanism and the selection of a method for restoring the hydrophobic properties of diamonds for increasing their recovery in separation processes [3,4].

An important task of the research aimed at achieving this goal is to study and determine the mechanism of mineral formation on the surface of diamond crystals. The concept of stepwise crystallisation was chosen as a working hypothesis for the mechanism of hydrophilization.
The historical 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 diamond recovery from kimberlite is achieved through the use of physical and physicochemical methods of treating solid and liquid phases of the pulp [5]. The use of electrochemical conditioning method allows controlling the mineral properties and increasing their floatability. The mechanism of influence of the electrochemical conditioning consists in optimising the ion composition of circulating water and effecting on the mineral surface and reagents [6,7].

2. An analysis of the mineral and phase composition of the surface of diamond crystals
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. 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 of Science, YAKUTNIPROALMAZ Institute and the Scientific Research and Geological Exploration Enterprise of company “ALROSA”.

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.

The assaying findings and preferential location of the surface mineral formations on the defects of the diamond crystals enabled, for analysis of the processes of their hypergene and technogenic hydrophilization, using the hypothesis of the formation and attachment of hypergene secondary minerals and salt-like substances on the diamond surface, with a broken crystal structure to be the most prone to the epitaxial growth. Spectral analysis enabled detecting calcium-magnesium-silicate-carbonate composition of the mineral formations on the diamond crystal surface. The noticeable contents of iron, titanium, and sulphur are found. There is a small amount of sodium and chlorine, indicating the presence of halite or calcium chloride in the studied surface formations. Such a set of elements corresponds, as a rule, to the elemental composition of kimberlite altered in hypergene conditions. The nature of the distribution of iron and oxygen allows assuming possible availability of goethite or hematite in the formations (figure 1a,b). The intensity of the distribution of calcium (b), sulfur (g) and oxygen (b) is diagnosed with gypsum (CaSO$_4$·2H$_2$O) (figure 1c,d).

In the case under consideration the diamond surface serves as a matrix forming the phase of the crystallising salt. The value of the variable of the crystallographic discrepancy $\delta$ is used as the criterion of the surface activity (substrate) [8,9]. The formation and growth of the crystal nuclei occur when the parameters of these crystal lattices differ by no more than 20% ($\delta = 0.2$) [10]. For example, the results of the micro-X-ray spectral analysis showed that the serpentine and the calcite are the main rock-forming minerals in kimberlite samples from the Mir pipe (Table 1). Goethite is the most abundant among the minerals prone to crystallisation on the diamond surface [11].
Figure 1. X-ray maps of distribution of chemical elements: iron (a), oxygen (b); calcium (c); sulfur(d).

Table 1. Mineral formations identified on the surface of diamonds.

| Mineral, formula | Lattice parameter a, Å | Crystallographic discrepancy with diamond | Crystallographic discrepancy with goethite | Crystallographic discrepancy with hematite |
|------------------|-------------------------|-------------------------------------------|-------------------------------------------|-------------------------------------------|
|                  | a       | b       | c       | δ(a)   | δ(b)   | δ(c)   | δ(a)   | δ(b)   | δ(c)   | δ(a)   | δ(b)   | δ(c)   | δ(a)   | δ(b)   | δ(c)   |
| Diamond          | 3.57    | 3.57    | 3.57    | 0      | 0      | 0      | 0.28   | 1.78   | 0.15   | 0.41   | -      | 2.85   |
| Goethite         | 4.59    | 9.94    | 3.02    | 0.28   | 1.78   | 0.15   | 0      | 0      | 0      | 0.10   | -      | 3.55   |
| Hematite         | 5.03    | -       | 13.7    | 0.41   | -      | 2.85   | 0.10   | -      | 3.55   | 0      | 0      | 0      |
| Phlogopite       | 5.3     | 9.2     | 10.3    | 0.48   | 1.58   | 1.88   | 0.15   | 0.07   | 2.41   | 0.05   | -      | 0.10   |
| Serpentine       | 5.8     | 9.2     | 7.3     | 0.48   | 1.57   | 2.17   | 0.15   | 0.07   | 1.42   | 0.05   | -      | 0.47   |
| Aragonite        | 4.95    | 7.95    | 5.73    | 0.38   | 1.22   | 0.6    | 0.07   | 0.2    | 0.89   | 0.01   | -      | 0.58   |
| Halite           | 5.64    | -       | -       | 0.58   | -      | -      | 0.23   | -      | -      | 0.12   | -      | -      |
| Gypsum           | 5.68    | 15.2    | 6.29    | 0.58   | 3.25   | 0.76   | 0.24   | 0.53   | 1.08   | 0.13   | -      | 0.54   |

According to the proposed mechanism for the formation of minerals on the surface of diamond crystals under the conditions considered, the initial alteration of the natural diamond surface may occur as a result of hypergene processes and lead to the formation of films of metal hydroxides [12].

Due to the crystallographic non-conformity of goethite lattice with diamond lattice, (δ(с) is 0.15), this mineral can crystallize on the diamond crystal surface and be a substrate for crystallisation of the other 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) - serpentine, aragonite, phlogopite, halite, gypsum.

The established fact of the participation of iron compounds in the formation of the hydrophilizing films is confirmed by electronic images of mineral impurities on the surface of diamonds extracted from kimberlite, illustrating the joint fixation of hypergene (serpentine, aragonite) and salt-like minerals (phlogopite, gypsum and halite) on the film of iron minerals (goethite, hematite).
3. The destruction covers on the surface of diamonds with the use of electrochemically treated water products

In the previous studies, we have shown the possibility of using water electrolysis products for desorption of surface films on diamond crystals [3,4]. Taking into account the findings of the present studies, testing of the products of the non-diaphragm electrolysis of saline water for removing the hydrophilic mineral formations from the diamond surface was performed.

As can be seen from figure 3, the increase in the wetting angle of natural hydrophilic diamonds is about 23%, technogenic hydrophilic diamonds – about 27%, and for natural hydrophobic diamonds containing mineral impurities in a minimum amount, the increase in the wetting angle is minimal and amounts to 8-10%.

![Figure 2. Change of the edge wetting angle of the diamond from the power consumption under the conditions of interaction with the products of non-diaphragm electrolysis of mineralized water: 1 – technogenic-hydrophilic crystals; 2 – natural-hydrophilic crystals; 3 – natural-hydrophobic crystals.]

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The reason for the change in the hydrophobicity of diamonds is the cleaning of their surface in an aqueous medium that has passed the stage of electrochemical conditioning (table 2). It was experimentally determined that the crystal surface, washed by the water electrolysis products, is characterised by low content of the impurity elements (< 5 %) and oxygen content of less than 15% (Table 3).

Table 2. Change in the surface composition of diamonds after interaction with the products of electrolysis of mineralized water in a non-diaphragm electrolyzer.

| Chemical element | Before treatment | After treatment | Mass fractions of elements, % | At power consumption, kWh/m³ |
|------------------|-----------------|----------------|-----------------------------|-----------------------------|
|                  |                 |                 |                            | 0.5                        | 1.0                        | 1.5                        |
| C                | 78,0            | 87,5            | 91,2                        | 94,0                        |                            |                            |
| O₂               | 9,4             | 6,8             | 4,3                         | 3,3                         |                            |                            |
| Ca               | 1,4             | 1,06            | 0,39                        | 0,19                        |                            |                            |
| Fe               | 1,3             | 1,12            | 0,61                        | 0,37                        |                            |                            |
| Si               | 2,5             | 1,7             | 1,2                         | 0,8                         |                            |                            |
| Mg               | 0,65            | 0,4             | 0,33                        | 0,17                        |                            |                            |
| Al               | 0,4             | 0,27            | 0,19                        | 0,1                         |                            |                            |
Table 3. Changes in the natural-hydrophilic diamond surface film composition before and after treatment with water electrolysis products.

| Subject of measurement          | Edged angle of wetting, degrees | Content on the surface, % | Film area, % |
|--------------------------------|---------------------------------|---------------------------|--------------|
|                                |                                 | C (diamond)               | Si | Fe | Mg | O   |                  |
| Hydrophilic diamonds before    |                                 | 63.5                      | 3.3 | 4.25 | 4.5 | 35.1 | 73.0             |
| treatment                     |                                 |                           |     |     |    |     |                  |
| Diamonds after treatment       |                                 | 80.1                      | 1.4 | 0.7  | 2.3 | 15.0 | 19.9             |

In order to evaluate the efficiency and select the best mode of electrochemical conditioning of mineralized water in order to give them the ability to activate the surface of diamonds in conditions close to industrial, a series of experiments on flotation of the studied diamond crystals in mineralized water and products of its non-diaphragm processing was conducted. Bench tests of the process of foam separation of the studied mineral objects were carried out in the laboratory of the Institute "Yakutniproalmas" on a pilot plant, which included sample preparation units, conditioning of circulating water, agitation of ore with reagents and subsequent foam separation (figure 2).

![Figure 3](image)

Figure 3. Schematic diagram of the circuit apparatus for bench testing of the process of foam separation of diamond-containing raw materials. 1-power supply; 2-water tank; 3-electrolyzer; 4-pump; 5-air conditioner; 6-tray; 7-foam separator; 8-sieve.

The obtained results served as the basis for the development of electrochemical technology of circulating water conditioning at the concentrators of the joint-stock company “ALROSA”. The results of the laboratory technological research showed that using products of non-diaphragm electrolysis of circulating water enables increasing the recovery of diamonds into the concentrate of foam separation from 19.5% to 66.7%. Under industrial conditions, it was confirmed that diamond recovery in the process of foam separation increased by 8.8%.

4. 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 diamond and the crystallizing substance is used as a criterion for the activity of the surface. 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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