Research and Classification of Mineral Formations on the Surface of Natural Diamonds

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Abstract. A set of analytical studies has established differences in the composition of mineral formations on the surface of natural diamonds of intensely altered kimberlites under the conditions of occurrence and processing of diamond-bearing ores. A classification of mineral formations on diamonds has been proposed depending on their origin, properties and mode of their attachment on the surface of crystals.

1. Introduction
Reduction of flotation activity of diamonds is caused by hydrophilic mineral formations on the surface of crystals, which is the reason for the decrease in the efficiency of their recovery by physical and chemical methods [1-6].

During diamond-bearing ore, processing polyminerall films and a functional cover represented by the molecules of compounds (CO, CO₂, N, H₂O, etc.) appear on diamond surfaces; their nature is caused by the conditions of their formation and has a significant impact on the modification of physical and chemical properties of the diamond surface [7-9]. A high degree of change in the groundmass of refractory kimberlites related with the content of secondary minerals (up to 80%-90%) leads to a reduction in diamond recovery by grease and froth separations [10-11].

The systematization of mineral formations on the surface of diamond crystals, as well as their subsequent classification, are required to justify and select the technique of restoring the hydrophobic properties of diamonds before the processes of grease and froth separation of refractory kimberlite ores with a high degree of metamorphism.

2. Targets of Research
To achieve this goal with the participation of IPKON RAN and ALROSA specialists, the composition and surface properties of hydrophilic diamonds not recoverable by physicochemical methods have been studied in the NIGP and the Yakutniproalmaz Institute laboratories.
3. Research methods and techniques

The composition and structural features of mineral formations on the surface of diamond crystals has been identified by the semi-quantitative X-ray diffraction method using the following equipment: X-ray diffractometers DRON-2.0 (Burevestnik), DMAX-2400 (Rigaku), ARL X’TRA-155 (Thermo scientific), DTG-60AH thermal analyzer (Shimadzu). The chemical composition of mineral components is determined by the micro-X-ray spectral analysis using a JXA-8800R microanalyzer. Surface formations on diamonds were studied using the IR spectroscopy method by comparing the reference infrared spectra of minerals transmission with impurity bands on diamonds.

4. Discussion of findings

The task of the present studies was to establish the particular features of the morphology and chemistry of mineral formations on the surface of rough diamonds of intensely altered kimberlites, followed by their systematization and classification.

With regard to the data previously obtained [2.5-12], it has been established that the surface of hydrophobic diamond crystals is fairly homogeneous, characterized by separate mineral formations of serpentine-type magnesium silicates and covered with a layer of gases such as CO2 and HCO3 radicals.

The hydrophilic surface of diamond crystals is characterized by relief mineral formations, carbonate films and individual mineral formations, represented mainly by magnesium silicates of the talc group. The area of distribution of mineral formations on the surface of hydrophobic diamonds does not exceed 25%, whereas on hydrophilic crystals this value reaches 70%.

The thickness of mineral formations on the surface of hydrophilic diamonds is 2-3 more than in hydrophobic crystals.

The analysis of images of natural diamond crystals of metasomatically altered kimberlites made it possible to establish that the mineral formations diagnosed on their surface are characterized by mixed relief forms and are concentrated near the diamond surface discontinuities (Fig. 1).

The discovered mineral formations are represented by three groups: macroscopic formation up to tens of microns thick; micro-formation with a thickness of 10 to 100 nm; films up to 150 nm thick.

Figure 1. The external view of mineral formations in various areas of the surface of diamond crystals: a — on a flat diamond surface; b - in depressions; c - in cracks and chips; d - on the steps of crystal growth and in the depressions.
The findings of the conducted research in the studied samples of mineral formations have recorded the distribution of calcite (CaCO3) also in a sharply subordinate amount of gypsum CaSO4*nH2O.

Calcium minerals are found on the surface of the studied diamond crystals both in the form of separate compact formations and in the form of uniformly distributed films and microglobules, where calcium minerals are scattered together with silicates (Figure 2).

![Figure 2. Images of combinations of mineral formations (a) and calcium distribution (b) on the diamond surface (calcium is highlighted in white).](image)

Of special interest are the results of semiquantitative analysis of very thin (up to 1 μm) film formations. The highest surface concentration of calcium is found in the diagnosed impurities (see Table 1). The ratio of the amount of magnesium, silicon and aluminum to calcium does not exceed 20%. Such results allow us to conclude that thin films on the diamond surface have mainly a calcium-carbonate composition.

**Table 1.** The findings of the analysis of surface film formations on the diamonds studied.

| Element | C | O | Na | Mg | Al | Si | S  | Cl | Ca  | Fe |
|---------|---|---|----|----|----|----|----|----|-----|----|
| Weight percent | 62.0 | 28.9 | 0.6 | 0.8 | 0.1 | 0.7 | 0.2 | 0.3 | 6.2 | 0.1 |

The identified features of the structure of surface formations of the studied diamonds of altered kimberlites are illustrated by X-ray spectra shown in Fig. 3.
Figure 3. Spectrograms of mineral formations on the surface of diamonds not extracted by the process of froth separation of altered kimberlites.

The analysis of the obtained results made it possible to re-systematize the aggregate of mineral formations on the surface of diamond crystals.

The first most common way of attachment is the adhesion of a rock to the hydrophilized diamond surface (Figure 3, a). The minerals in this case are represented by adhesively active clay minerals such as serpentine capable to form a large area contact with diamond crystals. Such "adhesion" is feasible only with the initial hydrophilization of the diamond surface.

The second, less common way of attachment is the adhesion of a rock to the hydrophobized diamond surface (Figure 3, a). These mineral formations will attach to the natural or hydrophobic surface of a diamond. The energy of attachment of such formations is much less than in the mutual attachment of hydrophilic formations.

The third type of mineral formations on diamonds are kimberlite rock elements, which have formed with the diamond crystal a mechanically strong complex under the impact of hypergenic factors (Figure 3, c).

The fourth type of surface formations is a thin film formed by the crystallization of carbonate, hydroxy carbonate, sulfate and other salts from supersaturated aqueous media typical for slurries of basic preparatory and enrichment processes (Figure 3, d). Despite a small thickness of the film, such mineral formations dramatically increase the wettability of the surface and reduce the floatability and adherence to the grease surface.

Thus, on the basis of the data obtained, the classification of mineral compounds on the surface of natural diamonds of refractory ores highly altered by metasomatic ore processes has been presented for the first time, and four types of formations are identified (see Table 2).
Table 2. Composition and properties of mineral formations of various origins.

| Type of a surface mineral formation | Thickness, mm | Linear size, mm | Carbonates | Ferric hydroxide | Layered aluminosilicates | Clays |
|-------------------------------------|---------------|-----------------|------------|-----------------|-------------------------|-------|
| 1. A conglomerate (adhesion) of rock minerals on the hydrophilized diamond surface | 20-280 | 0.01-1.5 | 4.16 | 0.5-1.9 | 21-42 | 46-75 |
|                                      | 145           | 0.44           | 8.8       | 0.91           | 29.6         | 54.4 |
| 2. A conglomerate (adhesion) of rock minerals on the hydrophobizated diamond surface | 20-280 | 0.01-1.5 | 3.14 | 0.1-1.5 | 42-82 | 16-28 |
|                                      | 145           | 0.44           | 7.3       | 0.73           | 59.6         | 21.5 |
| 3. A stable cluster of diamond and rock minerals | 20-350 | 0.03-3.0 | 23.74 | 1.5-6.5 | 12-22 | 6-18 |
|                                      | 198           | 0.88           | 47.1      | 3.72           | 17.1         | 10.8 |
| 4. Technogenic film formation on the surface of a diamond | 5-30 | 0.03-5.0 | 53.91 | 1.5-4.5 | 3.12 | 3.12 |
|                                      | 15.8          | 1.74           | 77.7      | 2.66           | 6.7          | 6.8  |

Based on the type of mineral impurities diagnosed on the surface of diamond crystals, it is possible to presuppose the most rational way of their removal or prevention of their formations.

5. Conclusion
A new classification of surface formations on diamonds having various origins and properties has been developed. Four types of surface formations have been identified:
- the remnants of the rock preserved on diamond crystals and having a common genesis with them;
- conglomerates (adhesions) and single grains of slurry classes of hydrophilic or hydrophobic minerals adhesively attached to the hydrophilic or hydrophobic surface of diamonds;
- technogenic products of crystallization of minerals (carbonates and hydroxydcarbonates) from supersaturated water systems of kimberlite ore treatment processes.

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