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PRODUCTION, STRUCTURE, PROPERTIES

Rare Diamond Microcrystals

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Abstract—Rare forms of diamond growth and dissolution are described using the example of diamond microcrystals from the Samotkan' Neogene titanium–zirconium placer on the Ukrainian Shield. These include diamond crystals with complex faceting, microblock crystals, skeletal crystals, vertex-shaped crystals, crystals with natural dissolution, and ideal twins. It is argued that microscopic diamond crystals differ from the macroscopic counterparts in the richness of crystallization forms.

Keywords: microdiamond, crystal morphology, simple crystal forms, microtopography, growth and dissolution forms

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INTRODUCTION

The variety of crystal forms is often found in the microrealm of many minerals. The cause of this phenomenon is not clear. This is probably due to a number of reasons, primarily the high symmetry of the medium that forms the mineral microcrystals. This phenomenon is also characteristic of diamond microcrystals from various sources, as was noted by the author of this study in, for example, [1, 2]. Among these diamond microcrystals, there are rare forms that are almost uncharacteristic of diamond macrocrystals, the author came across such rare forms among diamond microcrystals from the Samotkan' Neogene titanium–zirconium placer on the Ukrainian Shield. The placer can be attributed to the diamond deposit, since the content of microdiamonds here can reach almost 0.1 carats per 1 m^3 of sand ore concentrate.

The Samotkan' placer is located on the Middle Dnipro domain of the Ukrainian Shield. This lithosphere domain about 200 km in thickness is a typical granite-green stone terrane of the Archean era. In the domain, remains of the former oceanic crust have been preserved among plagiogranites and granodiorites. This is expressed by the presence of altered ultrabasic rocks and basalts converted into amphibolites and dark greenish shales.

The Samotkan' placer has a coastal and marine origin. Neogene placer sands are enriched with heavy minerals, including microdiamonds of various nature. In addition to crystals of endogenous (mantle) diamond, placer sands contain impact apographitic diamond (up to 3% of the total number of diamonds). Maternal sources for endogenous and impact diamonds are unknown. The nature of endogenous diamond has not been definitively elucidated; there are many hypotheses, the main one that it is of the mantle and metamorphic nature. Typical concomitant minerals from kimberlites and lamproites were not found in the placer. Endogenous microdiamonds of the Samotkan' placer have a number of specific features.

EXPERIMENTAL

Among several thousand microdiamonds of the Samotkan' placer, single crystals of microdiamond with rare morphology were found. Their morphological studies were conducted in the Semenenko Institute of Geochemistry, Mineralogy, and Ore Formation, National Academy of Siences of Ukraine on a JSM-6700F scanning electron microscope equipped with a JED-2300 energy dispersive microanalysis system (JEOL, Japan). Scanning electron microphotographs of diamonds were obtained with an accelerating voltage of 15 kV, a probe current of 6×10^{-10} A, and a probe diameter of 1–2 μm. Goniometric studies of complex faceted microdiamond crystals on a GD-1 two-circle goniometer were also performed in the institute mentioned above.

FEATURES OF MICRODIAMONDS

Most diamond crystals from the Samotkan' placer do not exceed 0.125–0.220 mm in diameter and sometimes reach 0.3–0.4 mm. Microdiamonds from this placer are characterized by great morphological diversity. Many of them have a cubic form (cubes and cuboids), as well as tetrahexahedra, octahedra, so-called "transitional" or "combinational" forms of the {111}+{110}, {111}+{100}, and {100}+{110}+{111} types, contact and penetration twins, complex fivefold octahedron twins, and various irregularly grown crystal aggregates are found among them, while rhombododecahedral crystals are relatively rare. There are also diamond crystals with coat and carbonado.

A number of diamonds are colored in different colors, such as purple, yellow, green, and brown. The nature of color of some purple crystals is unusual, since it is not a consequence of plastic deformation, but the absorption band with a maximum at 17850 cm^{-1} is detected in their spectra [3]. The yellow and green color of diamond crystals are determined by the known impurity of nitrogen as N, N_3V, and H3 centers, and GR-1 centers, respectively.

The orange photoluminescence of most microdiamonds of the Samotkan' placer, which is rare among diamonds from known deposits, is also unusual. Such luminescence predominates among luminescent cubic crystals. A characteristic feature of the spectra of these crystals is the line at 575 nm, which determines the orange luminescence. In addition, a number of lines (409 and 389 nm), which were previously unknown for natural diamond crystals, were also recorded in the photoluminescence spectra of purple microdiamonds [4].

Most microdiamonds are of nitrogen type, but nitrogen impurities were not detected in nearly a third of the studied crystals [5]. We can assume that a significant part of diamond crystals did not experience long residence in the mantle on the basis of the following contents of nitrogen types: 22% I*aA*, 27% I*ab*, and 13% I*b*, which reflects the low aggregation state of nitrogen impurities in the crystals. There are crystals with a high (up to 2000 ppm) nitrogen content, as well as crystals with a mature evolution of nitrogen centers. This indicates the long residence of the last type of diamonds in the depths of the mantle.

Both the inclusions of minerals of peridotite (lherzolite) and eclogite deep associations have been detected in microdiamond crystals [6]. They also contain various fluid inclusions that are characteristic of mantle diamonds and allow one to reproduce their carbonate and carbonate–silicate crystallization medium rich in alkalis and volatile components.

The $\delta^{13}C$ value for microdiamonds varies in a wide range from –32.5 to –2.5 ‰ [7]. Combining data on a wide range of isotopic compositions of carbon with such an important indicator as the dominant cubic form of microdiamonds, the eclogite environment of diamond crystallization can be preferred. However, the presence of olivine and enstatite inclusions in microdiamonds evidences their growth in the peridotite environment as well. Altogether, the above reasoning suggests the mantle origin of microdiamonds from the Samotkan' placer.

RARE DIAMOND CRYSTALS: DISCUSSION

Among the diamond polyhedra from the Samotkan' placer, there are crystals with flat and smooth faces of various simple forms (Fig. 1) that are characteristic of the hexoctahedral symmetry class (cubic system) of diamond crystals (octahedron, cube, rhombic dodecahedron, trisoctahedron, trapezohedron, tetrahexahedron, and hexoctahedron). As a rule, such forms are not holomorphic and develop mainly on crystals of the octahedral habitus. Flat and smooth faces of the cube occur more often, which is confirmed by goniometric measurements. This form is often holohedral (see Fig. 1a), but its habit development is not detected. The flat faces of a cube can independently complicate the faceting of diamond octahedra, less often in combination with other faces of various simple forms (see Fig. 1b). Hexoctahedron is the second frequently occurring simple form of microdiamond crystals after the cube faces. There are crystals on which the flat and smooth faces of the hexoctahedron are well developed. In addition to the cube, the following forms were found goniometrically among the simple forms: rhombic dodecahedron; hexoctahedra {251}, {592}, {594}, and {694}; trapezohedra {211} and {511}; trisoctahedra {991} and {881}; and tetrahexahedra {120} and {140}. In general, all these forms have a secondary development with the exception of the octahedron.

The presence of morphologically unique crystals is a specific feature characteristic of microdiamonds from the Samotkan' placer. The diamond crystals shown in Figs. 2–6 are rare among natural diamonds, and some of them are described for the first time. Cubes with the surfaces comprised of rectangular plates (see Fig. 2a) or microoctahedra (see Fig. 2b) are atypical. This indicates the microblock growth of such cubes. Usually natural diamond cubes are the result of degeneracy of the faces of the octahedron with tan-

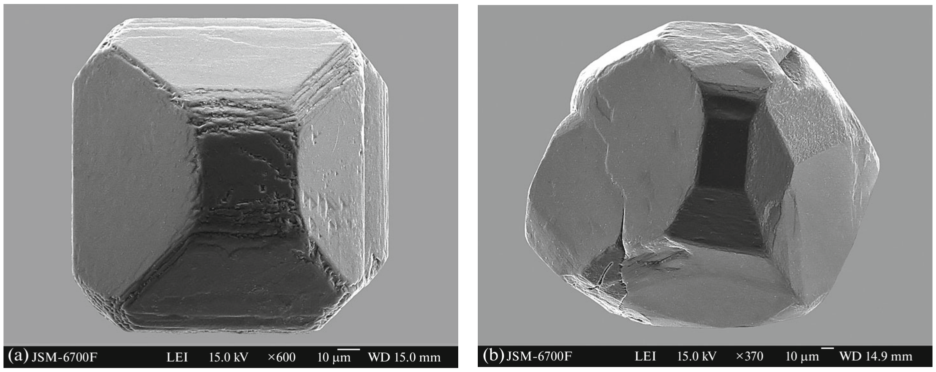

Fig. 1. SEM-images of complex faceted microdiamond crystals: (a) octahedron with flat and smooth faces of the cube and (b) octahedron with flat and smooth faces of the cube, rhombic dodecahedron, trapezohedron, and hexoctahedron.

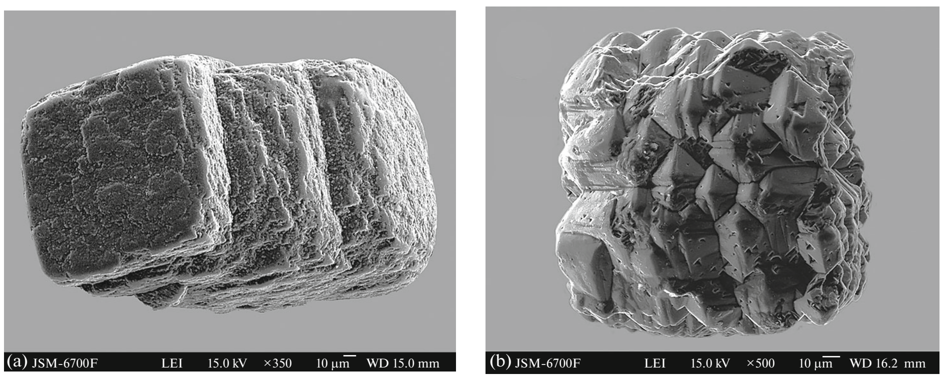

Fig. 2. SEM images of the microblock growth of microdiamond crystals: (a) formation of cube faces by layering of numerous parallel rectangular particles and (b) formation of cube faces by numerous miniature octahedra.

gential growth of the crystal or the result of the fibrous growth of the crystal. Therefore, such crystals exhibit different morphology of the {100} faces, which mainly consists of numerous bumps that vary in size and form or covered with numerous quadrangular pits.

Various skeletal crystals that show clear growth in the (111) planes are even rarer microdiamonds. They are negatively curved and only the vertices of the crystals can be blunted by small flat faces of the octahedron (see Fig. 3a). Upon intensive dissolution of such crystals their bodies seem to consist of eight rounded pyramids (see Fig. 3b). Vertex forms on diamond crystals are also extremely rare and barely described. These are forms that indicate a significant change in the growth conditions of crystals or their stepwise growth. Such crystals are shown in Fig. 4. If parallel plates on the octahedron faces have grown on the cuboid (see Fig. 4a), thereby complicating them, then rounded faces of the trapezohedron have grown on the vertices of the tetrahexahedron (see Fig. 4b).

Octahedral and cubo-octahedral crystals with obvious signs of natural dissolution are also rare among natural diamond macrocrystals. Typically, these features are triangular pits parallel to the edges on the surface of the octahedron faces (they can be pyramidal or flat-bottomed) and quadrangular pits on the faces of the cube, which are oriented at an angle of 45° to the edges of the cube habit. Such crystals were found among diamond microcrystals mined from the Samotkan' placer (see Figs. 5 and 6). Another form associated with dissolution of the faces of an octahedron is serrated notches of its edges, which have a clear orientation perpendicular to them (see Fig. 5b). The notches are wedge-shaped and developed along the (111) cleavage. The position of their walls corresponds to trapezohedra. These toothed notches can be interpreted as a new type of dissolution sculpture on diamond crystals. Straight parallel triangular pits on the faces of the octahedron and quadrangular pits on the faces of the cube are experimentally reproduced on diamond crystals.

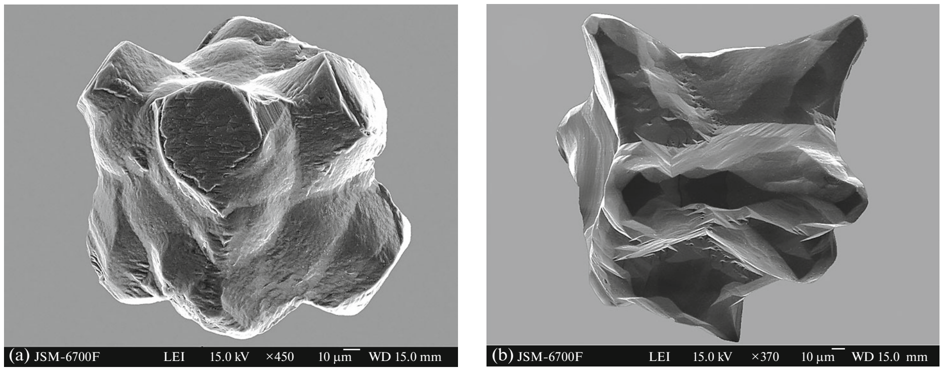

Fig. 3. SEM images of skeletal curved crystals of microdiamond with (a) octahedron faces and without (b) octahedron faces on the vertices.

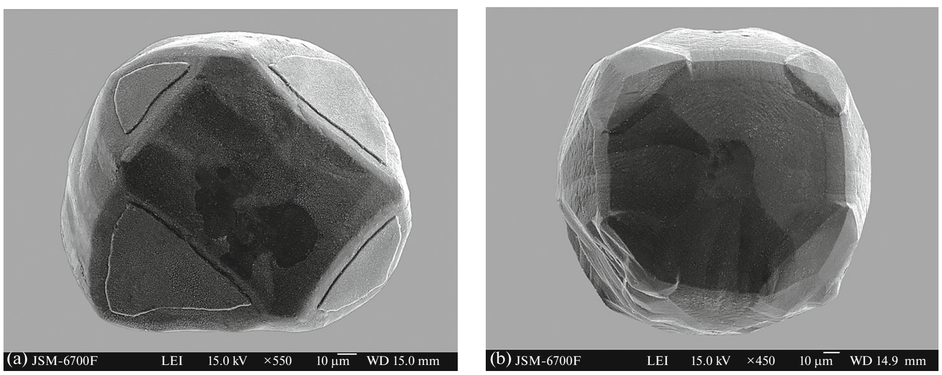

Fig. 4. SEM images of intricately faceted curved crystals of microdiamond: (a) a cuboid with outgrowths of flat octahedral plates and (b) a tetrahexahedron with outgrowths of faces of the trapezohedron.

Perfectly shaped twins are not so common among natural macroscopic diamond crystals. They are more common for microdiamonds mined from the Samotkan' placer. Figure 7 shows the following intergrowths: the contact fivefold twin of octahedra and the peneration twin of cubes.

Among the above forms, only some representatives of microdiamond crystallization forms are described for macroscopic diamond crystals in a number of well-known publications [8–13]. We have already noted earlier the development of flat and smooth faces of various simple forms on microdiamond crystals (especially the faces of a cube) for this mineral from kimberlites, metamorphic rocks, and placers.

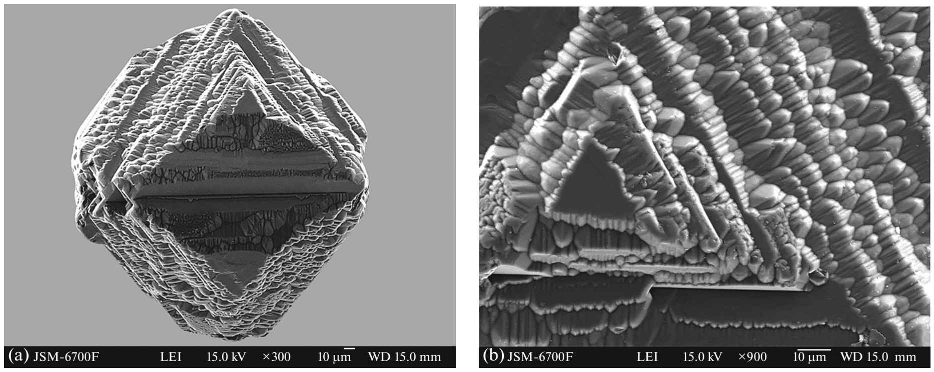

Fig. 5. SEM images of the microdiamond crystal with signs of dissolution: (a) intensely dissolved octahedron and (b) toothed protrusions on the face of the octahedron.

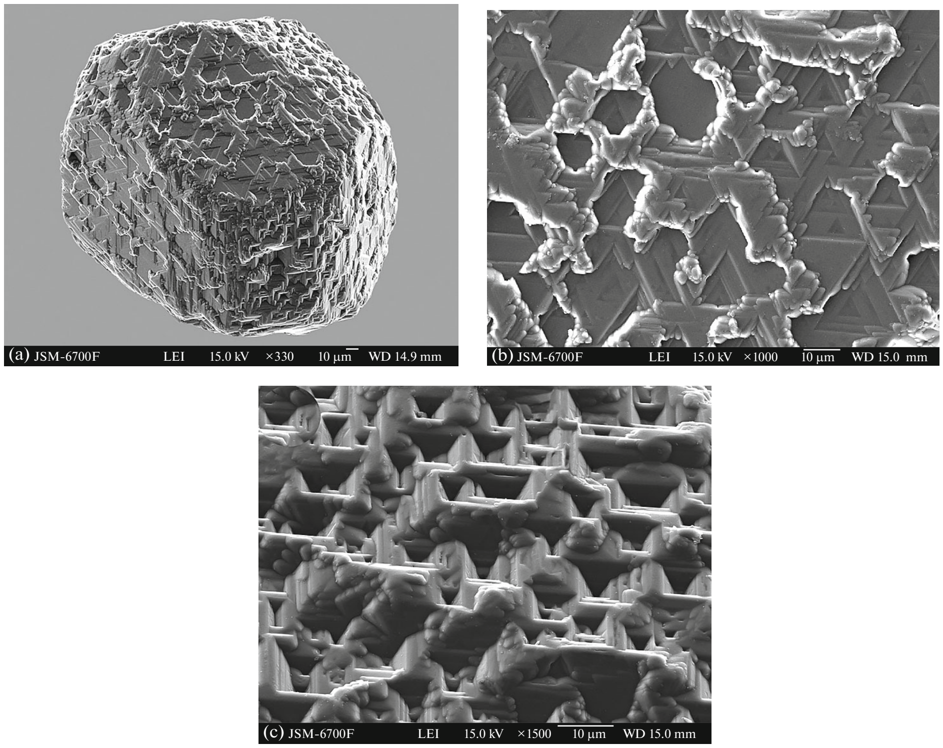

Fig. 6. SEM images of a microdiamond crystal with signs of dissolution: (a) intensely dissolved cube-octahedron, (b) straight parallel triangular pits on the surface of the octahedron face, and (c) rectangular pits on the surface of the cube face.

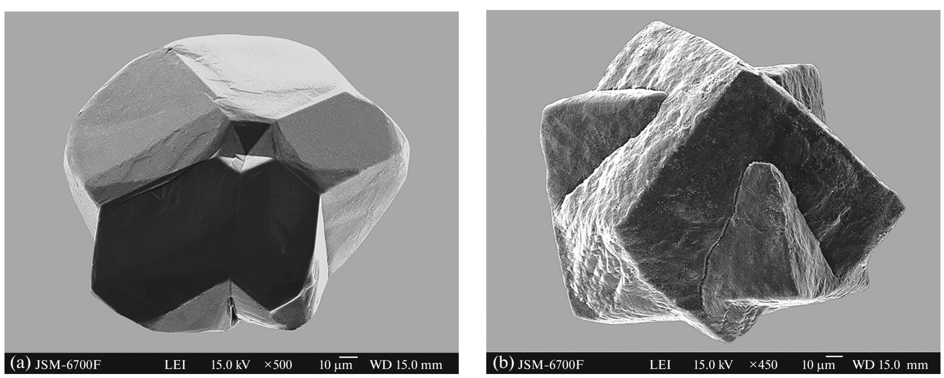

Fig. 7. SEM images of regular intergrowths of microdiamond crystals: (a) contact fivefold twin of octahedra and (b) penetration twin of cubes.

We have described a rare phenomenon, such as the microblock growth, for diamond micro- and nanocrystals developed on impact diamonds, the formation of which is associated with the fall of a meteorite [14].

The study of the morphology of natural microdiamond crystals shows an even more contrasting difference between the faceting of synthetic and natural diamond crystals. The morphology of synthetic diamond crystals is much poorer. However, it is the development of the flat faces of the cube that is characteristic of synthetic diamond crystals, on which they may have habitus significance. Such a variety of forms inherent in natural macroscopic and microscopic diamonds has not yet been obtained for synthetic HPHT and CVD diamonds, even in the cases when various crystallization systems were tried (composition of the medium, catalysts, volatile components, and pressure and temperature conditions of the growth). Obviously, synthetic diamond production mimics the simplest process of diamond growth. The determining reason for this is probably the short growth time of synthetic diamond crystals at a substantial crystallization rate and a much larger size of the building particles, from which the crystal is formed.

CONCLUSIONS

The realm of diamond microcrystals allows one to reveal less-known mechanisms of their growth and to show new growth and dissolution forms.

The form of diamond crystals strongly correlates with the size of the crystal. Unlike macroscopic crystals of diamond, microcrystals can exhibit a variety of simple crystalline forms and habitae. Macroscopic crystals of diamond mainly grow only in a structurally important growth form, such as the octahedron.

The rare microblock mechanism of diamond crystal growth is realized in a supersaturated medium. The dominance of cubic crystals among microdiamonds of the Samotkan' placer may be an additional indication of such a crystallization medium.

The growth of diamond crystals—even at the microlevel—is a multistage and stepwise process, as evidenced by the vertex forms on diamond microcrystals.

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