Effect of crystal defects on diamond morphology during dissolution in the mantle

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ABSTRACT

The influence of three-dimensional defects on the morphology of diamond dissolution in water-containing carbonate melts was studied at a pressure of 5.7 GPa and a temperature of 1300°C, using a BARS multi-anvil apparatus. Experiments on stage-by-stage dissolution were performed for four blocky synthetic diamond crystals. Initial crystals had polycentric structure of the faces, strong strains, block structure, numerous microtwins and microinclusions. It has been established that the main relief features of partly dissolved diamond crystals are shield-shaped laminae and negative trigons on remnants of \{111\} faces, deep etch channels, rectilinear steps on microtwins and hillocks on rounded surfaces. The produced dissolution forms have shagreen or block-type rounded surfaces. The main element of the relief are hillocks. Their shape is controlled by the orientation of the surface on which they are localized. For natural rounded diamonds it is found that the dissolution drop-like hillocks on the surfaces are also related to strong lattice strains occurring in the crystals. The established relation between the dissolution
hillocks and diamond deformation can be used for the reconstruction of the post-growth history of natural diamonds as well as for the preliminary evaluation of their quality.

Keywords: Diamond dissolution, crystal morphology, defect of crystals, dissolution hillocks.

INTRODUCTION

Natural rounded diamonds demonstrate a wide variety of surface structures. Some crystals have macroscopically smooth, glossy surfaces. Others show on their surfaces specific features, including serrate and shield-shaped laminae, drop-like hillocks, striations, ruts and many other patterns (Kukharenko 1955; Orlov 1977; Robinson 1978). There is no doubt that the rounded form of natural diamond crystals is a result of dissolution in water-containing kimberlitic melt (Moore and Lang 1974; Orlov 1977; Robinson 1978; Gurney et al. 2004; Kozai and Arima 2005; Khokhryakov and Palyanov 1990, 2007; Fedortchouk et al. 2007). Therefore the details of the micro-relief of natural diamond crystals reflect first of all the conditions of dissolution in natural processes. At the same time, diamond characteristically contains various structural imperfections ranging from point to three-dimensional defects. The dissolution at the defects outcrops proceeds in a different way than for perfect surfaces (Heimann 1975). As a result, the micro-relief elements may form, which to a greater extent reflect the features of the real structure of diamond crystals rather than the dissolution conditions. This question has not been adequately explored so far. Only for some micro-relief elements of natural rounded diamonds, their relation to the real structure has been determined. It is established that trigons on {111} faces are located at the dislocation outcrops (Lang 1964). It is shown that the intersecting striation is related to the bands of plastic deformations (Robinson 1978) and rhombic patterns of the etching channels to the surface cracks (Orlov 1977). The nature of many other widely abundant micro-relief elements and surface sculptures has not been clarified yet. The scarcity of experimental data on this
subject is partly due to the fact that in most cases only high-quality diamond crystals were used in the dissolution experiments (Kozai and Arima 2005; Khokhryakov and Palyanov 2007; Fedortchouk et al. 2007). Furthermore, most of previous experimental works on diamond dissolution were focused mainly on the effect of conditions and composition of the medium on dissolution morphology.

In the present study we have explored the dissolution of synthetic diamonds of block structure. The specific features of dissolution surfaces of mosaic crystals are established. It is shown that the origin of the drop-like hillocks on diamond tetrahexahedra is related to the occurrence of strong local strains in the diamond lattice.

**Experimental**

In the experiments we studied stage-by-stage dissolution of four blocky crystals of synthetic diamond weighting from 1.2 to 5.92 mg (Fig. 1). The diamond crystals were grown by the temperature gradient method in the Ni$_3$Fe$_3$-C system with nitrogen content from 0.25 to 0.3 at.% (Palyanov et al. 2010). A detailed investigation of these crystals was performed in (Palyanov et al. 2010). It was shown that the crystals had a polycentric structure of the faces, strong strains, block structure, numerous microtwins and microinclusions. Such characteristics are typical for many natural diamond crystals. Crystal No. 1 (5.92 mg) has small \{100\} faces (Fig. 1a). Approximately one third of the crystal has flat faces, and the rest surface is blocky with numerous microtwins. Crystal No. 2 (2.47 mg) has only \{111\} faces (Fig. 1d). The surface exhibits large blocks and twinning intergrowths. Crystals No. 3 (1.51 mg) and No. 4 (1.20 mg) are of octahedral habit. These crystals have a rough relief with numerous trigonal blocks and depressions (Fig. 1g,j). All crystals contained micro inclusions of metal catalyst. The amount of micro inclusions in the crystals increases with the degree of their blockiness from crystal No. 1 to crystal No. 4. From the infrared absorption measurements it was found that synthetic diamond
crystals contained approximately 120-130 ppm of nitrogen impurity predominantly in the form of single substitutional atoms, C-centers.

Experiments on diamond dissolution were carried out using a “split-sphere” type multi-anvil apparatus at 5.7 GPa and 1300°C in water-containing carbonate melts. Details on the high-pressure cell design, pressure and temperature measurements and calibration were presented in our previous works (Khokhryakov and Palyanov 2007, 2010). Starting materials for each experiment were 99.9% pure CaCO₃ (700 mg) with addition of H₂O (78 mg). Thus the water content in all experiments was 10wt.%. Starting materials and four diamond crystals were placed into sealed Pt capsules (6 mm in diameter, 5 mm long, and 0.2 mm thick walls). All four crystals were used in two experiments with duration of 30 and 45 hours.

Several rounded natural diamonds from Udachnaya and Yubileinaya kimberlite pipes were studied to reveal possible effects of lattice imperfections on the surface morphology. The selected crystals were 1.0-1.5 mm in size and exhibited nonuniform surface structure. Cross section plates 0.5-0.7 mm thick were prepared from three crystals by mechanical polishing. The plates were oriented so that areas with different types of surface relief were exposed.

The crystals before and after each experiment were weighed (±0.01 mg) and analyzed with optical and scanning electron microscopes. The micromorphology of diamond crystals was studied using a LEO420 scanning electron microscope. Internal structure of diamond plates in polarized light was studied using a Ziess AXIO Imager.Z2m” microscope. Infrared absorption spectra were measured using a Bruker Vertex 70 Fourier Transform Infrared (FTIR) spectrometer equipped with a Hyperion 2000 microscope.

**RESULTS AND DISCUSSION**

The overall view of the crystals and their weights before and after experiments are presented in Fig.1. The crystals dissolved to different degrees. The mass loss (LM) of crystal No.
1, which was the largest one, was only 19%, whereas smaller and more defective crystals No. 3 and No. 4 lost 58-59% of their initial mass.

The main relief features of partly dissolved diamond crystals are shield-shaped laminae and negative trigons on the remnant \{111\} faces; deep etch channels, rectilinear steps on microtwins and hillocks on rounded surfaces. The number and size of the negative trigons differ for the studied diamond crystals. A great number of trigons are present on the crystals which initially had numerous trigonal depressions (crystals No. 3 and 4). Trigons on these crystals did not disappear even when the weight loss was 58-59%. This apparently is connected with a large number of microinclusions in crystals No. 3 and 4.

Ditrigonal or shield-shaped dissolution laminae were present on the crystals only after the first experiment (LM from 6.4 to 34%). These laminae had rough, wavy edges (Fig. 2a) in contrast to the dissolution laminae on high-quality diamond crystals. As it was shown previously (Khokhryakov and Palyanov 2007, 2010) the ditrigonal laminae formed on the \{111\} faces of high-quality crystals had smooth rectilinear edges (Fig. 2b). The presence of microtwins and large trigonal depressions and cracks in the mosaic crystals resulted in polycentric lamination.

Typical elements of blocky crystals after dissolutions are the etching channels. The number and size of the channels increase with decreasing quality of the crystals from No. 1 to No. 4 (Fig. 1). The etch channels form, most likely, along the cracks and boundaries between the crystal blocks. Numerous microtwins appear after dissolution as single rectilinear steps or blocks of polysynthetic twinning (Fig. 3a).

The produced dissolution forms have shagreen or block-type rounded surfaces. The main elements of the relief are hillocks. Their shape is controlled by the orientation of the surface on which they are localized (Fig. 3). On the surfaces close to the \{100\} faces they have isometric irregular shape (Fig. 3b). Surfaces close in orientation to \{111\} are covered with flat hillocks forming a regular structure similar to the sculpture of roof tiles (Fig. 3c). Hillocks formed on the surfaces close to the \{110\} faces have an elongated drop-like shape (Fig. 3d).
It is known that hillocks are one of the widespread relief elements of tetrahedroids of natural diamond. Depending on the size, shape and degree of elongation of hillocks, their accumulations form various types of microrelief of rounded natural diamonds. These include block-type, drop-like, serrate and shagreen features (Orlov 1977). The origin of hillocks is still debatable. In earlier works considering the origin of rounded diamonds within the "growth" hypothesis, these sculptures were treated as vicinal growth hillocks and their growth occurred by the (110) layers (Evdokimova and Shemanin 1962, Shemanina and Shemanin 1964). Orlov (Orlov 1977) suggested that hillocks formed as a result of partial dissolution of polyhedra initially present on the surface of the diamond. In other studies it was supposed that the formation of hillocks took place at high intensity and duration of the dissolution of diamonds (McCandless et al. 1999) or when diamond resorption occurs in the CO₂ fluid (Fedortchouk et al. 2007).

The diamond crystals used in present study had strong stresses and possibly this was the reason for the formation of dissolution hillocks as the main element of the dissolution microrelief. For natural diamonds there is a number of observations indicating that hillocks are more typical for crystals with high level of internal strains. Orlov (1977) noted that hillocks are often located along the intersecting striation associated with the bands of plastic deformation in diamond. They are also very characteristic of natural diamond crystals of type II, which often exhibit anomalous birefringence of "tatami" type (Orlov 1977). Kaminsky et al. (2000) noted that dissolution of natural diamond crystals with plastic deformation produces sculptures consisting of hillocks appearing as shagreen, hackly, drop-like, grooved and block-type features. Recently, Gainutdinov et al. (2013) also suggested possible association of the dissolution hillocks in diamond with post-growth deformation events. In addition it has been demonstrated experimentally (Heiman 1975, Sangwal 1990) that dissolution hillocks on rounded surfaces of crystals form not only as a result of blocking of individual sections by impurities (for example,
MgO and KCl crystals), but also due to the presence of strong gradients of stresses in crystals (for example, Ag crystals).

To the best of our knowledge, there are no available literature data correlating the location of drop-like hillocks on the rounded surfaces of natural diamond crystals with the internal structure of the crystals. In order to clarify whether such a correlation exists we examined several natural diamond crystals with rounded surfaces exhibiting drop-like hillocks. The most illustrative of these crystals is shown in Fig. 4. For this crystal the boundary between the areas with different surface relief is the most sharp. Most of the crystal surface is smooth and glossy (area B in Fig. 4) and small fragments of the surface are composed of accumulations of small drop-like hillocks (area A in Fig. 4). The (110) cross section plates were cut from the crystals through the surface areas with drop-like hillocks, as shown in Fig. 4a. Using polarized light microscopy it was established that in the volume of the crystals there are distinct strongly strained regions whose borders coincide with the borders of distribution of hillocks (Fig. 4c,d). The birefringence patterns within these strained regions has a specific “tatami” form, which is attributed to plastic deformation (Lang 1967; Orlov 1977). To examine if other defects such as nitrogen impurity may be responsible for the observed surface morphology we measured infrared absorption spectra from several local areas on the sample. Figure 5 shows IR spectra recorded from the selected locations as indicated in the insert. It follows that the periphery area which exhibit high strains and which is bound by surfaces with hillocks contain relatively low nitrogen concentrations of approximately 100-120 ppm (spectrum 1 in Fig. 5). In this case, 90-95 ppm of nitrogen is in the form nitrogen pairs, A-centers and 15-20 ppm in the form of aggregates of four nitrogen atoms, B-centers. Moving from the periphery to the center the concentration of nitrogen significantly increases to approximately 580-600 ppm (spectrum 3 in Fig. 5). From this we can infer that nitrogen defects itself can not be responsible for the observed dissolution hillocks. On the other hand our results are in agreement with previous observations that diamond crystals or
local areas within the crystals with low nitrogen concentrations deform plastically more easily than crystals or areas with high nitrogen concentrations (e.g. Nailer et al., 2007).

The established correlation between the dissolution hillocks and defects due to lattice strains in diamond is preliminary and needs further verification over a greater amount of crystals with detailed investigations of surface micro-relief and internal structure with quantitative measurements of lattice strains. Nevertheless, the results obtained in this study allow us to suggest that the formation of dissolution hillocks occurs on strained natural diamonds.

The shape of hillocks is worth special consideration. In spite of the different external forms of hillocks, they have the same crystallography. Goniometric studies of hillocks on natural diamonds were performed in the middle of the last century (Fersman 1955; Kukharenko 1955). These data allow an accurate description of the dissolution hillocks. Fersman (1955) found that rounded surfaces with drop-like hillocks always gave reflection on the goniometer in the form of arcuate bands. On the stereographic projection the bands of reflections from the rounded surface of hillocks have the shape of an ellipse, designated by Fersman as band CE (Fig. 6). Such a shape of light reflexes corresponds to a conical surface with an elliptic cross section. It is known that conical surfaces are very characteristic forms of dissolution of crystals of various minerals and diamond is not an exception (Shafranovsky 1961; Glazov 1981). Also goniometric study of hillocks with flat faces was conducted by A.A. Kukharenko (Kukharenko 1955). He measured coordinates of faces which bound relatively large (up to 60 μm) conical hillock. The most prominent light reflexes from the surfaces of these hillocks corresponded to hexaoctahedron and tetrahexahedron series of faces. As shown in Fig. 6, the reflections from the flat areas of hillocks are located on bands CE. Thus, rounded and faceted dissolution hillocks have similar conical shape. The center of ellipses (i.e. the spherical projection of the axes of cones) of hillocks is calculated as the middle point between the reflections i(304) and e(102) located on the symmetry line. The calculation showed that it corresponds to the normal to plane (508) ρ=32°00´. Thus, the axis of the cone-shaped surface hillocks or hillocks vertexes are oriented along the <850>
directions. As is known the vertexes of the dissolution forms correspond to directions of minimal
dissolution rate (eg Heiman 1975). Thus, the <850> direction is the direction of minimal
dissolution rate of rounded surfaces of natural diamond tetrahexahedroids.

**IMPLICATIONS**

The results obtained in this study allow us to conclude that the hillocks on the rounded
surfaces of diamond do not reflect any specific features of the dissolution conditions, but indicate
the occurrence of strong deformations in the crystals. The drop-like shape of hillocks
corresponds to the conical surface with an elliptical cross section and the axis along <850>
directions. Thus, our results demonstrate that the morphologic features of rounded natural
diamonds do not indicate exclusively the composition of the dissolution media and dissolution
conditions. Sculptures on the diamond surface can also be related to the specific features of the
real structure of the diamond crystals. The established relation between the dissolution hillocks
and diamond deformation can be used for the reconstruction of the post-growth history of natural
diamonds as well as for the preliminary evaluation of their quality.

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Figure captions

Figure 1. SEM images of initial and partly dissolved diamond crystals in water-bearing carbonate melts after 30 and 75 h. LM = mass loss of crystals. Scaling bar corresponds to 200 μm.

Figure 2. A dissolution layer on the {111} faces. (a) block diamond crystals of No. 3 after dissolution for 30 h.; (b) high-quality diamond crystals. Figure 2f from the work (Khokhryakov and Palyanov 2007).

Figure 3. SEM image of surface textures of partly dissolved diamond crystals. (a) Microtwin on the crystal No 2 after 30 h of dissolution. Dissolution hillocks on the surfaces close to (b) {100} (crystal No. 4, 30 h), (c) {111} (crystal No. 1, 75 h) and (d) {110} (crystal No 2, 75 h) faces.

Figure 4. A natural diamond crystal with drop-like hillocks. (a) General view of the crystal. Black lines show the directions of cutting the crystal. (b) A fragment of the crystal surface. (c) A plate cut from the crystal and (d) a fragment of the plate viewed with cross polarizers. A - crystal surface without drop-like hillocks. B - crystal surface with drop-like hillocks.

Figure 5. Infrared absorption spectra recorded from a plate prepared from the natural diamond crystal shown in Fig. 4. The insert shows a fragment of the plate. Squares mark the areas with spectra were taken and their sizes correspond to the sizes of the microscope aperture (approximately 80×80 μm). Labels on the spectra corresponds to labels shown on the image.

Figure 6. A fragment of stereographic projection of hillocks on the surfaces of natural diamond crystals. Continuous bands of reflexes (gray) are from (Fersman 1955). Single reflexes are given
according to (Kukharenko 1955): k - {702}, a - {301}, g - {502}, e - {201}, i - {403}, r - {961},

t - {951}, I - {742}, p - {532}, Ξ - {731}, z - {531}, x - {321}, y - {432}, w - {431}, Σ - {541},

Φ - {651}, S - {833}.
Figure 6.