Dissolution of diamond crystals in a heterogeneous (metal-sulfide-silicate) medium at 4 GPa and 1400 °C

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As a result of artificial dissolution of diamonds at 4 GPa and 1400 °C in a heterogeneous solvent (Fe-S melt with the addition of natural kimberlite in an amount of 5 wt%), it is established that, in the dissolution process the diamond crystals of octahedron form with flat faces and sharp edges are transformed into rounded octahedroids. The role of silicate additives is to local screen the surface of diamonds with the formation of etch hillocks, which gives crystals a visually complex external morphology. Thus morphologically complex natural diamonds with irregular shapes may form by dissolution by heterogeneous solvents in the mantle. Metal-sulfide-silicate melts consisting of immiscible components with different carbon solubility are the most likely candidates for such solvents.

Keywords: Diamond, Morphology, High pressure, Dissolution

INTRODUCTION

Rounded diamond crystals in kimberlites were commonly considered as resulting from particular growth patterns while their origin by dissolution of planar crystals had little support (Fersman and Goldschmidt, 1911; Orlov, 1977; Robinson, 1978; Sunagawa et al., 1984) based solely on theoretical calculations and etching experiments with model materials. In 1977 Kanda et al. (1977) reported etching of a flat-faced octahedron of natural diamond by ditrigonal (shield-shaped) etching layers using water as an etchant at temperatures of 1100, 1300, and 1500 °C and at a pressure of 5 GPa. Their experience gave an idea of how the rounded shapes of natural tetrahexahedroid diamonds could be reproduced in an experiment. In 1985 diamond etching was effectuated in a basaltic silicate melt in the presence of H₂O (Chepurov et al., 1985) and then in a kimberlite melt (Arima and Inoue, 1995; Arima, 1996; Sonin et al., 2004; Kozai and Arima, 2005; Khokhryakov and Pal'yanov, 2007; Fedortchouk

et al., 2007; Arima and Kozai, 2008; Khokhryakov and Pal'yanov, 2010), both at high pressure. Thus, origin of tetrahexahedroid diamonds as a result of etching of octahedron diamonds is possible in silicate melts with the presence of H₂O at high pressure. The result was confirmed directly by chromatography of run products (Sonin et al., 1997, 2001). Currently it has been widely accepted that the natural rounded diamonds form by dissolution in hydrous kimberlite magma during transport to shallow lithosphere and surface (Robinson et al., 1986; McCallum et al., 1994; Afanasiev et al., 2000; Kaminsky et al., 2000; Win et al., 2001; Gurney et al., 2004; Banas et al., 2007, etc.).

In addition to hydrous kimberlite melts, an important role of metallic liquid in natural diamond crystallization and dissolution processes has been suggested. Many theoretical and experimental evidences suggest the presence of metallic iron in Earth's mantle (Frost et al., 2004; Rohrbach et al., 2007; Frost and McCammon, 2008). This hypothesis is supported by discoveries of iron metal inclusions in natural diamonds (Garanin and Kudryavtseva, 1990; Bulanova et al. 1998; Stachel et al., 1998; Smith et al., 2016). Earlier work by Zhimulev et al.

(2016b) has shown that flat-faced octahedral diamond crystals are transformed into curve-faced octahedroids with morphological surface features similar to those of natural diamonds in S-bearing iron melt at 4 GPa and 1400 °C. This indicates that the dissolution commonly observed on natural diamond may have occurred in liquid metal under more reducing mantle conditions. These studies suggest that some diamonds grew and dissolved in metallic liquids in the Earth's mantle.

Uniform dissolution of diamond crystals by homogeneous fluids or melts produces geometrically regular shapes of crystals. However, dissolution in heterogeneous media is of special interest as the morphology of etched crystals holds clues to the properties of the etchants, because specific morphological sculptures remain on the crystal surface.

For instance, pseudo-hemimorphic diamond crystals, with flat and rounded faces, are assumed to result from partial destruction of diamond-bearing xenoliths: some crystal parts come into contact with kimberlite magma and become resorbed (Orlov, 1977; Afanasiev et al., 2000) while the others remain shielded from the aggressive melt behind solid xenolith phases. Thus the process leads to incomplete dissolution with formation of semi-rounded crystals.

Natural diamonds can also demonstrate different etching figures: trigons, etching hillocks, cavities, striations, disc sculptures, and others (Orlov, 1977; Robinson et al., 1986; Evdokimov et al., 2001). Examples of etching patterns formed in a heterogeneous medium are disc sculptures (Figs. 1a and 1b). They are disc or elliptical flat morphologies, circular or crescent forms, or lines of small pits on rounded surfaces, which have no relation with the symmetry of crystal faces and can superpose upon other surface features. As Pandya and Tolansky (1954) hypothesized, these forms may be imprints of gas bubbles, which were confirmed by etching experiments with diamonds (Sonin et al., 1998). In fact, they appear late during the evolution of kimberlite magma when the overall pressure decreases and water, with reduced solubility, appears as bubbles in a silicate melt, and some bubbles contact with the diamond surface. If carbon oxide (inert to diamond) released during the reaction, its bubbles accumulate on the crystal surfaces and shield them from further dissolution. On the other hand, natural diamonds often have round or elliptical cavities on rounded surfaces (Orlov, 1977; Afanasiev et al., 2000), which likewise may be due to dissolution in a heterogeneous medium.

The surface textures of natural diamonds may be more intricate, and their origin remains unclear. Such diamonds are often called as abnormal or irregular. 'Diamonds are classified as irregular if they do not exhibit an

Figure 1. Optical microphotograph of natural diamond with complex morphology. (a) and (b) Tetrahexahedroids of natural diamond with disk sculptures from placers of the Anabar River basin (Yakutia, Russia). (c) Octahedroid with numerous pits and hillocks on the edges (kimberlite pipe Dalnyaya, Yakutia, Russia). (d) Enlarged view of the same crystal with hillocks near the edge of the crystal.

identifiable crystal shape or if their existing shape is largely incomplete' (Tappert and Tappert, 2011). In this case, they are not crystal pieces but rather single crystals of a complex shape, such as a natural single crystal of a complex morphology from the Dalnyaya kimberlite (Yakutia, Russia) shown in Figure 1c. The diamond crystal has a rounded surface and can be characterized as an octahedroid. The morphology of the crystal is greatly complicated by the presence of numerous pyramidal pits and hillocks with stepped lateral faces. Striation on faces of these pits and hillocks corresponds to parallel striation near the edges of the crystal. Surfaces with striation correspond to the form of a trigon-trioctahedron. Probably the presence of pits, hillocks and parallel striation evidence that dissolution of the crystals has occurred under natural conditions. Additionally, Figure 1c shows a part of rounded surface of diamond crystal with hillocks, rising above the surface of trigon-trioctahedron. The surface of trigon-trioctahedron has a parallel striation, but the hillocks have rough surface and do not have any striation. Such complex forms can result from dissolution in a heterogeneous medium, i.e., in a melt consisting of two segregated liquids with different carbon solubilities, like metal (sulfide)–silicate melt systems (Brenan, 2008; Kadik et al., 2015).

Therefore, our goal was to study the morphology of diamond crystals dissolved in a metal–sulfide melt with additives of kimberlite, that is, in a melt containing two immiscible liquids.

EXPERIMENTAL

The experiments were conducted on a pressless split-sphere multi-anvil apparatus (BARS) at a pressure of 4 GPa, and a temperature of 1400 °C, with a run duration of 1 h. The design of the BARS apparatus and the methods of pressure and temperature determination were detailed in (Chepurov et al., 1998; Zhimulev et al., 2016a). The solid-phase high-pressure cell was made of ZrO₂, CaO, and MgO refractory oxides and had a cylindrical graphite heater with molybdenum current conductors in its center (Fig. 2).

The high pressure and temperature experiments were performed as follows: the assembled cell was placed into the apparatus after drying at 120 °C. PbSe and Bi, which have specific resistances dependent at pressure were used as checkpoints to calibrate pressure in the cell. The rate of pressure increase in the working cell was 0.1–0.2 GPa/min and the pressure determination error for experiments was ± 0.25 GPa. The sample was heated through the graphite heater at a rate of 100 °C/min. The temperature in the high-pressure cell was measured with a platinum-rhodium thermocouple (Pt/Rh 30/6) fixed close to the sample with a temperature measurement error of ± 25 °C. The required experimental temperature corresponded to that in the central zone in the heater. A correction for the pressure changes during further heating was made according to the known position of the graphite-diamond *P-T* coordinate equilibrium line (Kennedy and Kennedy, 1976). The sample was quenched for 2–3 seconds by switching off the electric power immediately after the run. Pressure decreased at a rate of 0.3–0.5 GPa/min.

Two experiments were conducted in MgO capsules with powdered (crushed and ground on a ball mill to < 5 μm) and carefully mixed starting materials consisting of 99.98 wt% pure sulfur and metallic iron. The Nyurba and Udachnaya-East kimberlites (Yakutia, Russia) were used as a natural solvent. The two kimberlites contained: (SiO₂) 32.08 and 29.40 wt%, (TiO₂) 0.47 and 1.26 wt%, (Al₂O₃) 3.71 and 2.34 wt%, (FeO + Fe₂O₃) 6.91 and 9.21 wt%, (MnO) 0.14 and 0.15 wt%, (MgO) 31.05 and 32.00 wt%, (CaO) 7.63 and 8.78 wt%, (Na₂O) 0.47 and 0.01 wt%, (K₂O) 1.74 and 0.97 wt%, (P₂O₅) 0.31 and 0.40 wt%, (LOI) 16.18 (CO₂–6.02 wt%) and 15.60 wt% (CO₂–7.60 wt%), and the total made 100.68 and 100.12 wt%, respectively. It is believed that kimberlite from the Udachnaya-East pipe is fresh with a high content of carbonates (and chlorides) compared to other kimberlite pipes in Yakutia (Kamenetsky et al., 2004). According to petrogenic components, there are no significant differences in the composition of kimberlites used.

A half of the etchant powder was placed into a spe-

Figure 2. Vertical cross-section of the high-pressure cell assembly used for experiments in apparatus BARS. 1, high-pressure cell; 2, molybdenum electrode (four electrodes in the top and four in the bottom tablets); 3, graphite heater; 4, cylinder made of pressed metal-sulfur powder; 5, diamond crystal; 6, thermocouple.

cially cut cylindrical anvil and pressed. Then, synthetic and natural crystals of diamond were placed on the cylinder top, in the center, and covered by the other half of the powder pressed in the same way. Thus we obtained a cylinder of pressed starting material with diamond crystals in the center (Fig. 2). The weight of the etchant was 840 mg (Fe, 81 wt%; S, 14 wt%; kimberlites, 5 wt%).

The diamonds used were free from inclusions. The synthetic crystals were octahedron with additional faces of cube and tetragon-trioctahedron (Fig. 3a) and octahedron (Fig. 3b) with flat faces and sharp edges. The natural diamond was a rounded tetrahexahedroid (Figs. 3c and 3d). The synthetic diamonds were grown by the temperature gradient method in a Fe–Ni–C system at high pressure and temperature, as in (Chepurov et al., 1998). The natural diamonds were from the Ebelyakh placer (Yakutia, Russia). The synthetic and natural diamonds had different initial weights in two runs with different solvent kimberlites: 8.2 mg (Fig. 3a) and 4.94 mg (Fig. 3c), respectively, in run 2–27 with the Nyurba sample; 5.11 mg (Fig. 3b) and 5.34 mg (Fig. 3d), respectively, in run 2–28, with the Udachnaya-East sample.

After the experiments the diamond crystals were treated in acids and then studied under optical (MBS-10) and scanning electron (MIRA3 TESCAN) microscopes in

Figure 3. Initial diamond crystals before experiments at high P - T parameters. (a) and (b) Synthetic crystals. (c) and (d) Natural crystals.

a secondary electron mode. The diamonds were weighed before and after the runs to a precision of ± 0.02 mg.

RESULTS

The natural crystals lost 45.5 and 49% of their initial weight in two runs (final weights 2.69 mg in 2-27 and 2.73 mg in 2-28); the weight loss in the synthetic crystal was 24% (run 2-27, 6.25 mg) and 31% (run 2-28, 3.52 mg). After the experiments, the diamond crystals were completely in the solvent samples and did not contact with the MgO capsules.

The diamond crystals in our experiments were dissolved as 'normal' (perpendicular to the faces) and tangentially (layer by layer). As a result of the normal dissolution, etch pits were formed on the faces of the crystals: trigons on the faces of the octahedron and rectangular on the faces of the cube (Fig. 4a). It should be noted that the orientation of triangular etch pits corresponds to negative trigons on natural diamonds. At the locations of the cubic faces large cavities with pyramidal hillocks of etching were formed (Figs. 4b and 4c). Perhaps this is due to the higher defect content in the cube growth sectors of this crystal. As a consequence of tangential dissolution was the appearance of a fine parallel striation near the edges of a crystal forming rounded trigonal-trioctahedral surfaces. Hillocks on corners of diamond likewise truncated by curved planes close to $\{111\}$ with parallel striation on the edges (Figs. 4b and 4c). The synthetic diamond did not change octahedral habit with some parts of flat octahedral faces remained. A specific feature of the morphology of a diamond crystal is the appearance as a result of dissolution of particular texture elements such as flat rising forms (hillocks) with curved irregular contours, often on hillock corners (Figs. 4a and 4b).

The synthetic diamond from experiment 2-28 experienced a higher dissolution (Fig. 4d). Flat octahedral faces disappeared. They were replaced by curved surfaces, close to the $\{111\}$ form. Therefore, the diamond crystal shown in Figure 4d is an octahedroid. The pyramidal etching hillocks remained at the vertices of the diamond (Figs. 4d and 4e), as well as fragments of triangular plates corresponded to octahedrons with stepped walls on the octahedral faces (Fig. 4e). As in the case of the synthetic crystal from experiment 2-27, there are specific flat

Figure 4. SEM images of synthetic diamond crystals after the experiments 2-27 (a) whole view (b) and (c) enlarged view of the same crystal and 2-28 (d) Whole view (e) and (f) enlarged view of the same crystal. Morphological characterization of the crystals is given in the text.

Figure 5. SEM images of natural diamond crystals after the experiments 2-27 (a) whole view (b) enlarged view of the same crystal and 2-28 (c) whole view (d) enlarged view of the same crystal. Morphological characterization of the crystals is given in the text.

rising forms (hillocks) with curved irregular contours (Fig. 4f), similar to the hillocks on the natural diamond crystal shown in Figure 1d.

The natural diamonds acquired more complicated irregular shapes than the synthetic crystals, though the main morphological features were the same (Figs. 5a and 5c). On the diamonds after the experiments there were no flat faces and their entire surface was curved, rounded. The crystals changed habit from tetrahexahedroids to octahedroids with relatively large pyramidal etched hillocks and pyramidal etched pits on the surface. Hillocks and pits were truncated by rounded surfaces of trigon- and tetragon-trioctahedrons close to $\{111\}$. The crystals developed disc-shaped sculptures on the hillocks in run 2-27 (Fig. 5b) and little but distinct etched pits in run 2-28 (Fig. 5d); the pits have hexagonal or triangular contours on surfaces close to the octahedral faces and rectangular on surfaces close to the cubic ones. As in the case of synthetic crystals, the specific etching hillocks rising above the surface of natural diamonds are observed. Especially they appeared on a diamond from experiment 2-28 (Fig. 5d).

DISCUSSION

Dissolution of flat-faced octahedral diamond in a Fe (80 wt%)-S melt at 4 GPa and 1400 °C reported by Zhimulev et al. (2016b) produced octahedroids with curved faces and morphological features similar to natural diamonds:

negatively oriented trigons (pits) and flat triangular hillocks on the faces and striation parallel to the original edges. Photo-goniometry showed etch textures with curved faces and flat faces close to octahedron (Zhimulev et al., 2016b), or octahedroids (Orlov, 1977; Afanasiev et al., 2000). However, they were rather tetrahexahedrons, judging by the presence of pseudo-edges on the short and long diagonals of rhombic dodecahedral pseudo-faces.

We have observed similar etch textures in this study. However, unlike the results of Zhimulev et al. (2016b), the etched crystals developed cone-shaped and flat hillocks; the latter had irregular contours and often occurred on the cone tips. Conical hillocks were observed both on synthetic and natural diamond crystals. The natural crystals developed discs upon the conical hillocks in run 2-27, which produced multi-level irregular crystal surfaces.

The formation of etch hillocks may be due to heterogeneity of the solvent melt. The solubility of carbon in iron liquid at 5 GPa and 1400 °C reaches 5–6 wt% (Wood, 1993; Chabot et al., 2008), but decreases in sulfur-bearing systems as the content of S increases, both at ambient (Wang et al., 1991; Tsymbulov and Tsemekhman, 2001) and high (Tsuno and Dasgupta, 2015) pressures. Namely, the carbon solubility in a Ni-Fe-S melt at 6 GPa is about 1.5 wt% at 15 wt% S and 0.6–0.7 wt% at sulfur contents of 20–25 wt% (Tsuno and Dasgupta, 2015).

Prior to the experiments of this study, we estimated the solubility of carbon in a Fe-S melt at 4 GPa and 1400 °C according to weight loss in diamond crystals before re-crystallized graphite appeared in the system. It was ~1 wt% in a melt of 90 wt% Fe and 10 wt% S, 0.5–0.6 wt% in a melt with 85 wt% Fe and 15 wt% S, and ~0.3 wt% at 80 wt% Fe and 20 wt% S. For comparison, according to (Deng et al., 2013) in the Fe-S-C system with a total amount of S of 11.41 wt% at 5 GPa at 1400 °C the melt contains 2.13 wt% of carbon and at 1600 °C – 2.07 wt% of carbon. At 10, 15, and 20 GPa the solubility of carbon is almost unchanged over a wide range of temperatures. Zhang et al. (2015) summarizes the data on solubility of carbon in the Fe-(±Ni)-S-C system as a function of the sulfur content. Thus, at 20 wt% of S the solubility of carbon in a metal-sulfide melt is 0.3–0.9 wt% according to the data of different authors. Only in the work (Dasgupta et al., 2009) higher values are shown. Cooling in this system leads to crystallization of cohenite (Fe_3C), FeS, and a γ phase (solid solution of carbon in iron). Iron carbide Fe_7C_3 appears at a pressure exceeding 5 GPa (Dasgupta et al., 2009; Zhimulev et al., 2016a).

The solubility of carbon (diamond) in a dry silicate melt is as low as <0.1 wt% (Sonin et al., 2001) and dissolution is possible only in the presence of fluid, mainly H_2O . In our experiments, silicate components were as

low as 5 wt%. It is reasonable to infer that the specific conical shaped hillocks on the crystal surfaces could form due to shielding by drops of silicate melt. Note that diamond crystals become uniformly dissolved in the absence of silicate melt in the Fe-S system (Zhimulev et al., 2016b). In contrast to the dissolution process, during the growth of diamond crystals in a metal-carbon system with the addition of basalt or olivine, these silicate components can block the growth of diamonds resulting with the formation of cavities on faces of diamond crystals (Chepurov et al., 2002).

Inclusions in natural diamonds contain sulfides, metal phases, and cohenite (Garanin and Kudryavtseva, 1990; Bulanova et al., 1998; Stachel et al., 1998; Kaminsky and Wirth, 2011; Mikhail et al., 2014; Smith et al., 2016). According to Smith et al. (2016), diamonds of type-II (physical classification) crystallize in the mantle transitional zone in pockets with the Fe-Ni-S-C melt, while carbon input is of subduction origin as part of the deep carbon cycle.

Subducting slabs can also carry water which is required for partial melting and formation of kimberlite in the mantle. Serpentine has been assumed to be the principal H₂O carrier (Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997; Poli et al., 2009), but it decomposes and releases H₂O at high pressure already at 700 °C. Another hypothesis suggests H₂O transport to deep mantle as hydrogen and OH groups in nominally anhydrous minerals (NAMs) (Geiger et al., 1991; Scogby, 1994; Kohlstedt et al., 1996; etc.). On the other hand, experiments show that breakdown of serpentine leads to crystallization of olivine and orthopyroxene with aqueous inclusions, with H₂O up to 2 wt% relative to the solid phase (Chepurov et al., 2010). Perhaps, they are inclusions that carry encapsulated H₂O to the mantle transition zone. The delivery of such material by subducting slab causes not only partial melting, but allows percolation of molten silicates into metal-sulfide pockets leading to their carbon undersaturation and resulting with diamond dissolution.

However, the dissolution surface textures and irregular crystal shapes may arise in another way. The oldest known diamonds of 3–3.5 Ga (Richardson et al., 1984; Westerlund et al., 2006) are often older than their host kimberlites (Boyd and Gurney, 1986; Richardson, 1986; Gurney et al., 2010). Diamond crystals that had resided in the mantle for billions of years lived through a complex history, with growth gaps and dissolution events. Diamond nucleation may have occurred during Earth differentiation, at the stage of protoplanetary accretion. The existing models of iron melt segregation in the mantle of the early Earth imply percolation of liquid iron alloy through crystalline silicates which potentially played an

important role during core formation in planetary bodies of the early solar system (Terasaki et al., 2007, 2008). The cores of the Earth and the terrestrial planets may contain up to 10 wt% of light elements, including carbon and sulfur (Poirier, 1994; Campbell et al., 2007; Steward et al., 2008; etc.). Therefore, Fe-Ni melts may have entrained dissolved carbon and sulfur upon protoplanetary differentiation. The presence of carbon as graphite in interstitials between silicate minerals favors the percolation of metal liquid (Zhimulev et al., 2015). Diamond crystallization is inevitable under the appropriate *P-T* conditions in this system, while the inputs of additional sulfur-bearing metal melt should finally lead to partial or complete dissolution of diamond crystals.

This mechanism is consistent with the presence of central inclusions composed of metallic iron, sulfides and cohenite in natural diamonds (Bulanova et al., 1998). Furthermore, diamond crystals often have complex internal morphology demonstrating the interrupted original growth zoning by rounded surfaces, which is evidence of dissolution (Bescrovanov, 2000).

Note that many type-II diamonds (Bowen et al., 2009; Moore, 2009, 2014; Smith et al., 2016) are irregular crystals, and morphologically complex diamonds with disc sculptures and cavities are widespread in placers derived from unknown or debatable primary sources (Patel and Agarwal, 1965; Davies et al., 1999; McCandless et al., 1999; Evdokimov et al., 2001; Kaminsky et al., 2001; Tappert et al., 2009).

CONCLUSION

Thus morphologically complex natural diamonds with irregular shapes may form by dissolution by heterogeneous solvents in the mantle. Metal-sulfide-silicate melts consisting of immiscible components with different carbon solubility are the most likely candidates for such solvents.

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