1   **Revision 1**

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

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13   **ABSTRACT**

14

15   The influence of three-dimensional defects on the morphology of diamond dissolution in

16   water-containing carbonate melts was studied at a pressure of 5.7 GPa and a temperature of

17   1300°C, using a BARS multi-anvil apparatus. Experiments on stage-by-stage dissolution were

18   performed for four blocky synthetic diamond crystals. Initial crystals had polycentric structure of

19   the faces, strong strains, block structure, numerous microtwins and microinclusions. It has been

20   established that the main relief features of partly dissolved diamond crystals are shield-shaped

21   laminae and negative trigons on remnants of {111} faces, deep etch channels, rectilinear steps on

22   microtwins and hillocks on rounded surfaces. The produced dissolution forms have shagreen or

23   block-type rounded surfaces. The main element of the relief are hillocks. Their shape is

24   controlled by the orientation of the surface on which they are localized. For natural rounded

25   diamonds it is found that the dissolution drop-like hillocks on the surfaces are also related to

26   strong lattice strains occurring in the crystals. The established relation between the dissolution

27   hillocks and diamond deformation can be used for the reconstruction of the post-growth history

28   of natural diamonds as well as for the preliminary evaluation of their quality.

29   **Keywords:** Diamond dissolution, crystal morphology, defect of crystals, dissolution

30   hillocks.

31

32   **INTRODUCTION**

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34   Natural rounded diamonds demonstrate a wide variety of surface structures. Some crystals

35   have macroscopically smooth, glossy surfaces. Others show on their surfaces specific features,

36   including serrate and shield-shaped laminae, drop-like hillocks, striations, ruts and many other

37   patterns (Kukharenko 1955; Orlov 1977; Robinson 1978). There is no doubt that the rounded

38   form of natural diamond crystals is a result of dissolution in water-containing kimberlitic melt

39   (Moore and Lang 1974; Orlov 1977; Robinson 1978; Gurney et al. 2004; Kozai and Arima 2005;

40   Khokhryakov and Palyanov 1990, 2007; Fedortchouk et al. 2007). Therefore the details of the

41   micro-relief of natural diamond crystals reflect first of all the conditions of dissolution in natural

42   processes. At the same time, diamond characteristically contains various structural imperfections

43   ranging from point to three-dimensional defects. The dissolution at the defects outcrops proceeds

44   in a different way than for perfect surfaces (Heimann 1975). As a result, the micro-relief

45   elements may form, which to a greater extent reflect the features of the real structure of diamond

46   crystals rather than the dissolution conditions. This question has not been adequately explored so

47   far. Only for some micro-relief elements of natural rounded diamonds, their relation to the real

48   structure has been determined. It is established that trigons on {111} faces are located at the

49   dislocation outcrops (Lang 1964). It is shown that the intersecting striation is related to the bands

50   of plastic deformations (Robinson 1978) and rhombic patterns of the etching channels to the

51   surface cracks (Orlov 1977). The nature of many other widely abundant micro-relief elements

52   and surface sculptures has not been clarified yet. The scarcity of experimental data on this

53 subject is partly due to the fact that in most cases only high-quality diamond crystals were used

54 in the dissolution experiments (Kozai and Arima 2005; Khokhryakov and Palyanov 2007;

55 Fedortchouk et al. 2007). Furthermore, most of previous experimental works on diamond

56 dissolution were focused mainly on the effect of conditions and composition of the medium on

57 dissolution morphology.

58   In the present study we have explored the dissolution of synthetic diamonds of block

59 structure. The specific features of dissolution surfaces of mosaic crystals are established. It is

60 shown that the origin of the drop-like hillocks on diamond tetrahexahedra is related to the

61 occurrence of strong local strains in the diamond lattice.

62

63   **EXPERIMENTAL**

64

65   In the experiments we studied stage-by-stage dissolution of four blocky crystals of

66 synthetic diamond weighting from 1.2 to 5.92 mg (Fig. 1). The diamond crystals were grown by

67 the temperature gradient method in the Ni_7Fe_3-C system with nitrogen content from 0.25 to 0.3

68 at.% (Palyanov et al. 2010). A detailed investigation of these crystals was performed in

69 (Palyanov et al. 2010). It was shown that the crystals had a polycentric structure of the faces,

70 strong strains, block structure, numerous microtwins and microinclusions. Such characteristics

71 are typical for many natural diamond crystals. Crystal No. 1 (5.92 mg) has small {100} faces

72 (Fig. 1a). Approximately one third of the crystal has flat faces, and the rest surface is blocky with

73 numerous microtwins. Crystal No. 2 (2.47 mg) has only {111} faces (Fig. 1d). The surface

74 exhibits large blocks and twinning intergrowths. Crystals No. 3 (1.51 mg) and No. 4 (1.20 mg)

75 are of octahedral habit. These crystals have a rough relief with numerous trigonal blocks and

76 depressions (Fig. 1g,j). All crystals contained micro inclusions of metal catalyst. The amount of

77 micro inclusions in the crystals increases with the degree of their blockiness from crystal No. 1

78 to crystal No. 4. From the infrared absorption measurements it was found that synthetic diamond

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79   crystals contained approximately 120-130 ppm of nitrogen impurity predominantly in the form

80   of single substitutional atoms, C-centers.

81   Experiments on diamond dissolution were carried out using a "split-sphere" type multi-

82   anvil apparatus at 5.7 GPa and 1300°C in water-containing carbonate melts. Details on the high-

83   pressure sell design, pressure and temperature measurements and calibration were presented in

84   our previous works (Khokhryakov and Palyanov 2007, 2010). Starting materials for each

85   experiment were 99.9% pure $CaCO_3$ (700 mg) with addition of H_2O (78 mg). Thus the water

86   content in all experiments was 10wt.%. Starting materials and four diamond crystals were placed

87   into sealed Pt capsules (6 mm in diameter, 5 mm long, and 0.2 mm thick walls). All four crystals

88   were used in two experiments with duration of 30 and 45 hours.

89   Several rounded natural diamonds from Udachnaya and Yubileinaya kimberlite pipes were

90   studied to reveal possible effects of lattice imperfections on the surface morphology. The

91   selected crystals were 1.0-1.5 mm in size and exhibited nonuniform surface structure. Cross

92   section plates 0.5-0.7 mm thick were prepared from three crystals by mechanical polishing. The

93   plates were oriented so that areas with different types of surface relief were exposed.

94   The crystals before and after each experiment were weighed (±0.01 mg) and analyzed with

95   optical and scanning electron microscopes. The micromorphology of diamond crystals was

96   studied using a LEO420 scanning electron microscope. Internal structure of diamond plates in

97   polarized light was studied using a Ziess AXIO Imager.Z2m" microscope. Infrared absorption

98   spectra were measured using a Bruker Vertex 70 Fourier Transform Infrared (FTIR)

99   spectrometer equipped with a Hyperion 2000 microscope.

100

101   **RESULTS AND DISCUSSION**

102

103   The overall view of the crystals and their weights before and after experiments are

104   presented in Fig.1. The crystals dissolved to different degrees. The mass loss (LM) of crystal No.

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105   1, which was the largest one, was only 19 %, whereas smaller and more defective crystals No. 3

106   and No. 4 lost 58-59 % of their initial mass.

107   The main relief features of partly dissolved diamond crystals are shield-shaped laminae and

108   negative trigons on the remnant {111} faces; deep etch channels, rectilinear steps on microtwins

109   and hillocks on rounded surfaces. The number and size of the negative trigons differ for the

110   studied diamond crystals. A great number of trigons are present on the crystals which initially

111   had numerous trigonal depressions (crystals No. 3 and 4). Trigons on these crystals did not

112   disappear even when the weight loss was 58-59%. This apparently is connected with a large

113   number of microinclusions in crystals No. 3 and 4.

114   Ditrigonal or shield-shaped dissolution laminae were present on the crystals only after the

115   first experiment (LM from 6.4 to 34%). These laminae had rough, wavy edges (Fig. 2a) in

116   contrast to the dissolution laminae on high-quality diamond crystals. As it was shown previously

117   (Khokhryakov and Palyanov 2007, 2010) the ditrigonal laminae formed on the (111) faces of

118   high-quality crystals had smooth rectilinear edges (Fig. 2b). The presence of microtwins and

119   large trigonal depressions and cracks in the mosaic crystals resulted in polycentric lamination.

120   Typical elements of blocky crystals after dissolutions are the etching channels. The number

121   and size of the channels increase with decreasing quality of the crystals from No. 1 to No. 4

122   (Fig.1). The etch channels form, most likely, along the cracks and boundaries between the crystal

123   blocks. Numerous microtwins appear after dissolution as single rectilinear steps or blocks of

124   polysynthetic twinning (Fig. 3a).

125   The produced dissolution forms have shagreen or block-type rounded surfaces. The main

126   elements of the relief are hillocks. Their shape is controlled by the orientation of the surface on

127   which they are localized (Fig. 3). On the surfaces close to the {100} faces they have isometric

128   irregular shape (Fig. 3b). Surfaces close in orientation to {111} are covered with flat hillocks

129   forming a regular structure similar to the sculpture of roof tiles (Fig. 3c). Hillocks formed on the

130   surfaces close to the {110} faces have an elongated drop-like shape (Fig. 3d).

5

131   It is known that hillocks are one of the widespread relief elements of tetrahexahedroids of

132   natural diamond. Depending on the size, shape and degree of elongation of hillocks, their

133   accumulations form various types of microrelief of rounded natural diamonds. These include

134   block-type, drop-like, serrate and shagreen features (Orlov 1977). The origin of hillocks is still

135   debatable. In earlier works considering the origin of rounded diamonds within the "growth"

136   hypothesis, these sculptures were treated as vicinal growth hillocks and their growth occurred by

137   the (110) layers (Evdokimova and Shemanin 1962, Shemanina and Shemanin 1964). Orlov

138   (Orlov 1977) suggested that hillocks formed as a result of partial dissolution of polyhedra

139   initially present on the surface of the diamond. In other studies it was supposed that the

140   formation of hillocks took place at high intensity and duration of the dissolution of diamonds

141   (McCandless et al. 1999) or when diamond resorption occurs in the CO_2 fluid (Fedortchouk et al.

142   2007).

143   The diamond crystals used in present study had strong stresses and possibly this was the

144   reason for the formation of dissolution hillocks as the main element of the dissolution

145   microrelief. For natural diamonds there is a number of observations indicating that hillocks are

146   more typical for crystals with high level of internal strains. Orlov (1977) noted that hillocks are

147   often located along the intersecting striation associated with the bands of plastic deformation in

148   diamond. They are also very characteristic of natural diamond crystals of type II, which often

149   exhibit anomalous birefringence of "tatami" type (Orlov 1977). Kaminsky et al. (2000) noted

150   that dissolution of natural diamond crystals with plastic deformation produces sculptures

151   consisting of hillocks appearing as shagreen, hackly, drop-like, grooved and block-type features.

152   Recently, Gainutdinov et al. (2013) also suggested possible association of the dissolution

153   hillocks in diamond with post-growth deformation events. In addition it has been demonstrated

154   experimentally (Heiman 1975, Sangwal 1990) that dissolution hillocks on rounded surfaces of

155   crystals form not only as a result of blocking of individual sections by impurities (for example,

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156 MgO and KCl crystals), but also due to the presence of strong gradients of stresses in crystals

157 (for example, Ag crystals).

158   To the best of our knowledge, there are no available literature data correlating the location

159 of drop-like hillocks on the rounded surfaces of natural diamond crystals with the internal

160 structure of the crystals. In order to clarify whether such a correlation exists we examined several

161 natural diamond crystals with rounded surfaces exhibiting drop-like hillocks. The most

162 illustrative of these crystals is shown in Fig. 4. For this crystal the boundary between the areas

163 with different surface relief is the most sharp. Most of the crystal surface is smooth and glossy

164 (area B in Fig. 4) and small fragments of the surface are composed of accumulations of small

165 drop-like hillocks (area A in Fig. 4). The (110) cross section plates were cut from the crystals

166 through the surface areas with drop-like hillocks, as shown in Fig. 4a. Using polarized light

167 microscopy it was established that in the volume of the crystals there are distinct strongly

168 strained regions whose borders coincide with the borders of distribution of hillocks (Fig. 4c,d).

169 The birefringence patterns within these strained regions has a specific "tatami" form, which is

170 attributed to plastic deformation (Lang 1967; Orlov 1977). To examine if other defects such as

171 nitrogen impurity may be responsible for the observed surface morphology we measured infrared

172 absorption spectra from several local areas on the sample. Figure 5 shows IR spectra recorded

173 from the selected locations as indicated in the insert. It follows that the periphery area which

174 exhibit high strains and which is bound by surfaces with hillocks contain relatively low nitrogen

175 concentrations of approximately 100-120 ppm (spectrum 1 in Fig. 5). In this case, 90-95 ppm of

176 nitrogen is in the form nitrogen pairs, A-centers and 15-20 ppm in the form of aggregates of four

177 nitrogen atoms, B-centers. Moving from the periphery to the center the concentration of nitrogen

178 significantly increases to approximately 580-600 ppm (spectrum 3 in Fig. 5). From this we can

179 infer that nitrogen defects itself can not be responsible for the observed dissolution hillocks. On

180 the other hand our results are in agreement with previous observations that diamond crystals or

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181 local areas within the crystals with low nitrogen concentrations deform plastically more easily

182 than crystals or areas with high nitrogen concentrations (e.g. Nailer et al., 2007).

183   The established correlation between the dissolution hillocks and defects due to lattice

184 strains in diamond is preliminary and needs further verification over a greater amount of crystals

185 with detailed investigations of surface micro-relief and internal structure with quantitative

186 measurements of lattice strains. Nevertheless, the results obtained in this study allow us to

187 suggest that the formation of dissolution hillocks occurs on strained natural diamonds.

188   The shape of hillocks is worth special consideration. In spite of the different external forms

189 of hillocks, they have the same crystallography. Goniometric studies of hillocks on natural

190 diamonds were performed in the middle of the last century (Fersman 1955; Kukharenko 1955).

191 These data allow an accurate description of the dissolution hillocks. Fersman (1955) found that

192 rounded surfaces with drop-like hillocks always gave reflection on the goniometer in the form of

193 arcuate bands. On the stereographic projection the bands of reflections from the rounded surface

194 of hillocks have the shape of an ellipse, designated by Fersman as band CE (Fig. 6). Such a

195 shape of light reflexes corresponds to a conical surface with an elliptic cross section. It is known

196 that conical surfaces are very characteristic forms of dissolution of crystals of various minerals

197 and diamond is not an exception (Shafranovsky 1961; Glazov 1981). Also goniometric study of

198 hillocks with flat faces was conducted by A.A. Kukharenko (Kukharenko 1955). He measured

199 coordinates of faces which bound relatively large (up to 60 μm) conical hillock. The most

200 prominent light reflexes from the surfaces of these hillocks corresponded to hexaoctahedron and

201 tetrahexahedron series of faces. As shown in Fig. 6, the reflections from the flat areas of hillocks

202 are located on bands CE. Thus, rounded and faceted dissolution hillocks have similar conical

203 shape. The center of ellipses (i.e. the spherical projection of the axes of cones) of hillocks is

204 calculated as the middle point between the reflections i(304) and e(102) located on the symmetry

205 line. The calculation showed that it corresponds to the normal to plane (508) ρ=32°00′. Thus, the

206 axis of the cone-shaped surface hillocks or hillocks vertexes are oriented along the <850>

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207   directions. As is known the vertexes of the dissolution forms correspond to directions of minimal

208   dissolution rate (eg Heiman 1975). Thus, the <850> direction is the direction of minimal

209   dissolution rate of rounded surfaces of natural diamond tetrahexahedroids.

210

211   **IMPLICATIONS**

212

213   The results obtained in this study allow us to conclude that the hillocks on the rounded

214   surfaces of diamond do not reflect any specific features of the dissolution conditions, but indicate

215   the occurrence of strong deformations in the crystals. The drop-like shape of hillocks

216   corresponds to the conical surface with an elliptical cross section and the axis along <850>

217   directions. Thus, our results demonstrate that the morphologic features of rounded natural

218   diamonds do not indicate exclusively the composition of the dissolution media and dissolution

219   conditions. Sculptures on the diamond surface can also be related to the specific features of the

220   real structure of the diamond crystals. The established relation between the dissolution hillocks

221   and diamond deformation can be used for the reconstruction of the post-growth history of natural

222   diamonds as well as for the preliminary evaluation of their quality.

223

224   **ACKNOWLEDGEMENT**

225

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288

Figure captions

289

290

291   **Figure 1.** SEM images of initial and partly dissolved diamond crystals in water-bearing

292   carbonate melts after 30 and 75 h. LM = mass loss of crystals. Scaling bar corresponds to 200

293   μm.

294

295   **Figure 2.** A dissolution layer on the {111} faces. (**a**) block diamond crystals of No. 3 after

296   dissolution for 30 h.; (**b**) high-quality diamond crystals. Figure 2f from the work (Khokhryakov

297   and Palyanov 2007).

298

299   **Figure 3.** SEM image of surface textures of partly dissolved diamond crystals. (a) Microtwin on

300   the crystal No 2 after 30 h of dissolution. Dissolution hillocks on the surfaces close to (b) {100}

301   (crystal No. 4, 30 h), (c) {111} (crystal No. 1, 75 h) and (d) {110} (crystal No 2, 75 h) faces.

302

303   **Figure 4.** A natural diamond crystal with drop-like hillocks. (**a**) General view of the crystal.

304   Black lines show the directions of cutting the crystal. (**b**) A fragment of the crystal surface. (**c**) A

305   plate cut from the crystal and (**d**) a fragment of the plate viewed with cross polarizers. **A** - crystal

306   surface without drop-like hillocks. **B** - crystal surface with drop-like hillocks.

307

308   **Figure 5.** Infrared absorption spectra recorded from a plate prepared from the natural diamond

309   crystal shown in Fig. 4. The insert shows a fragment of the plate. Squares mark the areas from

310   with spectra were taken and their sizes correspond to the sizes of the microscope aperture

311   (approximately 80×80 μm). Labels on the spectra corresponds to labels shown on the image.

312

313   **Figure 6.** A fragment of stereographic projection of hillocks on the surfaces of natural diamond

314   crystals. Continuous bands of reflexes (gray) are from (Fersman 1955). Single reflexes are given

13

315   according to (Kukharenko 1955): k - {702}, a - {301}, g - {502}, e - {201}, i - {403}, г - {961},

316   t - {951}, I - {742}, p - {532}, Ξ - {731}, z - {531}, x - {321}, y - {432}, w - {431}, Σ - {541},
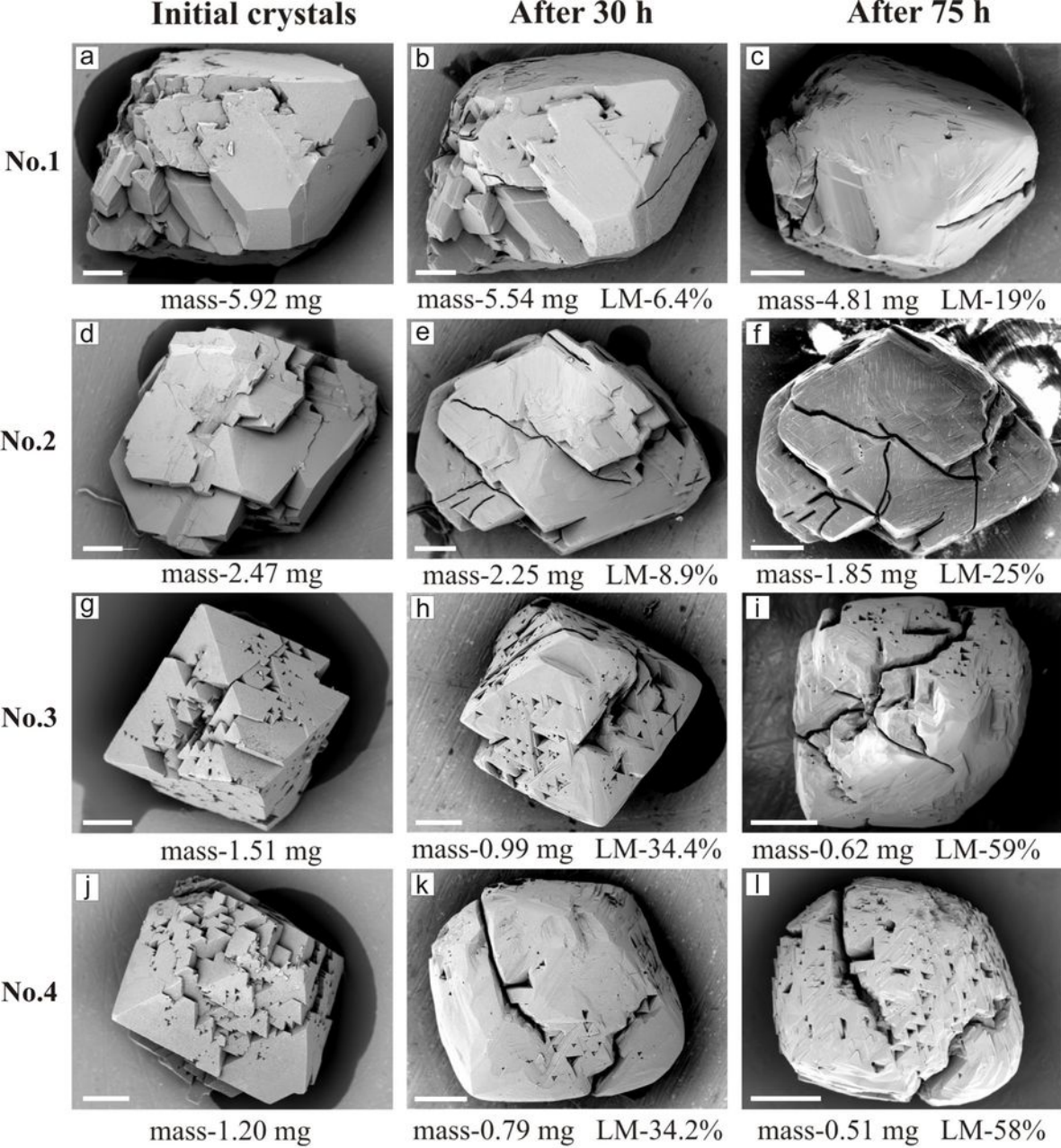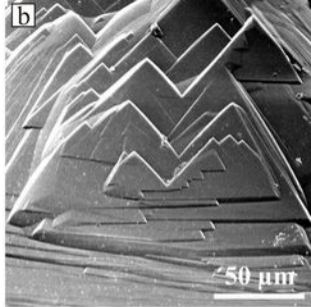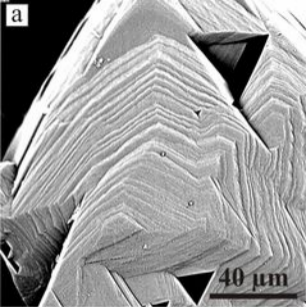
317   Φ - {651}, S - {833}.

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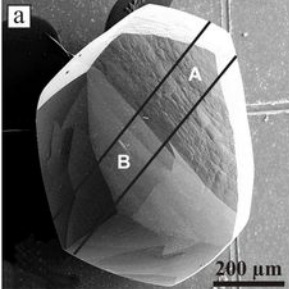|	Initial crystals	After 30 h	After 75 h
No.1	mass-5.92 mg	mass-5.54 mg LM-6.4%	mass-4.81 mg LM-19%
No.2	mass-2.47 mg	mass-2.25 mg LM-8.9%	mass-1.85 mg LM-25%
No.3	mass-1.51 mg	mass-0.99 mg LM-34.4%	mass-0.62 mg LM-59%
No.4	mass-1.20 mg	mass-0.79 mg LM-34.2%	mass-0.51 mg LM-58%
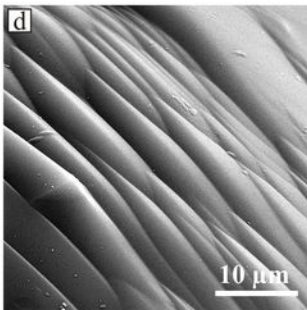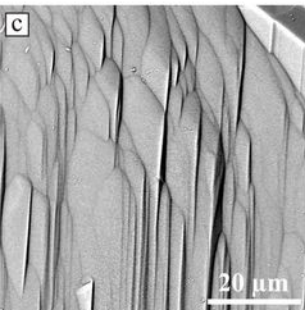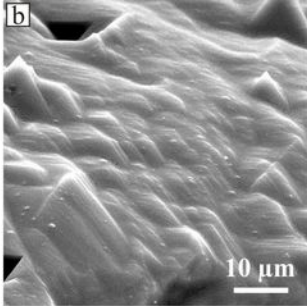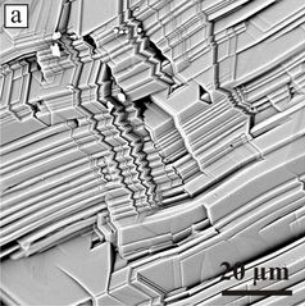
Figure 1.

Figure 2.

Figure 3.
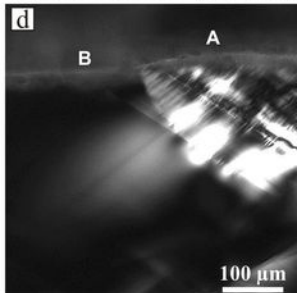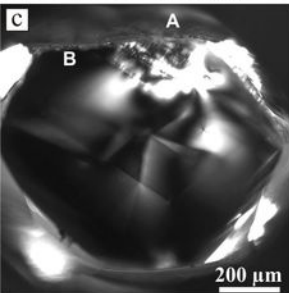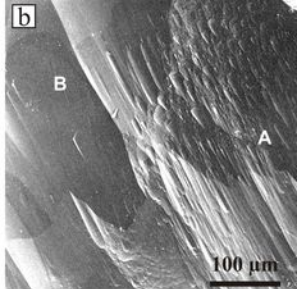
Figure 4.

Figure 5.

Figure 6.