

## DIAMOND MORPHOLOGY IN GROWTH AND DISSOLUTION PROCESSES.

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The morphology of diamond rather various and reflects growth conditions and further dissolution processes. Experimental modeling of these processes is of interest for solving problems of diamond genesis.

**Diamond growth.** The experiments were performed on device of "split sphere" type in the systems Ni-Fe-C and Ni-Mn-C at pressure 5.0-6.0 GPa and temperature range 1350-1500°C [Pal'yanov et.al,1990]. Generalized data on morphology, depending on growth rate in various crystallization processes, are given in Tables 1-3.

Table 1. Diamond growth from graphite by FG(film growth) method

Growth rate, $\mu\text{m/h}$	Size, $\mu\text{m}$	Shape	Morphology
$n \cdot 10^2 - n \cdot 10^3$	$n \cdot 10^2$	bulky	{111},{100}>{311},{110}
$n \cdot 10^3 - n \cdot 10^4$	$n \cdot 10^2 - n \cdot 10^3$	bulky+skeletal	{111},{100}
$> n \cdot 10^4$	$n \cdot 10^2 - n \cdot 10^3$	dendrites in [100] & [110] directions	{111},{100}
$> n \cdot 10^4$	$n \cdot 10^2 - n \cdot 10^3$	aggregative crystals*	{111},{100}
$> n \cdot 10^4$	$n \cdot 10^3$	aggregates*	{111}

\* - size of crystallites is  $n \cdot 10 \mu\text{m}$

Table 2. Diamond growth on seed by TGG(temperature gradient growth) method

Growth rate, $\mu\text{m/h}$	Growth rate, mg/h	Shape	Morphology
$n \cdot 10$	0, n -3	bulky	{111}>{311}>{100}>{110}
↓	3 - 6	bulky	{111}>>{311},{100},{110}
↓	5 - 10	bulky+skeletal	{111}>{100}
$n \cdot 10^2$	>10	skeletal	{111}, seldom {100}

Table 3. Diamond growth by RG(recrystallization growth) method

Growth rate, $\mu\text{m/h}$	Size, $\mu\text{m}$	Shape	Morphology
$V_l \approx n - n \cdot 10$	$l \leq 300$	needle in [111] direction	{110}>{111}
$V_d \approx 0, n - n$	$d \leq 30$	needle in [110] direction	{110}>{111}>{100}>{hkk}
l-length, d-thickness		needle in [211] direction	{111}>{110}>{100}

When growing diamond by FG method, supersaturation is determined by solubility differences of diamond and graphite at the same temperature. When growing diamond by TGG, supersaturation is determined by the difference in diamond solubilities in dissolution zone and growth zone and depends on the value of temperature gradient ( $\Delta T$ ). FG and TGG methods were described in paper (Kanda&Fukunaga,1982). Diamonds grown by RG method are formed in closed areas between crystals formed by TGG method, and in "shaded" sites where carbon transport is hindered due to shielding. RG diamond overgrows the dissolution surfaces of crystals in the form of needles. Faces {100} and {hkk} of RG crystals also have traces of dissolution. Needle-shaped crystals are always colorless and contain no inclusions. The growth of needle-shaped crystals is assumed to take place in active centers under conditions similar to equilibrium by redistributing carbon in metal melt owing to different solubility of diamond faces. Data from Tables 1-3 show that three different processes of diamond

growth cover the maximum range of growth rates which makes up nearly 5 orders.

A very important factor, influencing the diamond growth, is the presence of H<sub>2</sub>O in crystallization medium (Kanda et al., 1984). A more intricate picture was observed at spontaneous crystallization of diamond by TGG method in the Ni-Mn-C system. The diamond morphology with increasing H<sub>2</sub>O changes in the following order:

flat-faced crystals of {100} - {111} row → {110}\* → antiskeletal crystals\*\* → dendrites\*\*\* in [111] direction → growth of graphite.

\* in this case {110} faces have practically no growth sectors, \*\*studies on the morphology of antiskeletal crystals are reported in (Pal'yanov et al., 1985), \*\*\*dendrites were formed by crystallites with {110} and {111} faces.

**Dissolution of diamond.** The experiments on dissolution of diamond were conducted in sealed platinum ampoules. The procedure of experiments and investigation of crystals are described in (Khokhryakov and Pal'yanov, 1990). Main results are listed in Tables 4-6.

Table 4. Diamond dissolution in water at P=2,5 GPa.

T°C	Time min	H <sub>2</sub> O mg	diamond		etch pits		faces of dissolving
			quantity(mg)	loss,%	on {100}	on {111}	
1350	15	50	10 (0,64)	5	{111}	{111}	{322},{211}
1450	5	60	12 (0,91)	15	- " -	- " -	{322},{955}
1450	15	55	12 (0,90)	45	- " -	- " -	-
1450	20	68	12 (0,88)	75	- " -	- " -	-

Layers are observed only at initial dissolution stages; mainly etch pits and channels are formed. Finally, after 75% weight loss, the crystal acquires an irregular shape with cellular surface.

Table 5. Diamond dissolution in basalt at P=2,5 GPa (basalt was pre-annealed at 850°C)

T°C	Time min	basalt mg	diamond		etch pits		faces of dissolving
			quantity(mg)	loss,%	on {100}	on {111}	
1350	140	106,6	24 (0,75)	1	{111}	{855},{755}, {665}	-
1450	30	105,0	16 (0,45)	2,2	- " -	{755},{554}, {443}	{544},{755}, {998}
1450	180	101,0	24 (0,95)	6,5	{811},{611}, {411}	{775},{443}	{20.19.19}, {998}
1400	110	105,0	3 (0,20)	15	{23.1.1} {13.1.1}	- " -	{544}

Dissolution layers have a triangle shape. Finally, the crystal acquires trigontrioctahedral habit with striation along [110] direction.

Table 6. Diamond dissolution in water-bearing basalt.

T°C	P GPa	Time min	basalt mg	H <sub>2</sub> O mg	diamond		etch pits	
					quantity(mg)	loss,%	on {100}	on {111}
1100	2,5	120	175,5	20,0	7 (0,63)	< 0,01	-	-
1200	5,0	50	69,8	9,0	60 (1,82)	0,5	{11.1.1}	{443}
1300	2,5	40	165,5	26,0	7 (0,60)	3,5	{511}	{553}
1350	5,5	90	51,2	5,3	7 (0,45)	6,5	{411}	{221},{883}
1400	2,5	15	95,8	25,5	5 (0,46)	15	-	-
1300	2,5	150	167,7	29,9	10 (0,45)	18,0	-	-

Etch pits are typical of crystals at initial dissolution stages (to 10% of weight loss). Dissolution layers have a ditrigonal shape and form spherical triangles. Dissolution results in rounded surfaces with a sheaf-like striation and micro-disk patterns. Similar results on diamond morphology are obtained when diamond crystals were dissolved in the systems lamproite+diamond (with the content of H<sub>2</sub>O 0.38 wt.%) and basalt+ H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>(10-15%)+diamond.

**Discussion.** The shape of diamond crystals grown in metal melt at high temperatures and pressures to a greater extent depends on supersaturation and varies with increasing growth rate in the following order: needle, bulky, skeletal, dendrites, aggregative crystals, polycrystalline aggregates. Here the following regular changes in the morphology of crystals:

$\{110\}+\{111\}+\{100\}+\{hkk\} \rightarrow \{111\}+\{100\}+\{311\}+\{110\} \rightarrow \{111\}+\{100\} \rightarrow \{111\}$ .

An increase in H<sub>2</sub>O admixture results in: first, creation of {110} crystals, and farther antiskeletal growth is observed which lead to formation of dendrites. The results obtained on diamond morphology and earlier published data (Sunagawa, 1990, Kanda et al., 1984, Burns and Davies, 1992) allow determination of the main factors governing diamond morphology in growth processes: structure (PBC analyses), P-T parameters, composition of solvent, growth rate, and effect of admixtures.

Diamond morphology on dissolution in model systems is to a greater degree governed by the composition of solvent and rate of the process. The presence of water and its content in the system determines the dissolution rate and morphologic properties, including etch pits, features of relief and ways of dissolution. Flat-faced octahedra in a dry silicate system dissolve to form trigonal layers. On dissolution in water-containing silicate systems, crystals with ditrigonal dissolution layers are formed independent of silicate matrix composition. The rate of the process strongly depends on temperature. The presence of H<sub>2</sub>O is mainly responsible for the chemistry of the process, which is essentially oxidation of diamond, and respectively specific features of diamond morphology. Experimentally obtained dissolution forms are morphologic analogs of semirounded and rounded natural diamond crystals. Diamond morphology properties can be used as a qualitative (index) indicator of the presence of water-containing fluid in natural silicate systems. Comparison of natural diamond morphology and their morphological analogs obtained in model systems provides a possibility for estimation of the degree of dissolution of natural diamond crystals in various deposits.

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