=========================== **GEOCHEMISTRY** ===========================

Formation of Diamond Polycrystals in Pyrrhotite–Carbonic Melt: Experiments at 6.7 GPa

A. V. Shushkanova[a, b] and Yu. A. Litvin[b]

Presented by Academician V.S. Urusov November 24, 2005

Received November 24, 2005

The first syntheses of diamond polycrystals in pyrrhotite–carbonic melts are reported in this communication. The results obtained are directly related to the issue of diamond origin in the Earth's mantle, because pores in some natural polycrystalline varieties of diamond contain not only silicate, oxide, metallic, and other phases but also sulfide minerals [1, 2]. However, the experimental data [3, 4] showed that natural sulfide melts may serve (although, to a limited extent) as a medium for the growth of diamonds, but the main role belongs to carbonate–silicate (carbonatite) melts [5].

The main varieties of natural diamond polycrystals—diamondite and carbonado—occur as separate microcrystalline segregations and intergrowths with diamond monocrystals. Polycrystalline diamond aggregates occur in such intergrowths either within a diamond monocrystal or as an outer shell of a monocrystal [6]. These simple morphological observations suggest that the same mantle substance and processes are responsible for the growth of both diamond polycrystals and monocrystals.

The term *diamondite* as a name of a monomineral diamond rock was proposed in [1] for diamond polycrystals with syngenetic pore inclusions of mantle minerals similar to those in monocrystal samples [7], such as garnet, clinopyroxene, sulfides, ilmenite, and others. "Diamondite" is a generalized term for diamond varieties, such as bort, balas, framesite, and "diamond aggregate" [6]. Monocrystalline diamond and diamondite

[a] *Geological Faculty, Moscow State University, Leninskie gory, Moscow, 119992 Russia; e-mail: shushkanova@iem.ac.ru*
[b] *Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

were synthesized at a high pressure in the same carbonate–silicate–carbonic melts [8–10], and diamondite polycrystals ~2 mm in size were formed in a few seconds. The composition of growth melts in these experiments was set in compliance with mineralogical data on composition of syngenetic inclusions in diamonds. Carbonatites were also used. The experimental modeling of syngenesis of diamondite and primary garnet, clinopyroxene, sulfide, carbonate, and other inclusions allows us to consider the genesis of diamondite in the framework of the concept of a carbonate–silicate growth medium [11].

The origin of carbonado—diamond polycrystals with a cryptocrystalline (granulomorphic) texture and characteristic inclusions (native metals, oxides, sulfides, and others [2, 12])—is a matter of debate. The formation of carbonado is attributed to such unlikely phenomena as radioactive irradiation, shock metamorphism, specific tectonics, and so on (see review in [2]). At the same time, the thorough examination of carbonado-hosted syngenetic minerals demonstrates that they all are similar to the minerals known as primary inclusions in diamond monocrystals [2]. For example, zircon of peridotitic affinity and rutile of eclogitic mineral assemblage have been identified. This suggests that the carbonate–silicate–carbonic diamond-forming melts with the major (carbonate and silicate) and admixture (sulfide, oxide, phosphate, chloride, and fluid) components [5] might also be parental for carbonado. However, the primary phase and chemical compositions of syngenetic inclusions in porous carbonado might be altered by secondary reactions under strongly reducing conditions buffered by carbon of carbonado.

Sulfides are among the most abundant primary inclusions in natural diamond mono- and polycrystals. They were considered the probable major parental diamond-forming substance in the mantle for a long time [13].

The subsequent high *PT* experiments [3, 4] have shown that sulfide–carbonic melt solutions do serve as a high-efficient substance for spontaneous nucleation of diamonds. Further experimental investigations of phase relations in the garnet–pyrrhotite [4] and garnet–calcite–pyrrhotite [14] systems under *PT* conditions of diamond stability have shown that silicate, carbonate, and carbonate–silicate melts are completely immiscible with sulfide melts. It was established that solubility of silicate and carbonate components in sulfide melts is negligible under such conditions. This fact unequivocally indicates that the syngenetic crystallization of diamond together with silicate and carbonate minerals from sulfide–carbonic melts is impossible in terms of physical chemistry. Therefore, the hypothesis of sulfide substance serving as a parental material for the formation of bulk of diamonds in kimberlites should be turned down.

Nevertheless, the possibility of crystallization of both mono- and polycrystalline diamonds from natural sulfide–carbonic melts cannot be ruled out. However, diamond of such origin must be free of syngenetic silicate and carbonate inclusions.

The objective of this study was an experimental investigation of the possibility of the formation of diamond in sulfide–carbonic melts at high pressures and temperatures. While choosing the composition of a sulfide medium, we took into consideration the experimental results on the high efficiency of pyrrhotite ($Fe_{1-x}S$) melts for spontaneous nucleation and crystallization of diamond [4]. Such melts with simple compositions are representative components of mantle sulfide substances involved in diamond formation.

The starting materials were composed of mixtures of pyrrhotite and spectrally pure graphite powders (weight proportion 3 : 2). The pyrrhotite had the average composition of 52.79 at % Fe and 47.21 at % S (table), whereas the graphite was of analytical quality. The mixtures were homogenized by their grinding with alcohol in a WC–Co hard alloy mortar. High pressures and temperatures were created in an anvil-with-hole apparatus with the container made of lithographic limestone. The resistive tubular heater (height 7.2 mm, outer diameter 5 mm, and inner diameter 3 mm) was also made of graphite of the analytical quality. The experimental technique is described in [3]. The sulfide–carbonic mixtures were pressed into heater holes subsequently closed at both ends with graphite disks 1 mm thick. Pressure and temperature were determined by calibration curves based on reference phase transition of bismuth (pressure) and by measurements based on the $Pt_{70}Rh_{30}/Pt_{94}Rh_{06}$ thermocouple (temperature). The pressure correction for high temperature was based on the experimental curve of graphite–diamond equilibrium obtained by S. Kennedy and G. Kennedy. The accuracy of pressure and temperature determinations was ±0.1 GPa and ±20°C, respectively. After quenching at a rate of ~300°C/s, the samples were removed and

Chemical compositions of the quenched sulfide melt (growth substance for diamond polycrystals) and starting natural pyrrhotite, at %

Sulfide melt		Natural pyrrhotite from the Dalnegorsk deposit, Primorye	
S	Fe	S	Fe
50.22	49.78	53.86	46.14
55.47	44.53	52.74	47.26
55.59	44.41	52.99	47.01
55.17	44.83	52.57	47.43
55.63	44.37	52.53	47.47
52.44	47.56	52.70	47.30
51.88	48.12	52.69	47.31
52.47	47.53	52.87	47.13
51.82	48.18	52.79	47.21
52.05	47.95	52.83	47.17
52.13	47.87	52.69	47.31

split up. The SEM and microprobe examinations were performed on chip surfaces with carbon sputtering at the Institute of Experimental Mineralogy with participation of A.N. Nekrasov and K.V. Van on a CamScan M2300 (VEGA TS 5130MM) electron microscope equipped with a Link INCA Energy microprobe.

Diamond polycrystals formed at the contact of the graphite heater-ampule with the melted sulfide–graphite mixture at 6.7 GPa and 1660°C after 4 min (sample 1/1184). Figure 1 shows the sample after the run. The polycrystalline intergrowth consists of skeletal octahedral diamond crystals and their spinel twins. The pale substance in the polycrystalline diamond aggregate is a quenched growth (parental) sulfide melt. Its composition is given in the table. The solidified sulfide melt retains close contacts with growing diamond faces and tightly fills up holes between skeletal edge jugs and the interstitial spaces between the intergrown diamond microcrystals. This fact clearly indicates that the diamond microcrystals formed in the sulfide–carbonic melt.

Figure 2 shows the "sulfide-synthetic" diamond polycrystals after the removal of the parental sulfide substance by acid leaching. Polycrystals consist of diamond octahedrons and spinel twins varying from 1 to 100 μm in size. Figure 2a demonstrates a star-shaped intergrowth formed as a result of cyclic twinning. This type of morphology, well known for natural diamonds [6], has been recorded for the first time in a sulfide medium. Figure 2b shows the characteristic "cryptocrystalline" forms of distorted diamond microcrystals
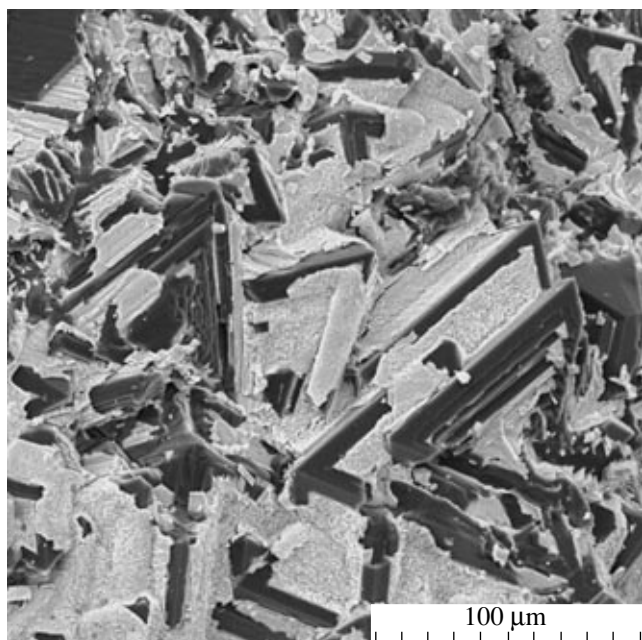
Fig. 1. A skeletal crystal grown in pyrrhotite–carbonic melt (microphotograph taken after run).

without distinct edges. Their formation is likely related to the much higher degree of oversaturation of sulfide melt with dissolved carbon and the consequent extremely high ("avalanche") rates of crystallization.

The edged skeletal forms of octahedral microcrystal faces are most typical in diamond polycrystals (Figs. 1, 2a, 2c). Sporadic smooth faces are likely related to the final (slower) stage of crystallization. During the layer-by-layer growth, the layers grow on skeletal faces near apices and edges. Then they spread toward the center with the formation of flat steps of variable width (Fig. 2c). Several fronts of crystallization can develop simultaneously. Their intersections and superpositions produce a complex sculpture with triangular projections and deeps oriented parallel to (111).

The formation of diamond polycrystals indicates that, like carbonate–carbonic and carbonate–silicate–carbonic melts, the sulfide–carbonic melts are highly efficient diamond-forming substances. In the sulfide–carbonic system, spontaneous crystallization of diamond with the formation of polycrystalline aggregate proceeds at a high pressure (6.7 GPa) immediately after melting of the starting pyrrhotite–graphite mixture at eutectic and higher temperatures. This is caused by oversaturation of sulfide melt with carbon relative to diamond because of a higher solubility of graphite (thermodynamically unstable phase in the PT field of diamond stability) in comparison with diamond (thermodynamically stable phase) at the same temperatures and pressures. Consequently, dissolution of the unstable graphite phase (source of carbon) in sulfide melt produces the labile (oversaturated with respect to diamond) carbon solution. The formation of diamond

polycrystals testifies to very high degrees of oversaturation and high densities of diamond phase nucleation, resulting in the simultaneous appearance of numerous nuclei, their fast growth, and intergrowth of crystallites. The dissolved carbon is transferred by diffusion mechanism to the growing faces with a high rate, so that polycrystallites ~1 mm in size are formed over a few seconds.

Microprobe analyses of the quenched sulfide melt at contacts with diamond polycrystallites (table) confirmed that its composition fits pyrrhotite. Sulfides are retained as individual substances in runs up to 4 min long. We did not establish reduction of sulfide to elementary iron and appearance of free sulfur or its oxygen-bearing compounds. This fact serves as evidence for stable redox conditions. The buffering is provided by the sulfide–carbon (graphite and/or diamond) system. It is noteworthy that sulfides are also stable with respect to reduction–oxidation at contacts with the parental carbonate–silicate substances [14].

Sulfide and homogeneous carbonate–silicate melts reveal complete immiscibility at PT parameters of diamond stability [14, 15]. Therefore, sulfide melts may occur as mechanical inclusions in diamond-forming parental carbonate–silicate (carbonatite) magmas. Carbon derived from mantle sources can dissolve simultaneously in carbonate–silicate melts and sulfide melt inclusions therein. When the concentration of oversaturated carbon solutions attains the labile state, the spontaneous nucleation and growth of natural analogues of carbonate-synthetic and sulfide-synthetic diamonds may occur simultaneously in both melts. Our previous and current experimental studies have shown that the formation of diamond polycrystals may be provided by growth substances similar to those in the case of diamond monocrystals. However, the common practice of crystal growth suggests that the formation of polycrystalline aggregates requires a higher concentration of labile carbon solutions in growth melts than for the spontaneous crystallization. The occurrence of diamondite and carbonado indicates that such concentrations most likely are achieved under natural conditions.

Several scenarios of origination of the highly oversaturated carbon solutions may be proposed for both carbonate–silicate and sulfide melts.

Increase in oversaturation of the saturated or slightly oversaturated melts with dissolved carbon may be caused by a fast change of pressure and/or temperature. This may occur, for instance, during the rapid propagation of magmatic melt in the relatively low-pressure region and at contacts with colder mantle rocks. Natural diamond polycrystals may form at contacts of diamond-bearing carbonate–silicate and sulfide melts with metastable graphite in the mantle. The presence of the metastable graphite is supported by findings of peridotite and eclogite xenoliths with graphite or graphite in combination with diamond [7]. However, it should be kept in mind that typomorphic attributes of natural
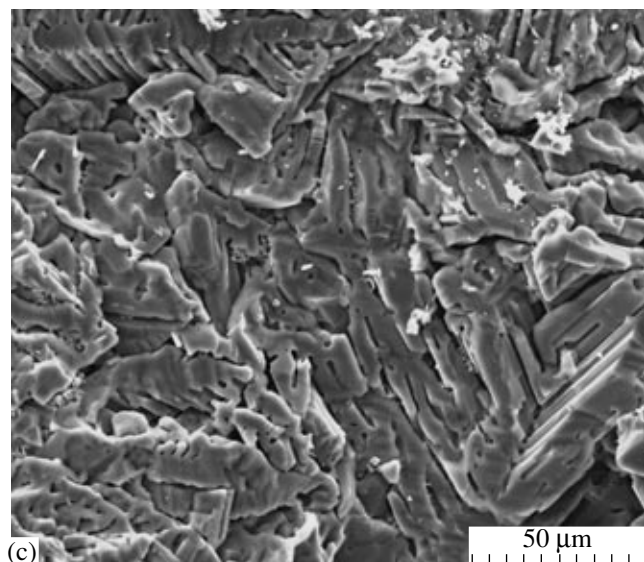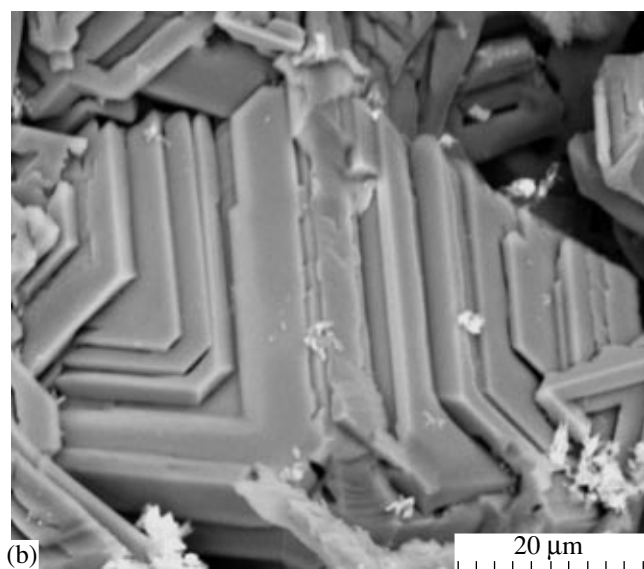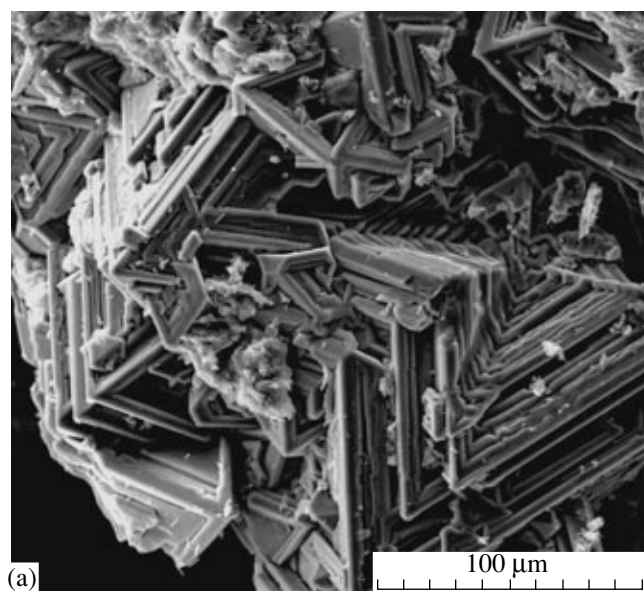
Fig. 2. (a) Star-shaped polysynthetic twin in diamond poly-crystal, (b) "cryptocrystalline" diamond polycrystal, and (c) products of layer-by-layer growth of skeletal microcrys-tals in diamond polycrystalline aggregate.

counterparts of carbonate-synthetic and sulfide-syn-thetic diamonds must differ because of the expected discrepancies in their admixture compositions and physical properties, on the one hand, and in the compo-sition of syngenetic inclusions, on the other.

CONCLUSIONS

(1) For the first time we have synthesized diamond polycrysts from the pyrrhotitic sulfide melt highly oversaturated with carbon at 6.7 GPa.

(2) The sulfide-synthetic diamond polycrystals rep-resent intergrowths of skeletal (edged) or cryptocrystal-line microdiamonds (1–100 μm in size) and their spinel-type and occasional star-shaped polysynthetic twins. Diamond polycrystals contain syngenetic sulfide inclusions.

(3) Experimental results demonstrate that natural counterparts of sulfide-synthetic diamond polycrystals can form under specific conditions of mantle sulfide melts highly oversaturated with dissolved carbon, in particular, at contacts with the mantle graphite.

REFERENCES

1. G. Kurat and G. Dobosi, Mineral. Petrol. **69**, 143 (2000).
2. S. V. Titkov, A. I. Gorshkov, S. F. Vinokurov, et al., Geochem. Int. **39**, 228 (2001) [Geokhimiya **39**, 261 (2001)].
3. Yu. A. Litvin, V. G. Butvina, A. V. Bobrov, and V. A. Zharikov, Dokl. Earth Sci. **382**, 40 (2002) [Dokl. Akad. Nauk **382**, 106 (2002)].
4. Yu. A. Litvin, A. V. Shushkanova, and V. A. Zharikov, Dokl. Earth Sci. **403**, 719 (2005) [Dokl. Akad. Nauk **402**, 719 (2005)].
5. Yu. A. Litvin, Dokl. Earth Sci. **389A**, 388 (2003) [Dokl. Akad. Nauk **389**, 382 (2003)].
6. Yu. L. Orlov, *Mineralogy of Diamond* (Izd. Akad. Nauk SSSR, Moscow, 1963) [in Russian].
7. N. V. Sobolev, *Deep Inclusions in Kimberlites and Compo-sition of the Upper Mantle* (Nauka, Novosibirsk, 1974) [in Russian].

8. Yu. A. Litvin and V. A. Zharikov, Dokl. Earth Sci. **373**, 867 (2000) [Dokl. Akad. Nauk **372**, 808 (2000)].

9. Yu. A. Litvin, A. P. Jones, A. D. Beard, et al., Dokl. Earth Sci. **381A**, 1066 (2001) [Dokl. Akad. Nauk **381**, 528 (2001)].

10. Yu. A. Litvin and A. V. Spivak, [Dokl. Earth Sci. **391A**, 888 (2003) [Dokl. Akad. Nauk **391**, 673 (2003)].

11. Yu. A. Litvin, G. Kurat, and G. Dobosi, Geol. Geofiz. **46**, 1300 (2005).

12. A. I. Gorshkov, S. F. Vinokurov, I. D. Ryabchikov, et al., Geochem. Int. **38** (1), 1 (2000) [Geokhimiya **38** (1), 3 (2000)].

13. G. P. Bulanova, W. L. Griffin, and C. G. Ryan, Mineral. Mag. **62**, 409 (1998).

14. A. V. Shushkanova and Yu. A. Litvin, Geol. Geofiz. **46**, 1331 (2005).

15. Yu. A. Litvin and V. G. Butvina, Petrology **12**, 377 (2004) [Petrologiya **12**, 426 (2004)]