DIAMONDITE FORMATION IN CARBONATE-CARBON MELTS

Litvin Yu.A., Spivak A.V.
(Institute of Experimental Mineralogy RAS, Chernogolovka, Russia)
litvin@iem.ac.ru

Diamondites [1] – single mineral diamond rocks; the varieties: bort, ballas, carbonado (framesite). More commonly, these are the intergrowths of nano- and micrometer crystallites with mineral inclusions of the both peridotite and eclogite mineral parageneses in their pores and cavities.

Diamondite genesis has been linked with rapid crystallization from hypothetic carbonatite or kimberlite "fluid" together with silicate minerals [2]. The assumptions of the linkage of diamondites with the "fluids" of carbonatites (alkaline varieties, dolomites, kimbertlites, orangeites) have been appeared at analyzes of data for rare earth elements in garnets and clinopyroxenes from inclusions [1,3]. In diamondite pores and cavities, fragments of carbonatite paternal medium similarly to the inclusions in fibrous diamonds [4] are not found for the present.

Specific conditions of diamondite formation are extremely interesting as a part of the diamond genesis problem. By the modern experimental [5, 6] and mineralogical [4] evidence, parental diamond-forming media are multicomponent carbonate – silicate melts composed of major (carbonate and silicates) and admixed (sulfides, haloids, phosphates, carbon dioxide, water, etc.) components and containing a dissolved carbon in the state of labile oversaturations in respect to diamond. This conception is of importance for the chemical conditions of diamondite genesis as well.

This method of approach made it possible to realize first a formation of diamondites in carbonate – carbon and carbonate – silicate – carbon melts over their contacts with graphites at the high – pressure high – temperature experiments. Starting materials in the runs were block graphite (MGOSCH) of a spectroscopic purity and carbonate and carbonate – silicate materials. Among them, (1) multicomponent carbonate mixture of a model carbonatite composition for the fluid – bearing inclusions in Botswanian diamonds [4]: K_2CO_3 27.21, Na_2CO_3 2.89, $CaCO_3$ 26.91, $MgCO_3$ 17.35, $FeCO_3$ 25.63, wt. %; (2) carbonate – silicate rock of Chagatai complex, Uzbekistan – melanocratic carbonatite (sample 79 [7]) of the composition, wt. %: SiO_2 18.20, TiO_2 0.65, Al_2O_3 6.24, Fe_2O_3 14.37, FeO 4.20, MnO 0.23, MgO 3.65, CaO 29.40, Na_2O 0.29, K_2O 0.89, P_2O_5 0.43, H_2O 0.46, CO_2 20.90, SO_3 0.13, the sum 100.04) in the phase composition of which garnet and clinopyroxene appear together with carbonate of essentially calcite composition for the diamond stability conditions [8]; (3) limestone (lithographic stone) from Algeti, Georgia composed in general of carbonate of essentially calcite composition (which contains less than 5 wt. % of oxides and silicates).

The known methods are used in experiments [9]: high – pressure apparatus of an anvil – with – hole type with Algeti lithographic stone cell, a tube graphite heater of 5 mm diameter and 1 mm wall thickness which contemporaneously serves as an ampoule for the sample under study inside of it; initial pressure and temperature were determined with accuracies of $\pm$ 0.01 GPa and $\pm$ 20 $^{\circ}$C , respectively (for the specific experiments their change in time may not be under control). Chemical treatment of the polycrystalline diamonds to remove fragments of solidified carbonate melts was carried out with the use of HCl and HNO_3. The samples were studied by the methods of scanning electron microscopy and microprobe analyses (electron microscope CamScan, in the IEM RAS).

Spontaneous nucleation and rapid growth of polycrystalline blocks of diamond over the contacts of graphite and carbonate and carbonate – silicate melts were observed at pressures above 7.5 GPa. More than 80% of the mass of diamond polycrystals were formed in doing so. Recrystallization lasts for the run duration to 40 min. A micropicture of the polycrystalline microdiamond intergrowth (after chemical treatment) from the run with Algeti limestone melt is presented by the Fig. 1; a view from the outer contact of the graphite heater with the melt. The sample which is an experimental analogue of diamondite is composed with octahedral microcrystals and spinel twins of diamond. Their dimensions are variable in the 0, 2 – 20 micron limits. In the diamondite intergrowths, both full-faced and skeletal crystals takes part.
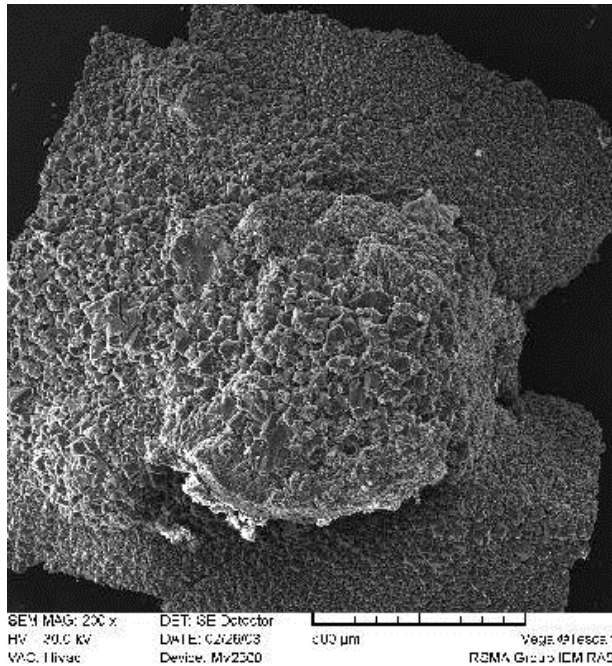
Fig. 1. Diamondite synthesized in carbonate-carbon melt (Algeti limestone is used); general view as viewed from an outer contact with graphite heater (sample. 937; 7.7 GPa; 1990°C, time duration 45 min).

The process of diamondite formation in the experiments above 7.5 GPa may be presented like this: in the heated to 1500 - 2000°C contact of graphite and carbonate, carbonate (mainly calcite) melt appears. The most effective rise of dissolved carbon concentration – in melt zone nearest to the contact with graphite. As soon as labile carbon concentrations are approached in these carbonate – carbon melts, a spontaneous nucleation of diamond with very high nucleus density happens (by calculations, a momentary nucleation density is no less than $5 - 10 \cdot 10^{4}$ nuclei in mm^{3}; thus a highest efficiency of diamond formation in carbonate and carbonate – silicate melts is obtained), and a thin polycrystalline diamond seeded layer forms in the interface between graphite and carbonate melt. The diamond seeded layer forms in several seconds after carbonate melt generation.

The subsequent scenario: over the graphite – melt contact, an intense dissolution of graphite and carbon transfer through a thin layer (or a melt – solution film of less than 100 micron thickness) to the diamond seeded layer is being continued allowing further diamondite crystallization and snowballing in size. In the process, most tiny crystals of diamondite intergrowths are formed (Fig. 2).
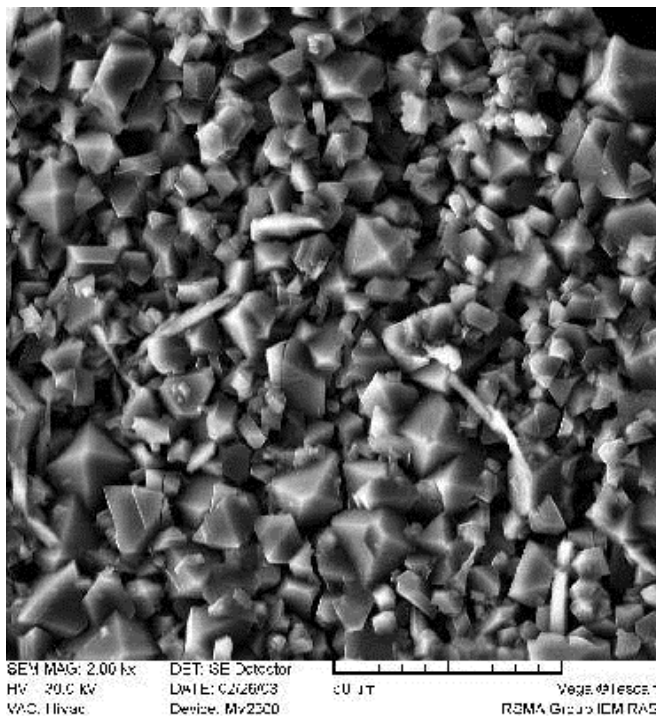

Fig. 2. Diamondite fragment from the zone of fine grained crystallization (sample 937; 7.7 GPa; 1990 ^{o}C, time duration 45 min).

It is of interest that judging from all a main moving force of recrystallization of metastable graphite into diamond in such a process is their solubility difference [9] in the acting carbonate melt because temperature gradients if even they exist over a melt film are obviously negligibly small.

A presentation of diamondite crystallization over the contact with the inner wall of graphite heater is given by the Fig. 3 for multicomponent carbonatite melt (which is compositionally similar to a boundary carbonatite constituent for the fluid – bearing inclusions in Botswanian diamonds) and Fig. 4 for carbonate – silicate melt of carbonatite of the Chagatai complex.
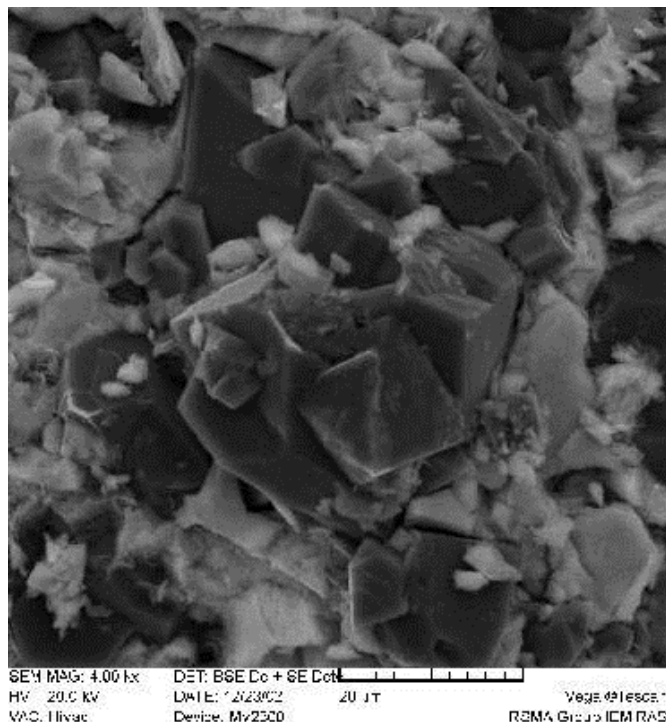

Рис. 3. Fragment of diamondite synthesized in multicomponent carbonate-carbon melt (a boundary carbonatite composition for the fluid–bearing carbonate–silicate inclusions in fibrous Botswanian diamonds is used) (sample 997; 8.0 GPa; 1990 ^{o}C; time duration 50 min).
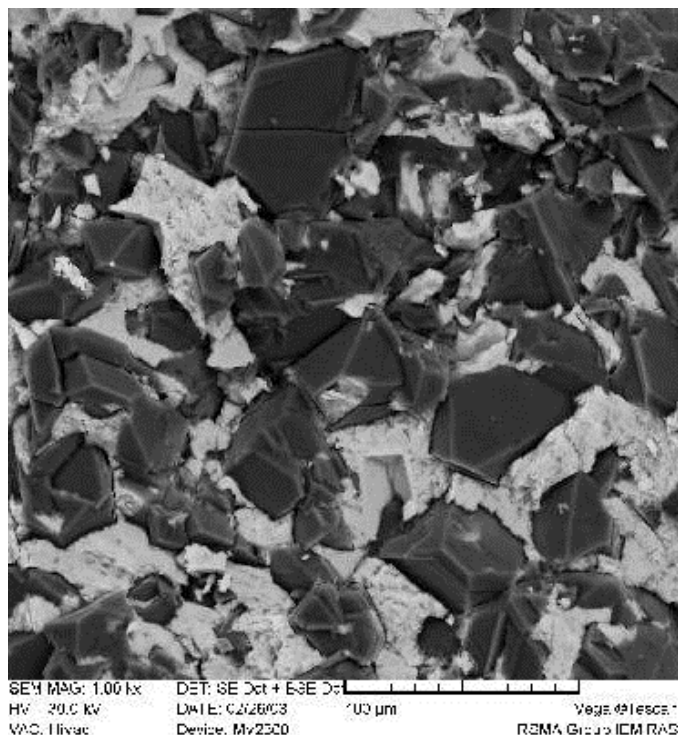

Рис. 4. Fragment of diamondite synthesized in a melt of the carbonate–silicate rock with carbon dissolved (melanocratic carbonatite of the Chagatai massif, Uzbekistan is used); the white material with garnets and clinopyroxenes–solidified and crystallized carbonate–silicate paternal melt (sample. 1007; 8.5 GPa; 1900°C, time duration 40 min).

In these cases, diamondites were not under a special chemical treatment; fragments of solidified parental melts - carbonate and carbonate – silicate, respectively, are presented. According to the study [8], there are garnets, clinopyroxenes, sulfides, etc. together with carbonates in the latter composition. The carbonate – silicate melts of Chagatai carbonatite rocks are of interest for modeling of parental carbonate – silicate diamond – forming media because they contain both carbonate and silicate major components and most interesting admixed ones in their compositions. Their use permitted to carry out experimental modeling of simultaneous crystallization of natural diamonds and minerals of syngenetic inclusions [7]. Their application for diamondite formation makes it possible to model the conditions of trapping syngenetic mineral inclusions (including garnets and clinopyroxenes of eclogite parageneses) by diamondites in the experiments. This work if the data of [7, 8] are taken into consideration shows that garnets and clinopyroxenes of eclogite parageneses are forming syngenetically with diamondites.

Thus, diamondite crystallization is first realized in carbonate – carbon and carbonate – silicate – carbon melts which compositions correspond to chemistry of natural parental media. Experimental data demonstrate a high efficiency of carbonate – carbon and carbonate – silicate – carbon melts with minimal contents of "fluid" and alkaline components or without these at all as parental media for diamondite formation. It should be taken into consideration along with it that a compositional variability in respect to the major and admixed components is characteristic for the parental carbonate – silicate melts. This is in connection with complicated petrological and geochemical conditions of their formation in the mantle peridotite substance combined with a subsequent evolution in the processes of fractional crystallization of silicate and carbonate minerals. Enhanced concentrations of alkaline and fluid components may appear at final stages of such an evolution.

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