Sulfide melts–graphite interaction at HPHT conditions: Implications for diamond genesis

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Abstract

The interaction of graphite with $(Fe,Ni)_9S_8$ and FeS sulfide melts has been studied at $P = 6.3–7.5$ GPa and $T = 1450–2200$ °C in experiments with a duration from 2 to 65 h. It has been found that both pentlandite and pyrrhotite melts interacting with graphite show similar behavior. At <7.5 GPa and 1450–1800 °C and at 7.5 GPa and <1600 °C carbon crystallizes predominantly as metastable graphite and to the minor extent as diamond on the seed crystals. Only at a pressure of 7.5 GPa and a temperature of 1600 °C and higher, sulfide melts provide spontaneous diamond nucleation at the melt–graphite interface and directly within carbon-saturated sulfide melt. In this case no metastable graphite was found in the products. Diamond crystals synthesized in the $(Fe,Ni)_9S_8$–C system were found to contain nitrogen impurity with concentrations of an order of 1000 ppm and exhibited IR absorption peaks due to hydrogen. The luminescence measurements revealed specific optical centers related to nickel impurity in the crystals. It is concluded that sulfide melts are less efficient diamond forming media as compared to carbonate, carbonate–silicate–fluid and fluid systems. The results of the study suggest that diamond nucleation from carbon-supersaturated sulfide melt as supposed in the sulfide model of diamond genesis seems improbable at the UHP conditions of the formation of most natural diamonds.
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1. Introduction

The origin of diamond represents one of the outstanding problems of modern Earth sciences. During the last 10–15 yrs convincing evidences have been obtained indicating a substantial role of metasomatic processes in diamond formation in the Earth's mantle [1–3]. At the same time, the question about diamond's crystallization environment still remains debatable. Based on the analysis of inclusions in diamond, it has been established that the composition of metasomatic melt/fluid may include volatile species of the C–H–O–N–S system, as well as silicates, carbonates, sulfides, chlorides, etc. This renders a great importance to the problem of recognizing the specific components of the diamond forming media, which are directly responsible for the nucleation and growth of diamond. The solution of this problem is indispensable for developing adequate models of diamond formation and is possible only with the attraction of methods of experimental modeling of diamond formation in different systems. With the lack of sufficient experimental research, most models of diamond formation assume *a priori* that *P–T* conditions corresponding to thermodynamical

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stability of diamond are sufficient for nucleation and growth of diamond in the mantle. However there are experimental data evidencing that this is not always the case and the problem is much more complicated than it was supposed in many models.

Of key importance for the experimental studies on diamond formation in modeling systems are syngenetic inclusions in diamond and deep seated xenolith, which are unambiguously recognized to be the main source of information about the mineralogy of the mantle (e.g. [4–7]). It has been established that sulfide minerals are the commonest among inclusions observed in diamond [6–17]. The history of the identification of inclusions is given in [10]. Detailed studies of sulfide minerals in diamonds and deep seated xenoliths have shown that most of them correspond in composition to the Fe–Ni–S system with minor to moderate amounts of Cu [2,7,13,18]. The review of the state-of-the-art data on geochemistry of sulfide inclusions and discussion on their paragenetic classification are presented in [18].

A number of facts including relatively low melting temperatures at high pressures [19,20], presence as abundant inclusions in diamond, and involvement of Fe and Ni, which are the well-known catalysts for diamond synthesis, served as the basis for the development of a concept of an essential role of sulfides in the natural diamond formation processes. One of the first studies in this line was made by Marx [21], who suggested a reaction between pyrrhotite and CO_2 as a possible mechanism of diamond formation. Haggerty [22] considered sulfur as a possible catalyst in the upper mantle reacting with hydrogen and carbon to produce different volatiles such as H_2S, COS or CS_2 and assumed the possibility of diamond crystallization from sulfide melts saturated with carbon. Based on the detailed study of sulfide inclusions in diamonds and xenoliths from Yakutia, it was concluded [11,23] that diamond crystallized from sulfide–silicate melt slightly oversaturated with carbon. Spetsius [24] also noted a special role of sulfide melts in diamond formation both in the field of thermodynamic stability of diamond and at metastable conditions. Taylor and Anand [2] suggested that in any scenario the C–O–H–N–S components must be accounted for the diamond-precipitating media.

Possible influence of sulfides on the diamond formation processes was considered in the analysis of metamorphic diamond genesis. It has been found that metamorphic micro-diamonds were associated with submicron-size metal sulfides from the UHP gneiss from Soxonian Erzgebirge in Germany [25]. Hwang et al. [26] have identified submicron metal sulfides, microdiamonds and phlogopite as multiphase inclusions in garnet of garnet–clinopyroxene–quartz crustal rock from the Kokchetav Massif in Kazakhstan.

The ideas of different authors above cited, taken as a whole, can be referred to as the sulfide model of diamond genesis, which represents one of the models of diamond formation currently developed. However, despite the sulfide model of diamond genesis has been broadly discussed in the literature, experimental studies on the interaction between sulfide melts and graphite under the mantle *P,T*-parameters are scarce and somewhat controversial in results.

Most of experimental investigations of sulfides under high pressures are concerned with the Fe–FeS system, since sulfur is considered as one of the most likely elements in the Earth core, which consists essentially of iron. The melting curve for FeS was determined by Ryzhenko and Kennedy [20] for pressures 1.8–3.8 GPa, Sharp [19] for 3.6–6.5 GPa and Boehler [27] for pressures up to 50 GPa. Wentorf [28] has studied the reactions of graphite with different sulfides including Cu_2S, ZnS and FeS at 6 GPa and 1400–1600 °C and concluded that sulfide melts correspond to graphite-forming solvents.

Recently synthesis of diamond in sulfide-carbon systems has been principally achieved [29] and studies into determining the conditions of diamond crystallization in these systems have started [30]. First results on diamond synthesis in the model carbonate–silicate–sulfide systems have been presented [31]. The results on diamond synthesis in the S–C system at 8–8.5 GPa and 1600–1800 °C
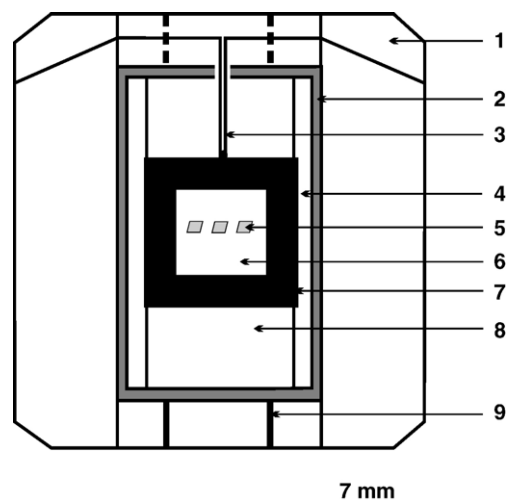

Fig. 1. The sample assembly used in the study: (1) container (ZrO_2 based pressure medium); (2) cylindrical graphite heater; (3) thermocouple; (4) MgO based insulating sleeve; (5) seed crystals; (6) sulfide; (7) graphite capsule; (8) ZrO_2 based pressure medium; (9) leads.
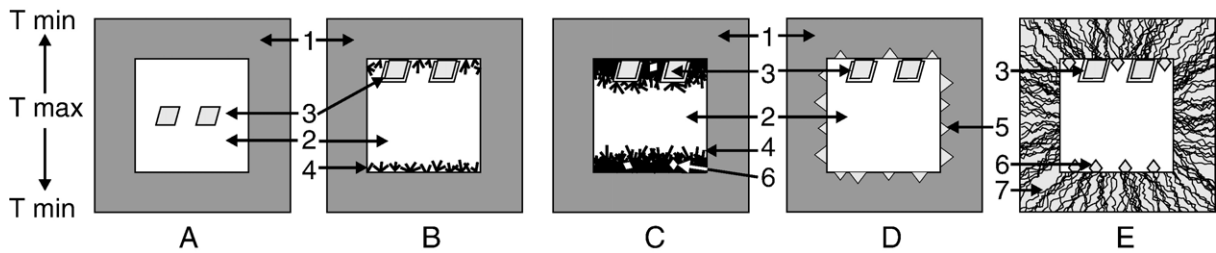
Fig. 2. The schemes of diamond and graphite crystallization in the sulfide melt–graphite system. A—initial capsule assembly; B, C, D, E—crystallization schemes observed at different $P-T$ conditions (see text for explanation). 1—Graphite capsule, 2—sulfide, 3—diamond seed crystals, 4—newly formed metastable graphite, 5—diamonds crystallized via FG*process, 6—diamonds crystallized via TGG* process, 7—polycrystalline diamond aggregate (FG-process) *FG and TGG refer to the film growth and temperature gradient growth processes, respectively. Although in both cases diamond crystallizes from carbon dissolved in the sulfide melt, driving forces for the crystallization are different. In the first case it is a difference in solubility of graphite and diamond in the sulfide melt at constant $P-T$ parameters. In the second case diamond crystallization is driven by the difference in solubility of diamond at the different temperatures within the thermal gradient field. The FG and TGG processes were first suggested by Kanda and Fukunaga [37] for metal–carbon systems. Later it was shown that these processes also take place in non-metallic systems [38].

[32] and at 7 GPa and 1750–1850 °C [33] may also be of interest for the sulfide model of diamond genesis.

Thus, investigations of inclusions in diamond and deep seated xenoliths evidence that sulfides were present in the mantle diamond forming media, but the existing experimental data do not permit to evaluate clearly the possible role of sulfides in natural diamond formation processes.

In the present work we report the results of the experimental study on the interaction of graphite with (Fe, Ni)$_9$S$_8$ and FeS sulfide melts, which can be regarded as model sulfide melts in the mantle. In order to assess the applicability of sulfide model to natural diamond formation, it is high of interest and importance to define the main factors controlling the nucleation and growth of diamond and also constrain the conditions of diamond and graphite crystallization form carbon solution in sulfide melts.

2. Experimental procedure

Experiments on the graphite–sulfide interaction were carried out using a multi-anvil high-pressure apparatus of a "split-sphere" type [34]. A high pressure cell (Fig. 1) had a shape of a tetragonal prism $19 \times 19 \times 22$ mm. The temperature was measured in each experiment using a PtRh$_{30}$/PtRh$_6$ thermocouple, whose junction was placed near the crystallization capsule. Details of the calibration of $P-T$ parameters have been presented elsewhere [35]. The starting materials were a graphite rod (99.99% purity) as the carbon source and crystallization capsule material, sulfide powder (pentlandite or pyrrhotite) and cube-octahedral synthetic diamond crystals ca 500 μm in size as the seed crystals. Graphite rod was machined into a capsule 7.2 mm in diameter and 7 mm high. Sulfide powder together with the seed crystals was pressed into a cylindrical sample and placed into the graphite capsule. The sample assembly is shown in Fig. 2A. Compositions of the initial sulfides are given in Tables 1 and 2. The experimental products were studied by X-ray and microprobe analyses. Formation of small diamond crystals was confirmed by Raman spectroscopy. Graphite and diamond were also studied using a scanning electron microscope (LEO 420).

Infrared (IR) absorption spectra of diamonds crystallized in the sulfide melts were measured using a Bruker Vertex 70 FTIR spectrophotometer fitted with a Hyperion 2000 microscope. Square apertures providing ca

Table 1
Composition of the initial pentlandite and sulfides in the run products

Wt. %	Initial pentlandite	MS-9						MS-4					
		Mss$_1$			Mss$_2$			Mss$_1$			Mss$_2$		
Fe	32.4	39.2	38.5	39.1	31.5	32.6	33.0	38.3	38.8	38.9	27.1	27.4	27.3
Ni	33.9	24.7	26.1	25.1	35.3	33.5	34.7	25.4	25.0	25.1	42.2	41.9	40.4
S	33.1	35.0	34.5	34.8	30.8	31.9	31.8	34.7	34.7	34.8	29.5	28.9	29.6
Co	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.4
Cu	0.1	0.3	0.3	0.3	0.9	0.3	0.6	0.3	0.3	0.3	0.5	0.3	0.9
Total	100	99.7	99.9	99.8	99.0	98.8	100,6	99.2	99.3	99.6	99.7	98.9	98.6

Table 2
Composition of the initial pyrrhotite and sulfides in the run products

Wt. %	Initial pyrrhotite	IS-1			IS-7			IS-11		
		Troilite			Troilite			Troilite		
Fe	62.6	63.6	63.5	62.8	63.5	62.9	62.8	62.9	62.3	62.8
Ni	0.1	0.3	0.3	0.1	0.2	0.1	0.1	0.2	0.2	0.2
S	37.1	35.7	35.6	36.9	36.0	36.8	37.0	36.7	36.9	37.2
Co	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cu	0.1	0.2	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1
Total	100	99.9	99.7	100	100	100	100.1	100	99.6	100.4

50×50 μm sampling area were applied. The absorption coefficients were determined from the intensity of the intrinsic two-phonon absorption of diamond. Concentrations of nitrogen impurities were derived from the infrared spectra using standard procedures [36]. The photoluminescence (PL) was measured at 80 K under excitation with an N_2 laser (337 nm) operated with a repetition frequency of 100 Hz. The PL spectra were recorded using an MDR-23 diffraction monochromator fitted with a 1200-grooves mm^{-1} grating. The signal was detected by a photomultiplier and a lock-in amplifier.

3. Experimental results

3.1. Diamond and graphite crystallization in the (Fe, Ni)$_9$S$_8$–C system

The results of experiments on the interaction between the sulfide melt of pentlandite composition and graphite are summarized in Table 3. At 6.3 GPa and 1450 °C the reaction was slow. In the run MS-1 with duration of 12 h only tiny (5–7 μm) metastable graphite crystals were found on the capsule walls. In a longer 65-h run larger

Table 3
Experimental results on the crystallization of diamond and graphite in the (Fe,Ni)$_9$S$_8$–C system

Run number	P (GPa)	T (°C)	Time (h)	Diamond nucleation		Diamond growth			Graphite crystallization	
				N(FG)	N(TGG)	D	h(111)	h(100)	G	Size (μm)
MS-1	6.3	1450	12	−	−	−	−	−	+	5–7
MS-2	6.3	1450	65	−	−	+	3	8	+	20–25
MS-3	7.0	1550	20	−	−	+	2	6	+	10–15
MS-4	7.0	1550	41	−	−	+	4	15	+	50–70
MS-5	7.0	1600	12	−	−	+	4	6	+	10
MS-6	7.0	1650	46	−	−	+	14	25	+	30–40
MS-7	7.0	1700	8.5	−	−	+	<1	7	+	20
MS-8	7.0	1800	15	−	−	+	2	10	+	15–20
MS-13	7.0	1900	16	−	+	+	18	40	+	300
MS-14	7.0	1900	40	−	+	+	20	70	+	500
MS-15	7.0	1950	4	−	−	+	6	20	+	30–50
MS-16	7.0	1950	40	−	+	+	33	125	+	700
MS-17	7.0	2000	20	−	+	+	34	125	+	500
MS-9	7.5	1550	18	−	−	+	4	8	+	10–15
MS-10	7.5	1600	15	+	−	+	*	*	−	
MS-11	7.5	1750	15.5	+	+	+	*	*	−	
MS-12	7.5	1800	12	+	+	+	*	*	−	
MS-18	7.5	1950	16	+	+	+	*	*	−	
MS-19	7.5	2200	2	+	+	+	*	*	−	

N(FG) (+)—nucleation of diamond by FG method was observed; (−)—not observed.
N(TGG) (+)—nucleation of diamond by TGG method was observed; (−)—not observed.
D (+)—growth of diamond on seeds was observed; (−)—not observed.
h(111) and h(100)—thickness of the diamond layer on seeds (μm).
G (+)—metastable graphite was observed; (−)—not observed.
*—diamond growth established, but sizes could not be determined due to high amounts of spontaneous crystals.

graphite crystals, up to 20–25 μm, and traces of diamond growth on the seed crystals were found. These results are schematically illustrated in Fig. 2B. As opposed to the initial capsule assembly (Fig. 2, scheme A) the seed crystals after the experiments were found in the upper part of the capsule that unambiguously evidence melting of the sulfide, that holds for all the experiments described in this paper.

At 7 GPa and temperatures in the range of 1550–1800 °C no diamond nucleation was established. Metastable graphite crystals formed druse aggregates in the "cold" parts of the capsules, indicating that the bulk of the melt was saturated with carbon. As temperature and duration increased the sizes and particularly the amount of graphite crystals increased accordingly (Table 3). The traces of diamond growth on the seed crystals were observed in all experiments. As a general tendency diamond growth rates on both [111] and [100] increased with the temperature. However, even at 1800 °C (MS-8) the maximum rate of diamond growth on the {100} faces was only 0.66 μm/h. It should be noted that the {100} faces of the seed crystals regenerated with the formation of pyramids built by the {111} micro-faces, sometimes

with minor {100} faces. Different stages of the regeneration of the cube-octahedral diamond seed crystals are shown in Fig. 3. The features of the regeneration were determined by the ratio of diamond growth rates on the {111} and {100} faces. As usual v_{100} was 2–3 times higher than v_{111}. No dissolution features were observed on the seed crystals, indicating that saturation of the sulfide melt with carbon was exclusively due to metastable phase—graphite of the capsule.

At higher temperatures in the range of 1900–2000 °C and pressure of 7 GPa (MS-13, 14, 15, 16, 17) the results correspond to scheme C in Fig. 2. In these runs a lot of relatively large (up to 500–700 μm) graphite crystals, diamond layers on the seeds and some individual spontaneous diamond crystals of 10 to 100 μm in size were found (except for the run MS-15 where the duration was only 4 h). Spontaneously nucleated diamonds were transparent, almost colorless and had octahedral habit.

AT 7.5 GPa and 1550 °C (MS-9) crystallization of metastable graphite and slight diamond growth on the seeds were established, that corresponds to scheme B in Fig. 2. The increase in the temperature for only 50 °C yielded principally different results corresponding to

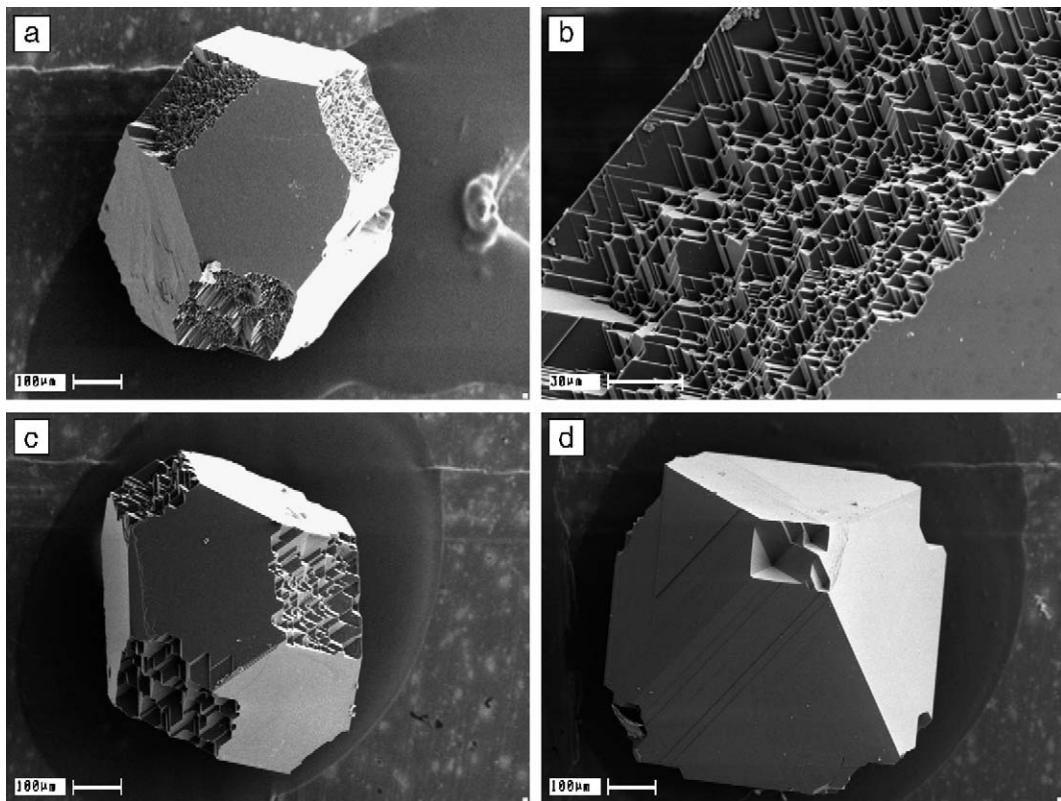Fig. 3. SEM micrographs of seed diamond crystals after the experiments in the (Fe,Ni)$_9$S$_8$–C system: (a) overall view and (b) growth patterns on the (100) face (run MS-17); (c) seed crystal from run MS-14; (d) seed crystal from run MS-16.

scheme D in Fig. 2. At 1600 °C (MS-10) no metastable graphite was observed and octahedral diamond crystals were found at the interface between sulfide melt and graphite capsule (Fig. 4a). An intensive spontaneous crystallization of diamond from carbon of the graphite capsule took place at higher temperatures with the experiment times of 12–16 h. For the runs MS-11, MS-12 and MS-18 conducted at 1750, 1800 and 1950 °C, respectively, the resultant crystallization scheme corresponds to Fig. 2E. In all these runs the degree of graphite-to-diamond conversion (α) was 100%. Diamond of black or gray color was present as a polycrystalline aggregate of octahedral crystals (Fig. 4b). Partial recrystallization of the diamond aggregate in the thermal gradient field resulted in the formation of colorless transparent diamond crystals in the cold parts of the capsule (Fig. 4c), which is schematically shown in Fig. 2E. At 2200 °C even 2 h was enough for diamond to crystallize in considerable amount, with the conversion degree (α) being 50%. In this case diamond crystals overgrowth were preferentially formed (Fig. 4d). No metastable graphite was observed in the experiments at 7.5 GPa and 1600–2200 °C.

The main phase of the quenched samples was mono-sulfide solid solution (mss_1) of pyrrhotite structure. Additionally small amounts of mss with violarite (Fe, Ni)$_3$S$_4$ structure was also present. Microprobe analysis revealed that the compositions of these mss phases differed considerably, approximately for 10–15 wt.% in Ni and Fe, and 5 wt.% in S. Throughout this series of experiments we did not find any differences in phase and chemical compositions of the samples from runs with either graphite or diamond synthesis.

To illustrate the effect of the temperature on diamond crystallization in the (Fe,Ni)$_9$S$_8$–C system Fig. 5 shows the dependence of diamond growth rates on the seeds upon the temperature for experiments conducted at 7 GPa. At 1550 °C the growth rate was very low and estimated to be approximately 0.1–0.2 and 0.3–0.35 μm/h for the (111) and (100) faces, respectively. The rate of diamond growth on the seeds in the metal–carbon systems at similar P–T conditions is about 10–150 μm/h [39], that is 2–3 orders of magnitude higher. At higher temperatures in the range of 1600–1800 °C the growth rate rose to 0.3 μm/h for the (111) faces and 0.8 μm/h for the (100) faces, and
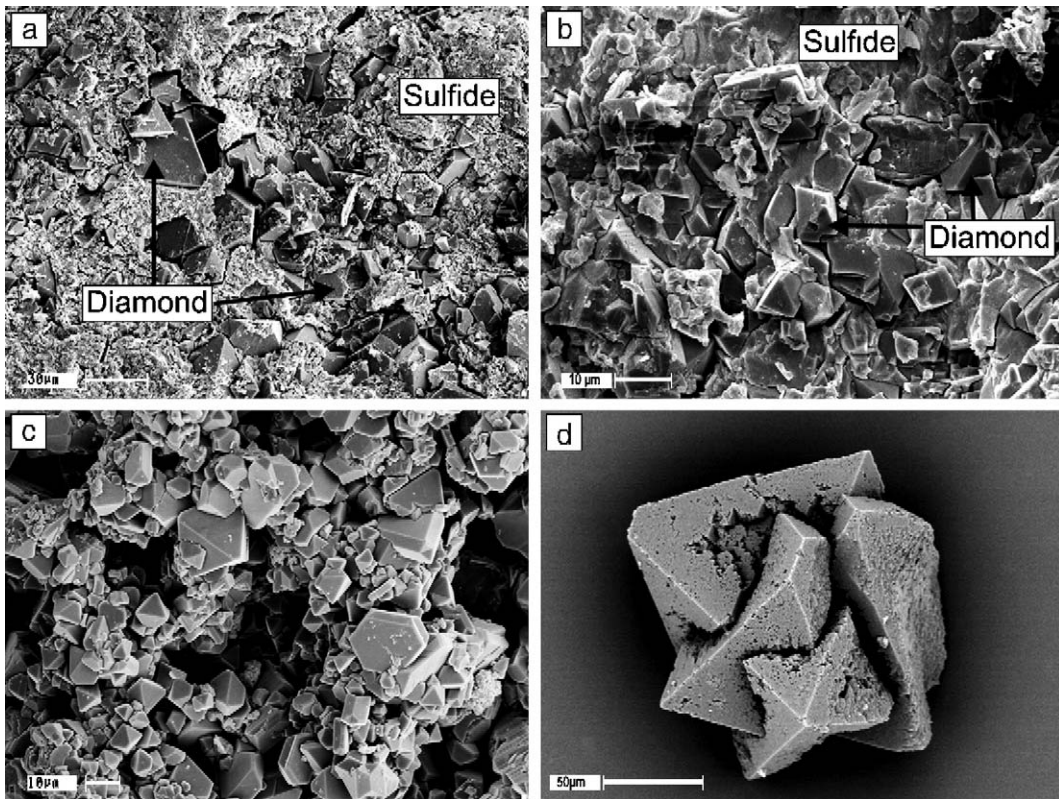

Fig. 4. SEM micrographs of spontaneous diamonds crystallized in the system (Fe,Ni)$_9$S$_8$–C: (a) diamond crystals (FG) at the sulfide–graphite interface (run MS-10); (b) diamond aggregate (FG) (run MS-12); (c) diamond crystals (TGG) cleaned from sulfide (run MS-11); (d) diamond crystals overgrowth (FG) (run MS-19).
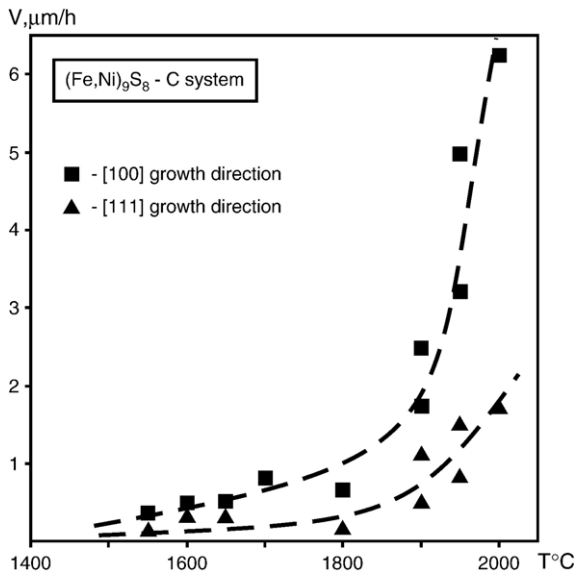
Fig. 5. The temperature dependence of the diamond growth rates in the (Fe, Ni)$_9$S$_8$–C system at 7 GPa.

starting from 1900 °C it sharply increased for several times, although the absolute values remained still low.

3.2. Diamond and graphite crystallization in the FeS–C system

In the second series of experiments we used pyrrhotite as the initial reagent, whereas sample assembly and experimental technique were the same as those for the

first series with pentlandite. The experimental results on diamond and graphite crystallization are given in Table 4. At pressures 6.3–7 GPa and temperatures 1500–1800 °C in experiments with duration from 8 to 65 h crystallization of metastable graphite and diamond growth on seeds with growth rates less than 1 μm/h were established. Spontaneous nucleation of diamond was not observed. The sizes and amount of metastable graphite crystals increased with the temperature. The results of the runs IS-1–IS-6 correspond to scheme B in Fig. 2. At 7.5 GPa and 1550 °C (IS-7) the results were similar and also correspond to scheme B. Significant changes were observed in the run IS-8 (7.5 GPa, 1600 °C), where recrystallized metastable graphite was absent and spontaneous diamond crystals were found at the interface between sulfide melt and graphite capsule (Fig. 6a). These results correspond to scheme D in Fig. 2. Fig. 6b shows a sulfide film with diamond imprints illustrating the FG process of diamond synthesis. At higher temperatures (IS-9, 10, 11) the intensity of the reaction between sulfide melt and graphite increased considerably. The graphite capsule converted into a polycrystalline diamond aggregate (Fig. 6c), as illustrated in Fig. 2E. The degree of graphite-to-diamond conversion was 70% and 100% in the runs IS-9 and IS-10, respectively. In a short 2-h run at 2200 °C (IS-11) approximately 20% of graphite converted to diamond. Similarly to the experiments with pentlandite, crystallization of diamond by the TGG process was possible on the polycrystalline diamond aggregate (Fig. 6d).

Table 4
Experimental results on the crystallization of diamond and graphite in the FeS–C system

Run number	P (GPa)	T (°C)	Time (h)	Diamond nucleation		Diamond growth			Graphite crystallization	
				N(FG)	N(TGG)	D	h(111)	h(100)	G	Size, μm
IS-1	6.3	1500	65	−	−	+	2	6	+	20–25
IS-2	7.0	1550	40	−	−	+	2–4	20	+	25
IS-3	7.0	1600	12	−	−	+	3–4	6	+	15
IS-4	7.0	1650	45	−	−	+	4–6	20	+	25–35
IS-5	7.0	1700	8	−	−	+	2	6–8	+	15–20
IS-6	7.0	1800	15	−	−	+	2–4	15	+	15–20
IS-7	7.5	1550	20	−	−	+	2–4	6–8	+	10
IS-8	7.5	1600	15	+	−	+	*	*	−	
IS-9	7.5	1750	15	+	+	+	*	*	−	
IS-10	7.5	1950	15	+	+	+	*	*	−	
IS-11	7.5	2200	2	+	+	+	*	*	−	

N(FG) (+)—nucleation of diamond by FG method was observed; (−)—not observed.
N(TGG) (+)—nucleation of diamond by TGG method was observed; (−)—not observed.
D (+)—growth of diamond on seeds was observed; (−)—not observed.
h(111) and h(100)—thickness of the diamond layer on seeds (μm).
G (+)—metastable graphite was observed; (−)—not observed.
*—diamond growth established, but sizes could not be determined due to high amounts of spontaneous crystals.
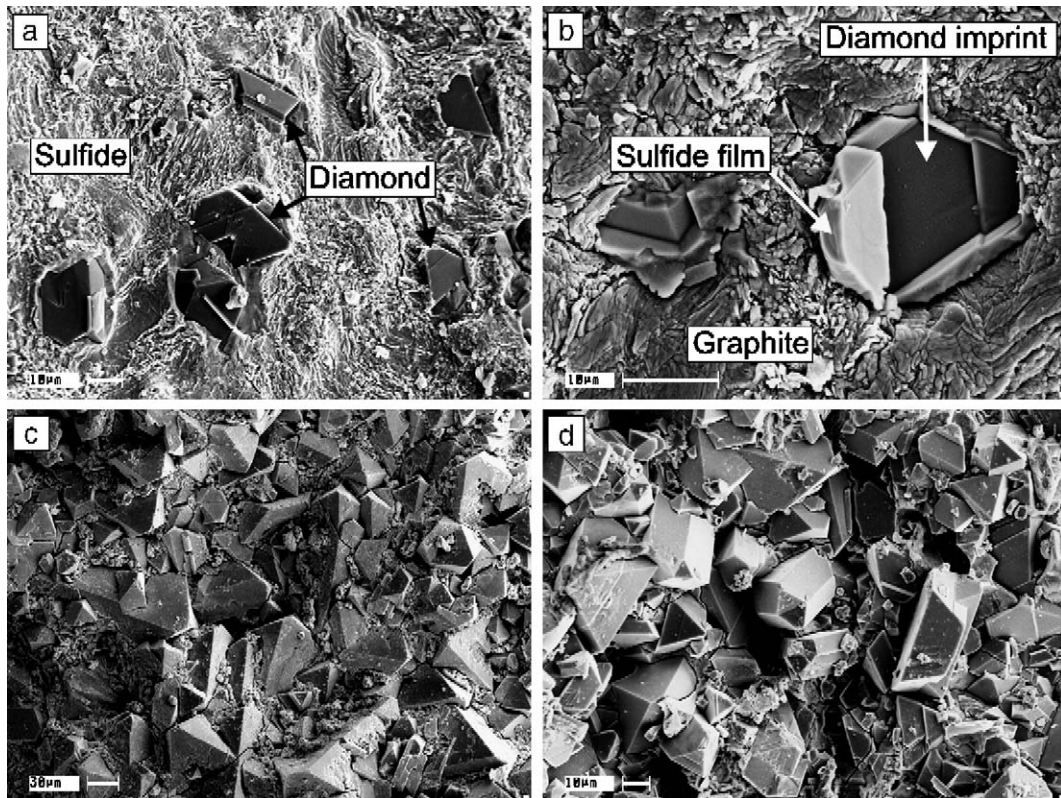
Fig. 6. SEM micrographs of spontaneous diamonds crystallized in the system FeS–C: (a) diamond crystals (FG) at the sulfide–graphite interface (run IS-8); (b) imprints of diamond crystals in graphite (run IS-8); (c) a diamond aggregate (FG) (run IS-9); (d) diamond crystals (TGG) cleaned from sulfide (run IS-9).

X-ray analysis showed that the samples of quenched sulfide melt were composed of troilite. Depending on the growth conditions X-ray patterns also exhibited reflexes of graphite and/or diamond (Table 4). Microprobe analysis of the sulfide phase did not reveal any considerable inhomogeneity over the samples (Table 2). An interesting feature of all the samples was that the troilite was somewhat depleted with sulfur and enriched with iron relatively to the initial composition. However, no new phases were observed for the whole series of experiments and the composition of the quenched sulfide melts did not vary, regardless of whether diamond or metastable graphite crystallized in the runs.

3.3. Spectroscopic characterization

For the spectroscopic characterization a number of spontaneous diamond crystals were selected from runs MS-13 and MS-14. Fig. 7 shows typical IR spectra recorded. Most of the spectra were somewhat distorted due to small sizes, rough surfaces and low quality of the crystals, that, however, did not hinder their interpretation and impurity content estimations. As it follows from the spectra the one-phonon defect-induced absorption is dominated by a band of A-aggregates of nitrogen (pairs of nitrogen atoms on the nearest-neighboring substitutional sites). The concentrations of nitrogen for the spectra presented in Fig. 7 were estimated as 850 and 1100 ppm, these were typical average values for the samples studied. The predominance of A-form nitrogen is obviously a consequence of relatively high crystallization temperatures. Of particular interest is that the nitrogen content in these crystals is considerably higher than that typical of diamonds grown in the conventional metal–carbon systems. This apparently is a characteristic feature of diamonds synthesized in a variety of non-metallic systems [40–44]. Another feature present in the IR spectra is a sharp absorption peak at 3107 cm^{-1}. As is known this absorption peak is due to hydrogen-related defects and commonly observed in natural type Ia diamonds. For the crystals studied the intensity of the 3107 cm^{-1} peak was in the range 5–20 cm^{-1} and seemed to correlate with nitrogen concentration. Recent studies on diamonds crystallized in non-metallic systems

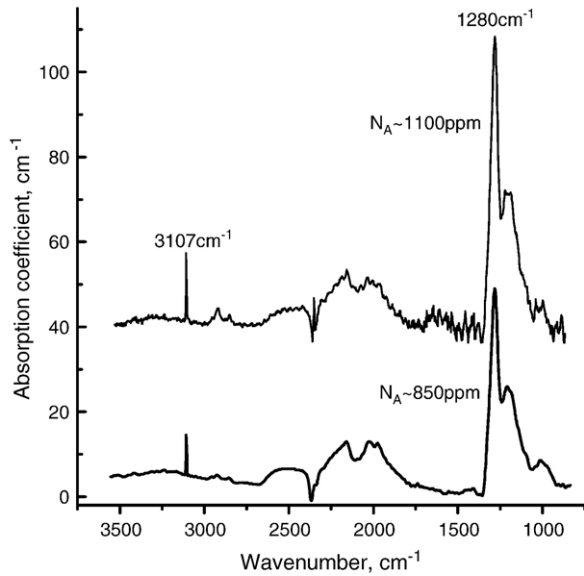Fig. 7. Infrared absorption spectra of diamond crystals synthesized in the (Fe,Ni)$_9$S$_8$–C system. The spectra have been displaced for clarity.

Fig. 9. Experimental data on diamond and graphite crystallization in sulfide and sulfur melts.

showed that the 3107 cm^{-1} hydrogen-related peak was commonly observed in the IR spectra, providing nitrogen concentrations in the samples was relatively high [41–44].

Photoluminescence spectra were recorded for the same diamond crystals as for the FTIR measurements. All the samples under UV laser excitation showed relatively intense yellowish-green emission. No significant sample-depended variations were observed in the spectra and the representative PL spectrum is shown in Fig. 8. It consists of a number of vibronic bands with zero-phonon lines (ZPLs) at 2.56, 2.49 and 2.37 eV and
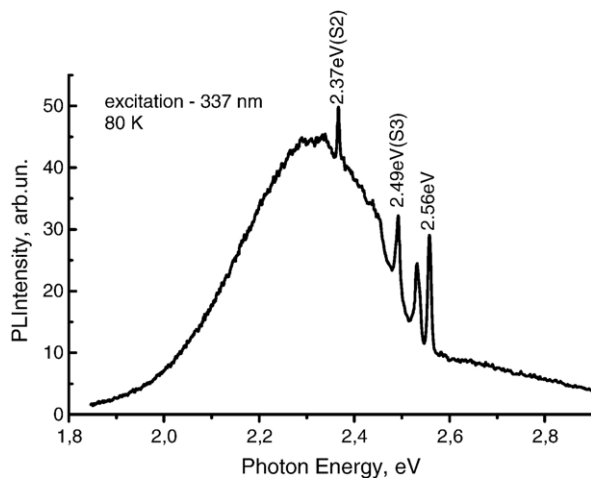
accompanying phonon sidebands. All these vibronic systems are due to the well-known nickel-related centers, characteristic of synthetic diamonds grown with nickel-containing solvent-catalysts [45]. The PL systems with ZPLs at 2.49 and 2.37 eV correspond to so-called S3 and S2 centers, which are frequently observed in some natural diamonds. These centers are due to nickel–nitrogen complex defects, which form during the nitrogen aggregation process.

4. Discussion of the experimental results and implication for the diamond genesis

In the present study we found that pentlandite and pyrrhotite melts reacting with graphite show similar behavior. This allows us to discuss on the main regularities of the interaction of sulfide melts with graphite in a wide range of P–T parameters and also ascertain the features of diamond and graphite formation in these systems.

The sulfide melts studied when reacting with carbon at temperatures in the range of 1450–1800 °C and pressures up to 7 GPa are capable of providing dissolution and transport of carbon. However, long reaction times are necessary for the carbon phases (metastable graphite and diamond growth layers on the seeds) to form in significant amounts. Even at relatively high temperatures (1600–1800 °C at 7 GPa) the amount of metastable graphite was small. This indicates that the sulfide melts have low carbon solubility, as well as low ability for carbon transport. Low solubility of carbon is also attested by the fact that no quenching graphite or other carbon phases were observed in sulfides after the

Fig. 8. Typical PL spectrum recorded at 80 K of diamond crystals synthesized in the (Fe, Ni)$_9$S$_8$–C system.

experiments. Our inference on the low solubility of carbon in the sulfide melts is in good agreement with the experimental results of Wang et al. [46] obtained for the Fe–S–C system at 1200–1600 °C.

At temperatures 1450–1800 °C and pressures up to 7 GPa carbon dissolved in sulfide melts crystallizes preferentially as metastable graphite and only small fraction of carbon deposits as diamond on the seed crystals. Only at 7.5 GPa and temperatures in the range of 1600–1800 °C sulfide melts provide spontaneous nucleation of diamond at the melt–graphite interface, with no metastable graphite being formed. Since chemical and phase compositions of the quenched sulfides from the runs both with and without diamond nucleation did not show significant variations, one may suppose the changes of some structural properties of the sulfide melt, which favor the crystallization of carbon in sp^2 and sp^3 forms at low and high $P–T$ conditions, respectively.

The results obtained in this study evidence that the metastable graphite cannot be considered as an intermediate carbon phase preceding diamond formation, since at 7.5 GPa and ≥ 1600 °C no metastable graphite was found. This finding implies that the interpretation of the $P–T$ conditions of formation of natural diamonds containing sulfide and graphite inclusions should be made with caution. Based on the experimental data we may suggest that such graphite is most probably a metastable phase captured by diamond together with sulfide melt. It should be noted that crystallization of metastable graphite at the $P–T$ parameters of thermodynamical stability of diamond was previously observed for a number of non-metallic solvents, such as alkali halides [47], fluid-containing carbonates [48], C–O–H fluids [49,50] and for carbonate–silicate interactions [41,51,52]. The reasons for this phenomenon are still not well understood.

Our results confirm the possibility of diamond crystallization from carbon solution in sulfide melts under high $P–T$ conditions, that principally agrees with the sulfide model of diamond genesis. However, it is of particular importance to discuss on the boundary conditions of the sulfide model applicability and compare these conditions with the data for other potential diamond-forming media. Fig. 9 presents experimental data on diamond and graphite crystallization in sulfide melts obtained in previous works and present study. It is evident that diamond nucleation directly from carbon saturated sulfide melts under conditions corresponding to those ascribed for the majority of natural diamonds (5–6 GPa, 900–1400 °C) seems unlikely. The experimentally determined $P–T$ parameters of diamond nucleation in sulfide melts, which are not less than 1600 °C at 7.5 GPa,

could be admissible for diamonds from the lower part of the asthenosphere [53–56].

It should also be noted that the minimal temperature of diamond synthesis in the studied sulfide–carbon systems is considerably higher than melting temperature of sulfides. Consequently, addition of components capable of reducing sulfide's melting temperature (e.g. copper) does not seem to decrease the $P–T$ parameters of diamond nucleation in these systems.

Comparing the results of this study with previously published data on diamond crystallization in carbonate [35,38,48], carbonate–chloride [57], fluid [49,50] and carbonate–silicate–fluid [41,52] systems one may conclude that sulfide melts are less efficient as possible media for diamond formation under the mantle conditions. It will suffice to note that the minimal $P–T$ parameters of diamond nucleation in the alkaline carbonate fluids are 5.7 GPa and 1150 °C [48], whereas for the $(Fe,Ni)_9S_8$–C and FeS–C systems these are 7.5 GPa and 1600 °C. However, it should be borne in mind that only relatively simple sulfide–carbon systems (sulfide melt + graphite) were considered in the present study. Natural diamond forming media are more complex and, as shown in a number of studies [58–60], involve fluids. Diamond formation in the mantle may be due to redox reactions [22,61,62]. Experimental evidences of diamond crystallization in the result of reactions of carbon reduction have been presented in [41,51,52,63]. For diamond formation from carbon of carbonates or CO_2 sulfides could be most probable reducing agents. In this case the role of sulfides in natural diamond crystallization may appear in reactions with their participation. For example, the reaction $2FeS + CO_2 = 2FeO + S_2 + C$ suggested by Marx [21] has not been studied experimentally yet. The complexity in experimental realization of such reactions is caused by the involvement of fluids.

5. Conclusions

(1) Interaction of graphite with pyrrhotite and pentlandite melts, modeling the composition of the mantle sulfides, follows common regularities. At pressures lower than 7.5 GPa and 1450–1800 °C and at 7.5 GPa and temperatures lower than 1600 °C carbon crystallizes predominantly as metastable graphite and to the minor extent as diamond on the seed crystals.

(2) The minimal $P–T$ parameters for spontaneous diamond nucleation in the FeS and $(Fe, Ni)_9S_8$ sulfide melts are 7.5 GPa and 1600 °C.

(3) The metastable graphite cannot be considered exclusively as a carbon phase preceding diamond

formation and the interpretation of the P–T conditions of formation of natural diamond containing sulfide and graphite inclusions should be made with caution.

(4) The stable growth form of diamond in sulfide melts of pentlandite and pyrrhotite compositions is octahedron and does not depend on the P–T parameters.

(5) Diamond crystals synthesized in the $(Fe,Ni)_9S_8$–C system contain nitrogen impurity with concentration of order of 1000 ppm and exhibit hydrogen-related IR absorption. Specific Ni-related optical centers were revealed in the photoluminescence, which confirms the possibility of Ni incorporation in diamonds from sulfide melts.

(6) Sulfide melts are less efficient diamond forming media as compared to carbonate, carbonate–silicate–fluid and fluid systems. However the role of sulfides in the diamond genesis may appear in their reactions with fluids, which have not been studied experimentally yet.

Acknowledgements

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