ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 4, pp. 399–404. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © V.M. Sonin, E.I. Zhimulev, V.P. Afanas'ev, I.I. Fedorov, A.I. Chepurov, 2007, published in Geokhimiya, 2007, No. 4, pp. 450–455.

SHORT COMMUNICATIONS

Diamond Interaction with Silicate Melts in a Hydrogen Atmosphere

V. M. Sonin, E. I. Zhimulev, V. P. Afanas'ev, I. I. Fedorov, and A. I. Chepurov

Instititute of Geology and Mineralogy, Siberian Division, Russian Academy of Sciences, pr. Akademika Koptyuga 3, Novosibirsk, 630090 Russia

e-mail: sonin@uiggm.nsc.ru

Received February 13, 2006

DOI: 10.1134/S0016702907040076

INTRODUCTION

Diamond crystals from different bedrock sources have specific typomorphic features, which are controlled by the conditions of growth (physical and structural characteristics, trace element composition, etc.) and postgrowth transformations. The latter are most distinctly expressed in changes in crystal morphology (dissolution patterns) [1]. The relation of certain macro- and micromorphological features of crystals to dissolution can be convincingly supported by the experimental reproduction of their analogues [2, 3]. The genesis of rounded diamonds was hotly debated until they were produced by high-pressure etching of initially flat-faced crystals in silicate melt in the presence of water–carbon dioxide fluid [4, 5]. At present, an important problem is not only the simulation of natural forms and sculptures on diamond crystals during etching but also the determination of the boundary physicochemical conditions of their appearance.

According to current concepts, diamonds from main bedrock sources, kimberlites (lamporites), crystallized in the mantle. The Earth's mantle is heterogeneous in terms of the redox potential and fluid regime. At high oxygen fugacity, the composition of the fluid is dominated by H_2O and CO_2, and carbonate phases are stable; however, there is evidence for the existence of mantle domains with low oxygen fugacity providing the prevalence of H_2 and CH_4 in the fluid and stability of free carbon [6–11]. Magmas can be generated in the presence of both hydrogen–methane and water–carbon dioxide fluid, which must probably be reflected in the post-growth transformations of diamond crystals during their transportation into the upper lithosphere. However, the stability of diamond and the character of its etching in silicate melts in the presence of hydrogen–methane fluid were never studied. It is known that at temperatures less than 1300°C, hydrogen reacts with diamond only in the presence of catalysts: free transition metals (elements with incompletely filled *d*-shells) [12, 13]. According to available data, diamond shows no interaction with the melts of alkali carbonates and hydroxides in a hydrogen atmosphere [14].

Diamond etching in silicate melts can be simulated to a first approximation at atmospheric pressure. This paper reports the results of experimental interaction of diamond crystals with silicate melts in a hydrogen atmosphere. The goal of this study was to evaluate the possibility of diamond etching in natural systems under reducing conditions.

METHODS

Experiments were performed in a specially designed microscopic thermal stage with internal heating, water cooling, and a window for visual observation using a method described elsewhere [15]. The furnace was made from a molybdenum wire. Temperature was monitored by a W–Re thermocouple with an accuracy of ±5°C. The sample was placed on a ceramic base in the center of the heated volume. The process was observed using a binocular microscope.

The experiments were conducted with natural and synthetic diamonds of octahedral habit 10–20 mg in weight. The synthetic diamonds were grown in the field of diamond thermodynamic stability by the method of recrystallization in the Fe–Ni–C system [16].

The diamonds were etched by a melt of a natural basaltic glass of the following composition (wt %): 47.0 SiO_2, 2.20 TiO_2, 16.3 Al_2O_3, 3.79 Fe_2O_3, 8.12 FeO, 0.15 MnO, 6.4 CaO, 4.55 MgO, 5.69 Na_2O, and 5.0 K_2O and a synthetic melt consisting of 20 wt % Na_2O, 40 wt % B_2O_3, and 40 wt % SiO_2. The latter composi-

tion was prepared by fusing preliminarily dried high-purity SiO_2 and Na_2CO_3 and reagent-grade B_2O_3.

Since the experiments were performed under strongly reducing conditions, the ampoule problem was eliminated by placing silicate glass particles directly on a diamond face. During the experiments, the silicate glass was melted and occurred as drops on diamond crystals. Visual observation allowed direct estimation of the extent of the diamond interaction with the silicate melt. The experiments were performed in a flow of hydrogen, which was produced by an SGS-2 generator and conveyed into the thermal stage with a rate of 3 l/h. Wet hydrogen was produced by preliminarily passing it through distilled water at room temperature (partial pressure of water vapor of 3×10^{-2} kPa).

The experiments were carried out at 1100°C and lasted up to 60 min, but every 10–15 min the samples were quenched and examined in detail at high magnification under an MBS-15 microscope. The diamond crystals were also studied using a LEO 1430VP scanning electron microscope equipped with an EDX OXFORD energy-dispersive system running in a back-scattered mode.

RESULTS AND DISCUSSION

The Fe-free silicate glass was synthesized by fusing the components in air. In experiments with this glass in a dry hydrogen atmosphere, numerous small gas bubbles appeared beneath the silicate melt drops over the entire contact area with the diamond after heating for 15 min. When the desired temperature was attained, the bubbles inflated and burst. These bubbles were probably formed owing to the presence of air entrapped by the melt during the preparation of the starting glasses. One to three gas bubbles with a lifetime of up to 5 minutes were simultaneously observed. During the repeated heating of the diamond crystals with a silicate globule fused in a hydrogen atmosphere, no gas bubbles were formed.

After the experiments (1 hour), the crystals showed no change in weight and surface morphology. The faces remained lustrous both beneath the silicate melt and over the entire diamond area; i.e., no traces of diamond etching were found. The contact surface between the silicate globule and the crystal face also remained flat and lustrous with imprints of irregularities and micromorphological sculptures present on the face prior to the experiment.

Experiments performed in a wet hydrogen atmosphere yielded the same results. Thus, the silicate melt of the Na_2O–B_2O_3–SiO_2 composition does not interact with diamond in the presence of wet hydrogen.

Different results were obtained in the basalt–hydrogen system, which was caused by the presence of iron in the silicate melt. In a hydrogen atmosphere, iron contained in the melt was reduced to a free state. It occurred on the surface of silicate globules as tabular hexagonal grains and tiny particles grouped in "convective jets." Irregular cavities were formed beneath relatively large (tenths of a millimeter and larger) drops of silicate melt on the faces of diamond crystals. The depth of the cavities depended on the duration of the experiments.

The energy-dispersive spectra of silicate glass particles support silicate melt differentiation and iron reduction and aggregation during the experiments. Figure 1 exemplifies the section of a basaltic glass globule, which was cooled directly on the diamond face after a 10-min experiment, and the EDS patterns of its zones. The light areas in the section correspond to iron segregations. This indicates that the hydrogen-mediated differentiation of the basaltic melt occurred already during the first minutes of the experiments, which is even more clearly seen in Fig. 2.

When smaller basaltic particles (powder) were applied to the diamond surface, flat-bottomed etch pits of complex shape were formed. It is noteworthy that the individual etch pits often showed triangular outlines and were oriented opposite to the triangular faces of the octahedra (Fig. 3). Some etch pits acquired truncated triangular or hexagonal shapes. Each pit contained a sphere of solidified silicate glass, the size of which positively correlated with the linear size of the etch pits. In addition, the size and depth of the etch pits depended on the duration of the experiments. For example, heating of a diamond crystal for 15 and 60 min resulted in the formation of etch pits up to 0.04 and 0.08 mm across and 0.2 and 0.42 mm deep, respectively.

The etch pits formed in these conditions are similar in appearance to trigons known on natural diamonds. However, there are some differences. The experimental pits are always flat-bottomed, whereas natural diamonds contain pits of several morphological types (pyramidal and truncated pyramidal), their linear contours are disturbed with increasing size, and the seemingly flat bottom consists of a few fragments with curved margins.

Thus, diamond etching by Fe-bearing silicate melt was caused by interaction with iron, which is reduced from the melt in a hydrogen atmosphere and adheres

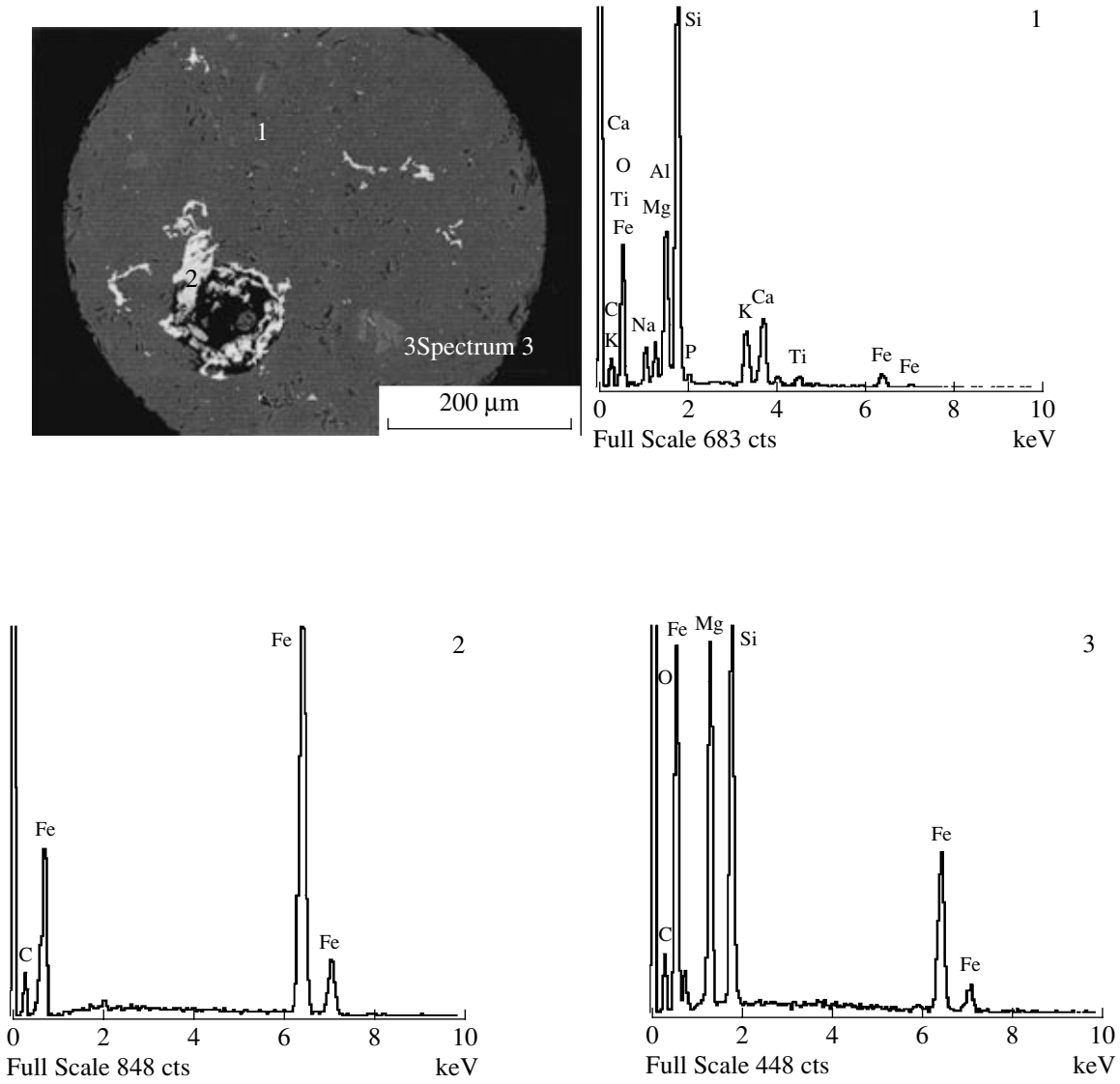
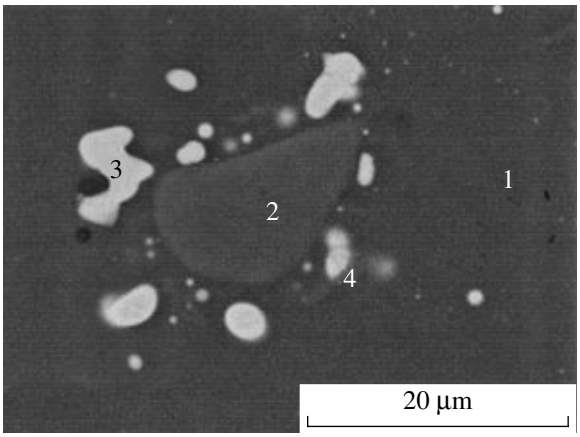


Fig. 1. Image and energy-dispersive spectra of a polished basaltic globule, which was melted on a diamond face in a hydrogen atmosphere at1100°C for 10 minutes.

more strongly to diamond than the silicate melt. Figure 4 shows the surface of a diamond crystal after its 10-min interaction with basalt, which was applied as a powder and mechanically removed after the experiment. The etch surface consists of numerous adjoining flat-bottomed etch pits. The EDS patterns of the diamond surface show the presence of Fe in the etch pit. The presence of Cu in the spectrums is presumably related to the fact that the remelted basaltic powder was removed with a copper needle.

An increase in the sizes of the pits and cavities with increasing experimental duration indicates that the etching is not controlled by carbon solubility in iron but is promoted by the catalytic hydrogenation of diamond. It is known that iron is the most efficient catalyst of this process [17, 18]. The process was accompanied by the blackening of etch patterns owing to surface graphitization. It was found that the etch patterns, including triangular and hexagonal ones, were formed at temperatures below the iron–carbon eutectics (1153°C). It should be noted that the character of the etching of natural and synthetic diamonds is similar under the aforementioned conditions.



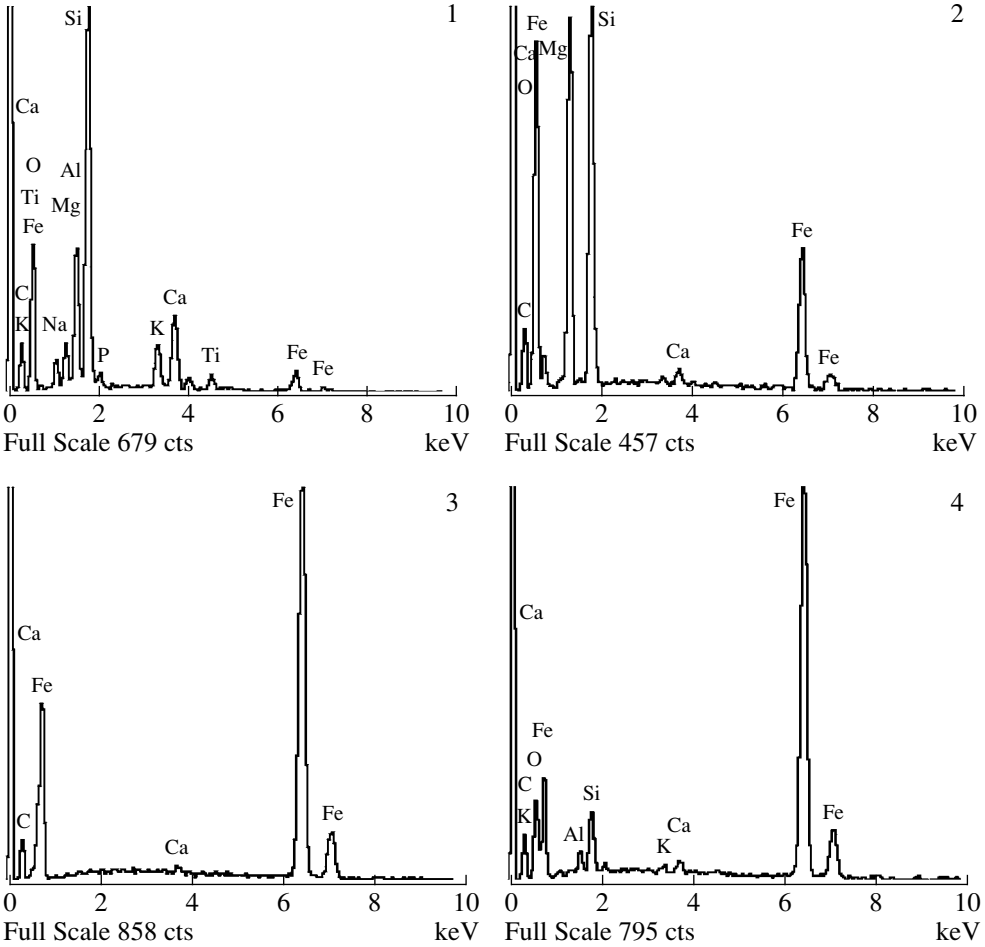


Fig. 2. Images and energy-dispersive spectra of a fragment of a polished basaltic globule, which was melted on a diamond face in a hydrogen atmosphere at 1100°C for 20 minutes.

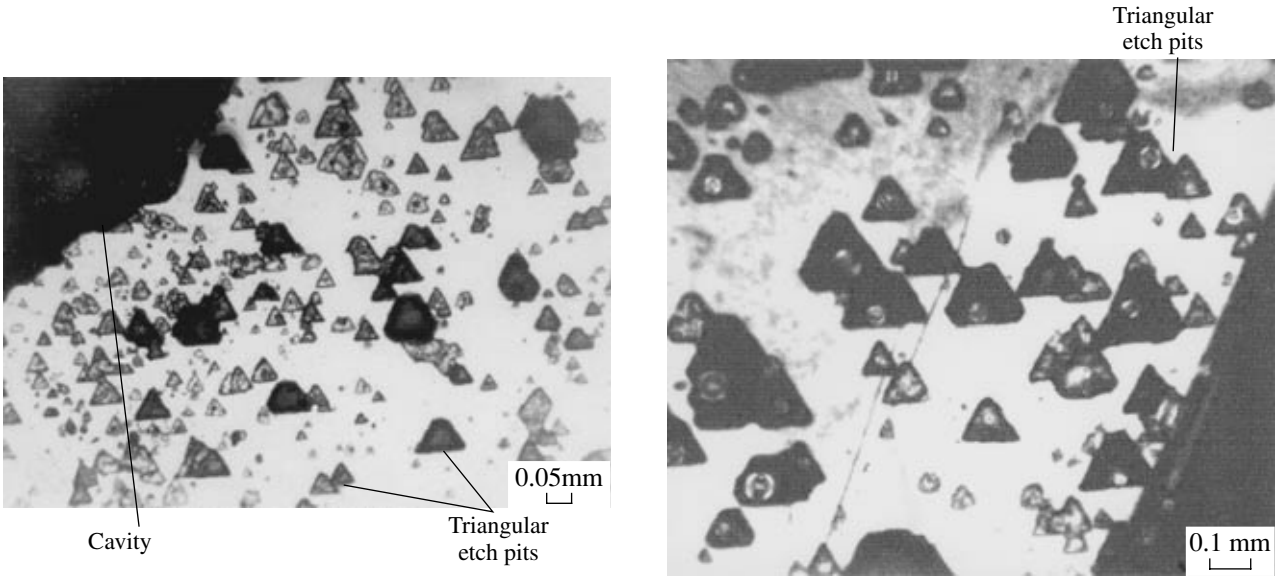


Fig. 3. Etch pits on an octahedral diamond face after its interaction with molten basaltic particles in a hydrogen atmosphere.

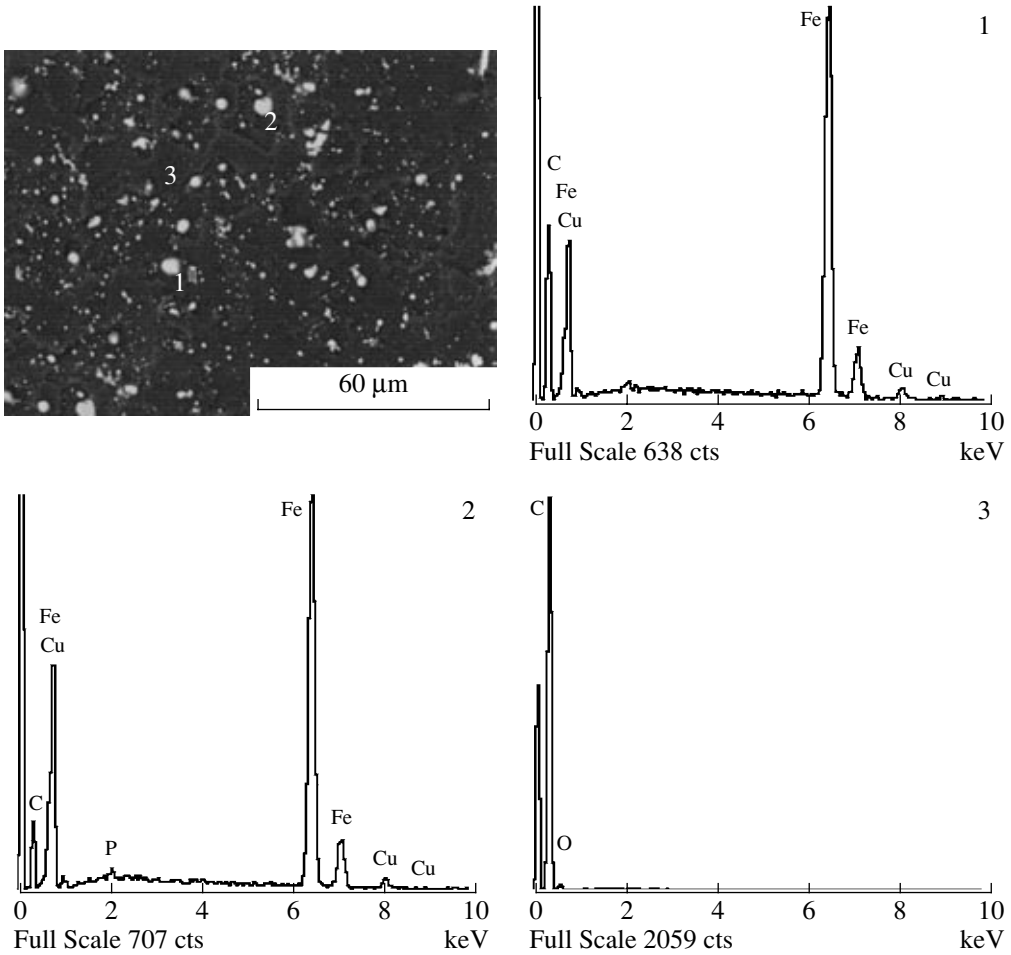


Fig. 4. Image and energy-dispersive spectra of the etch surface of a diamond crystal after its interaction with basaltic melt in a hydrogen atmosphere at 1100°C for 10 minutes.

CONCLUSIONS

The following conclusions can be drawn from our study.

Iron-free silicate melt does not interact with diamond in a hydrogen atmosphere. Iron-bearing silicate melt interacts with diamond through hydrogenation catalyzed by free iron, that is reduced from silicate melt. Therefore, the morphology of diamond crystals produced by etching in the aforementioned conditions is controlled by local interaction with iron aggregations.

This micromorphological study of diamond crystals and previous data on iron–diamond interaction (without silicate melt) [15, 18–22] indicate that natural diamonds, at least those borne by kimberlites, were probably not affected by dissolution under reducing conditions. Alternatively, the morphological evidence of this process could be eliminated by subsequent dissolution in a medium with more oxidizing conditions in the presence of water–carbon dioxide fluid. Further experiments on diamond etching in iron-bearing silicate melt in a hydrogen environment are required to answer this question.

REFERENCES

1. V. N. Kvasnitsa, N. N. Zinchuk, and V. I. Koptil', *Typomorphism of Diamond Microcrystals* (OOO Nedra-Biznestsentr, Moscow, 1999) [in Russian].
2. V. N. Kvasnitsa, *Small Diamonds* (Nauk. Dumka, Kiev, 1985) [in Russian].
3. Z. V. Bartoshinskii and V. N. Kvasnitsa, *Crystal Morphology of Diamond from Kimberlites* (Nauk. Dumka, Kiev, 1991) [in Russian].
4. A. I. Chepurov, A. F. Khokhryakov, V. M. Sonin, et al., "On the Patterns of Diamond Crystal Dissolution in Silicate Melts in the Presence of Essentially Aqueous Fluid at High *P–T* Parameters," Dokl. Akad. Nauk SSSR **285**, 212–216 (1985).
5. V. M. Sonin, E. I. Zhimulev, I. I. Fedorov, and N. Yu. Osorgin, "Etching of Diamond Crystals in Silicate Melt in the Presence of Aqueous Fluid under High *P–T* Parameters," Geokhimiya, No. 4, 451–455 (1997) [Geochem. Int. **35**, 393–397 (1997)].
6. A. A. Kadik and O. A. Lukanin, *Upper Mantle Degassing during Melting* (Nauka, Moscow, 1986) [in Russian].
7. I. D. Ryabchikov, *Geochemical Evolution of the Earth's Mantle* (Nauka, Moscow, 1988) [in Russian].
8. R. J. Arculus and J. W. Delano, "Oxidation State of the Upper Mantle: Present Conditions, Evolutions, and Controls," in *Mantle Xenoliths*, Ed. by P. H. Nixon (Wiley, Chichester, 1987), pp. 119–124.
9. C. Ballhaus, "Redox States of Lithospheric and Asthenospheric Upper Mantle," Contrib. Mineral. Petrol. **107**, 331–348 (1993).
10. A. A. Kadik, "Mantle-Derived Reduced Fluids: Relationship to the Chemical Differentiation of Planetary Matter," Geochem. Int. **41**, 844–855 (2003).
11. A. A. Kadik, "Oxygen Fugacity Regime in the Upper Mantle as a Reflection of the Chemical Differentiation of Planetary Materials," Geokhimiya, No. 1, 63–79 (2006) [Geochem. Int. **44**, 56–71 (2006)].
12. E. S. Simkin, "Graphitization of Diamonds during Heating in Various Gaseous Media," Adgeziya Raspl. Paika Mater., No. 16, 90–94 (1986).
13. S. Evans, "Surface Properties of Diamond," in *The Properties of Natural and Synthetic Diamond*, Ed. by J. E. Field (Academ. Press, London, 1992), pp. 181–214.
14. S. Kh. Lifshits, V. V. Botvin, A. P. Grigor'ev, and V. V. Koval'skii, "Hydrogen Effect on Diamond Interaction with Nickel and Melts of Carbonates and Hydroxides of Sodium and Potassium," in *Interaction of Diamonds with Liquid and Gas Media* (ISM AN USSR, Kiev, 1984), pp. 92–96 [in Russian].
15. A. I. Chepurov, V. M. Sonin, and J.-M. Dereppe, "The Channeling Action of Iron Particles in Catalyzed Hydrogenation of Synthetic Diamond," Diamond Relat. Mater. **9**, 1435–1438 (2000).
16. A. I. Chepurov, I. I. Fedorov, and V. M. Sonin, *Experimental Modeling of Diamond Formation* (SO RAN, Novosibirsk, 1997) [in Russian].
17. A. P. Grigor'ev, S. Kh. Lifshits, and P. P. Shamaev, "Mechanism of Carbon Hydrogenation in the Presence of Nickel, Iron and Platinum," Kinet. Katal. **18**, 948–952 (1977).
18. V. M. Sonin and A. I. Chepurov, "Interaction of Diamond with Dispersed Transition Metals in a Hydrogen Atmosphere," Neorgan. Mater. **30**, 435–438 (1994).
19. A. I. Chepurov, V. M. Sonin, I. P. Khokhryakova, and D. G. Bagryantsev, "Interaction of Free Metals with Diamond at High-Temperature Annealing," Geol. Geofiz. **36** (7), 65–72 (1995).
20. A. I. Chepurov, V. M. Sonin, P. P. Shamaev, et al., "The Action of Iron Particles at Catalyzed Hydrogenation of Natural Diamond," Diamond Relat. Mater. **11**, 1592–11596 (2002).
21. V. M. Sonin, A. I. Chepurov, and I. I. Fedorov, "The Action of Iron Particles at Catalyzed Hydrogenation of {100} and {110} Faces of Synthetic Diamond," Diamond Relat. Mater. **12**, 1559–1562 (2003).
22. V. M. Sonin, "Interaction of Fine Fe Particles with Structural Defects on {111} Faces of Synthetic Diamond Crystals in a Hydrogen Atmosphere," Neorgan. Mater. **40**, 25–27 (2004) [Inorgan. Mater. **40**, 20–22 (2004)].