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Graphite pseudomorphs after diamonds: an experimental study of graphite morphology

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Introduction

Complete graphite pseudomorphs after diamonds (e.g. (1) sharp-edged octahedra, with or without rounded fibrous graphite coats (the most abundant form); (2) rhombicuboctahedra exhibiting well formed cube and octahedral faces; (3) contact twins or macles, with and without re-entrant angles, most of which are coated; (4) irregular to rounded masses whose surface morphology resembles framesite have been described by Slodkevich (1982) and Pearson et al. (1989); Pearson et al. (1995) from Beni-Bousera (Morocco) and Davies et al (1992a); Davies et al. (1992b) from Ronda (south-west Spain). Findings of graphite cuboids from Maksutov complex interpreted also as graphite pseudomorphs after diamonds Leech and Ernst (1998), but so far no trace of an UHPM events were recognized from this complex (O'Brien, 2002 personal communication).

Contrary to kimberlites, where back and/or graphite-coated diamonds rarely occur (Grenville-Wells, 1952), in the ultrahigh pressure metamorphic rocks diamonds often coexist with graphites. Cuboids are predominant morphology of metamorphic diamonds, however perfect octahedral crystals occur in clinozoisite gneisses and quartz-tourmaline-muscovite metasomatic rocks (Lavrova et al., 1999; Korsakov et al., 2002). Therefore the presence of graphite cuboids in UHPM rocks is predominantly interpreted as partial graphitization of diamonds (Zhang et al., 1997; Massonne et al., 1998; Ogasawara et al., 2000; Zhu and Ogasawara, 2002). Recently metastable growth of graphite in the diamond stability field has been proposed by Korsakov and Shatsky (2004). Aim of this study to present the diagnostic features of graphite pseudomorphs after diamonds, which allow to distinguish it from metastable graphite-coating around diamonds.

Experiment

In this study we used synthetic diamond crystals of cubo-octahedron form with 111, 100 faces (synthesized in Fe-Ni-C system at P=5.5-6GPa and T=1350-1450°C for details see (Chepurov et al., 1997) and natural octahedron and cuboid diamonds. The size of crystals was 0.5–0.7 mm. All crystals were perfectly faceted, with sharp edges, smooth faces, and contained inclusions of sizes less than 5 μm.

Several crystals were placed inside MgO powder of grain size 1–2 μm, which subsequently was pressed into solid tablets. Experiments were made in a split sphere type apparatus at a pressure of 2.0 GPa, temperature 1800, 2000 and 2300 K. Additional experiments were run at 10^{-4} MPa at 2300 K. Heating time was up to 60 min at P= 10^{-4} MPa, T=2300 K, and 20 min P=2.0 GPa, T=2300 K, and 5 min in all other experiments.

At these pressures soft, compressible MgO has negligible small porosity and acts as a perfect isolator. After treatments crystals were extracted from MgO by heating in acid (to prevent the destruction of the pseudomorphs) and were studied by Raman, and scanning electron microscopy (SEM) methods.

Raman spectra were obtained using a Raman microimaging system. Excitation wavelength, 514 was used. Spectral resolution was about 3.0 cm^{-1}. An Olympus BH-2 microscope with a 100x objective allowed collection of scattered light from spots as small as 1 μm in diameter. Peak intensities and bandwidths were computed immediately after the spectra were saved.

A SEM microscope, JEOL 6380LA, was used to study the structure of diamond faces and graphite layers. The probe current ranged from 10^{-12} to 10^{-6} A and the maximum magnification was 20000. Typical accelerating voltage in the measurements was 20 kV.

Reflected optical microscopy (ROM) provides important information about the internal morphology of graphite pseudomorphs after diamond. An Olympus BH-2 microscope with a 10, 20, 50 and 100x objective were used.

Results

All experiments with temperature below 1800K and different duration (up to 12 hours) reveal that only thin layer of graphite appear on diamond crystals during first 10 minutes and no changes in thickness or morphology of graphite coatings were detected at long term experiments.

P=10^{-4} MPa, T=2300 K, t=20 min

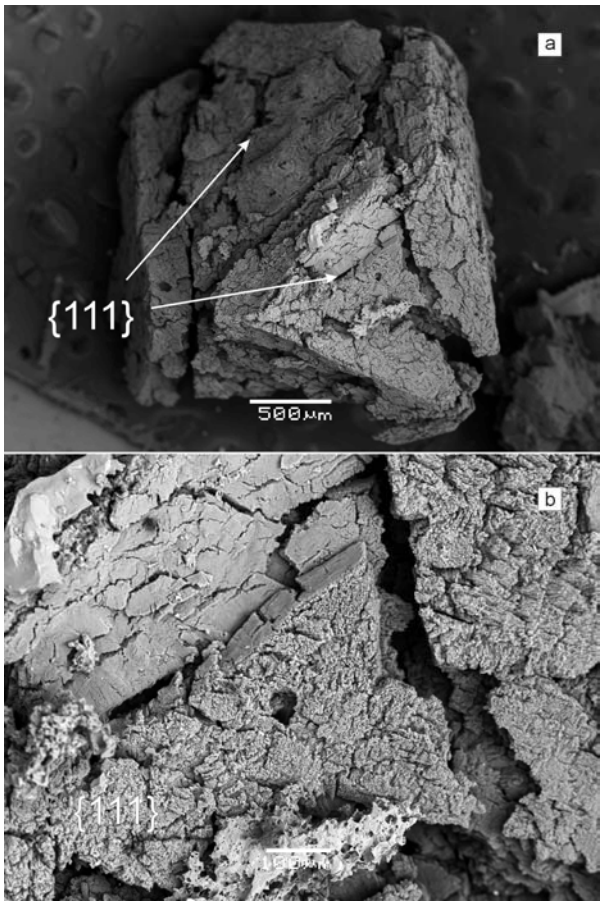

Fig. 1 SEM photograph of graphite pseudomorphs after diamond (a) an overview and (b) detail morphology of graphite aggregates formed at {111} diamond faces at P=10^{-4} MPa, T=2300 K, t=20 min)

The crystal habitus of initial diamonds crystals still can be recognized (Fig. 1a). However details of original morphology of diamond crystals almost never preserved on diamonds graphitized at low pressure conditions (Fig. 1b). Usually these graphite pseudomorphs are very fragile and some of them were damaged during extraction from MgO. Graphite aggregates of this type of pseudomorphs are very fine grained. They have preferred orientation: {0001} graphite crystals oriented parallel to {111} diamond facies. Similar features were described in pioneer study of Grenville-Wells (1952). The graphites obtained at low pressure runs characterized by presence of D, G and D' graphite bands in Raman spectra, indicating that the pseudomorphs consist of microcrystalline graphite.

P=2.0 GPa, T=2300 K, t=20 min

In contrast to pseudomorphs obtained at low pressure conditions, graphite pseudomorphs obtained at high pressure runs not only preserved habitus of initial crystals, but perfectly preserved even tiny growth features, inherited from original diamond crystal. In some experiments distortion of octahedral facies were observed. Originally flat octahedral facies became concave and curved (Fig. 2).

SEM and ROM show that {0001} of the graphite crystallites forming the aggregates is parallel to {111} of the octahedral forms (Figs. 2 and 3). This is the preferred orientation expected for graphitized diamonds (Grenville-Wells, 1952).

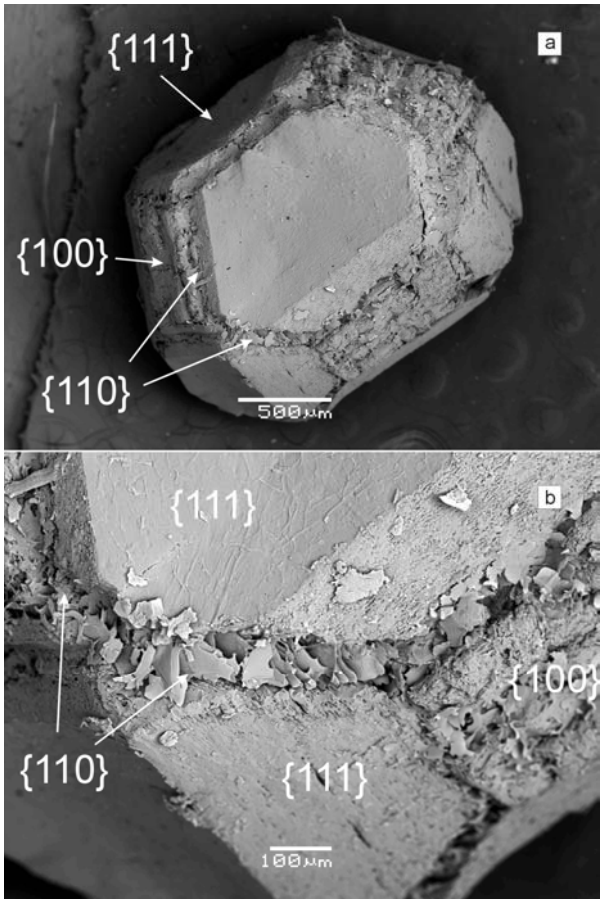

Fig. 2 SEM photograph of graphite pseudomorphs after diamond (a) an overview and (b) detail morphology of graphite aggregates formed at {111}, {100} and {110} diamond faces at P=2 GPa, T=2300 K, t=20 min)

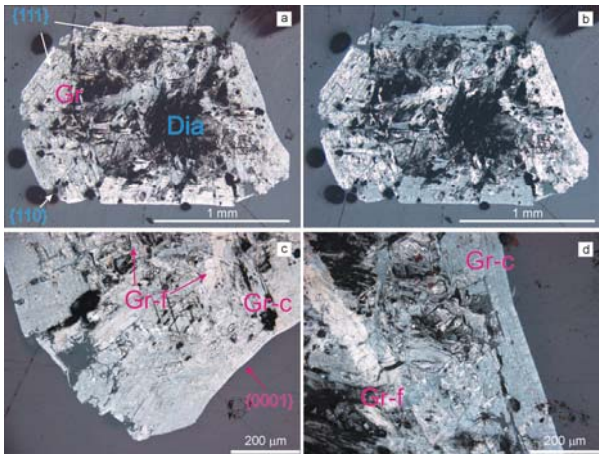

Fig. 3 Reflected light photomicrographs showing textural changes in different growth sectors of graphite pseudomorphs presented on Fig. 2. (a-b) An overview of pseudomorphs and (c-d) details of graphite morphology replacing {111} and {110}. Gr-c = coarse-grained graphite plane (0001) oriented parallel to (111) of diamond crystal, Gr-f=fine-grained randomly oriented graphite, Dia=Diamond relics.

ROM study of texture graphite pseudomorphs reveal that their external zones consist of coarse-grained

graphite (Fig. 3), while in the core and mantle there are zones consisting of fine-grained randomly oriented graphite. Raman spectra collected from the surface of HP pseudomorphs are well ordered and characterized by presence only G band.

Discussion and Conclusions

Graphitization of {100} and {111} faces of synthetic diamond crystals at pressures of 10^{-4} MPa and 2 GPa and temperature 2300K was studied by Raman spectroscopy, scanning electron microscopy. Different morphology of newly formed graphite at {100} and {111} faces of diamond crystals are discussed. The growth of oriented graphite crystallites was observed only on the {111} diamond faces. Randomly oriented graphite crystallites were observed on {100} and especially {110}. Internal morphology of graphite pseudomorphs were studied by reflected light optical microscopy. Contrary to external morphology no differences in mechanism or growth rate of graphite between {111}, {110} and {100} sectors of diamond crystals were observed. Predominant orientation of graphite {0001} plane in respect to {111} diamond face was found all over the crystal. Diagnostic feature of graphitized diamonds can be summarized as follow. - Oriented graphite crystallites observed on {111} diamond faces at different degree of graphitization. It should be noted that even at complete graphitizations some typical surface diamond features can be recognized. - Size of newly formed graphite crystals does not exceed 100 μm, even at very high temperature - Graphitization of {100} and especially {110} diamond sectors proceed by different mechanism (Pantea et al., 2002) and most probably rate, and reflected in morphology of graphite aggregates (Fig. 2). Our observations provide important information that metastable graphite (e.g. formed in the diamond stability field) can be distinguished from graphite formed by partial graphitization of diamond by criteria listed above.

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