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PRODUCTION, STRUCTURE, PROPERTIES

Octahedral Overgrowth Structures on Impact Diamond

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Abstract—Nano- to micrometre-sized overgrowths on the (0001) surface of impact apographitic diamond were characterized. The structures are documented as octahedra, occasionally cubes, their contact and penetration twins, and irregular intergrowths. The internal of these overgrowths structures and their chemical composition were studied. Their postulated globular structure and block growth mechanism published earlier were disproved. A mechanism for the formation of these overgrowth structures is presented.

Keywords: diamond, crystal morphology, paramorphose, growth mechanism

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INTRODUCTION

In 2018, we published an article about unusual nano-microdiamonds as overgrowths on the apopinacoidal face of an impact apographitic diamond from the Bilylivka meteorite crater on the Ukrainian Shield in *Journal of Superhard Materials* [1]. In that and the following publication [2], a mechanism of their crystallization and their growth was presented. It was based on the results of a study of the morphology and chemical composition of these nano-structures using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). However, new results of a more detailed transmission electron microscopy (TEM) study of the overgrowth structures refute the conclusions in these publications.

PREVIOUS STUDY

Morphology, crystal structure and chemical composition are the most important criteria to classify nano-micrometre-sized crystals. In the case of diamond, their crystal-morphological features are octahedral shape and especially the presence of contact and penetration twins along (111) plane among them (Fig. 1). The crystals-overgrowths size is usually less than 1 micron. The surface of the octahedra is covered with globules less than 30–40 nm in size. From these observations we concluded that the globular structure and blocky growth of the crystals was a result of gas phase condensation, similar to the growth conditions of CVD diamond microcrystals.

Figure 2 shows EDS spectra from two microcrystals (analysis locations—points # 010 and # 011) on the (0001) surface of the impact apographitic diamond and from the diamond surface itself (point # 012). The EDS spectra represent the carbon composition of both the overgrowth structures and the diamond surface itself. In more than 12 EDS spectra recorded from overgrowth structures, in addition to the dominant CK_α line, relatively intense FeK_α lines are often observed. The calculated chemical composition of overgrowth structures is up to 99.2–99.9% C and up to 1.3% of FeO. Additionally, there are minor concentration of Ca, Mg and S.

ADDITIONAL TEM STUDY

Seven thin foils[1] measuring 15 × 10 × 0.15 μm were cut with focused ion beam technique (FIB) vertical to the (0001) plane from the same black crystal of the lamellar impact apographitic diamond (Figs. 1a, 3a). The

[1] The foils were obtained in the TEM laboratory of GFZ Potsdam, Section 3.5: Interface Geochemistry. Telegrafenberg, Potsdam, Germany, where they were studied on a FEI Tecnai F20 XTwin electron microscope. Foil numbers examined are # 7117, # 7118, # 7134, # 7135, # 7259, # 7260, and # 7261. The overgrowth images and analysis of foils # 7259 and # 7260 were close, so only foil # 7259 is reported in the text.

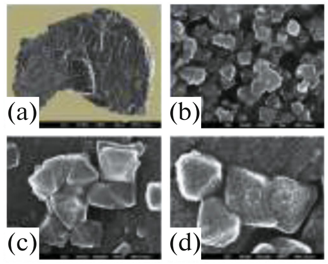

Fig. 1. A lamellar crystal of an impact apographitic diamond 0.3 mm in size (a) and the morphology of nano-microcrystals on its surface (0001) (b–d). SEM images.

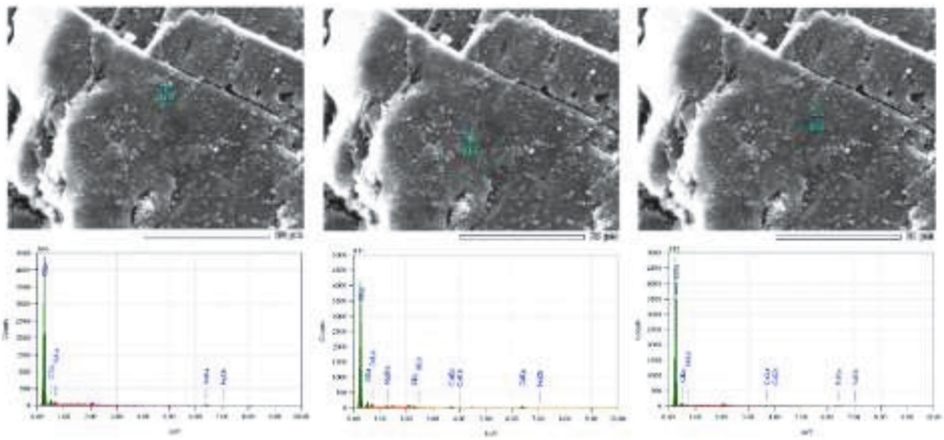

Fig. 2. EDS spectra from microcrystals on the (0001) surface of the impact apographitic diamond (points # 010 and # 011) and the surface itself (point # 012). SEM images.

FIB sample preparation technique and details of TEM application are described elsewhere [3]. The TEM study of such foils allows obtaining morphological, structural and chemical parameters from the crystalline and amorphous substances.

The TEM study confirmed that this apographitic crystal of impact diamond is polycrystalline with polysynthetic twinning along the $(11\bar{2}1)$ plane (Fig. 3b). Each TEM foil comprises the crystal matrix (diamond) and overgrowth structures on it (Figs. 3c, 3d). Figure 3c shows one # 7118 of the 7 foils, documenting linear deformation of the impact diamond crystal together with overgrowths structures on its surface.

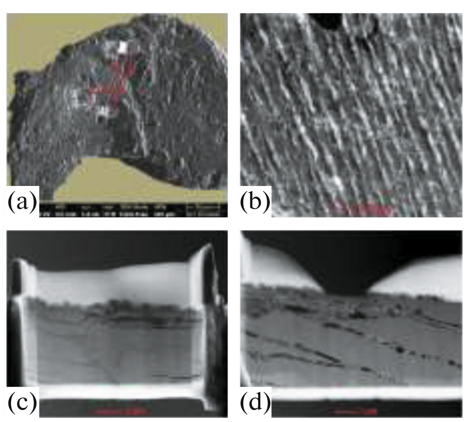

Fig. 3. The impact apographitic diamond ((a) the locations where four foils were cut and extracted (FIB) are indicated by arrows), its internal twin structure (b) and two foils cut from the diamond (c, d). (a) SEM image, (b–d) TEM high-angle annular dark field (HAADF) images, foils # 7118 and # 7117.

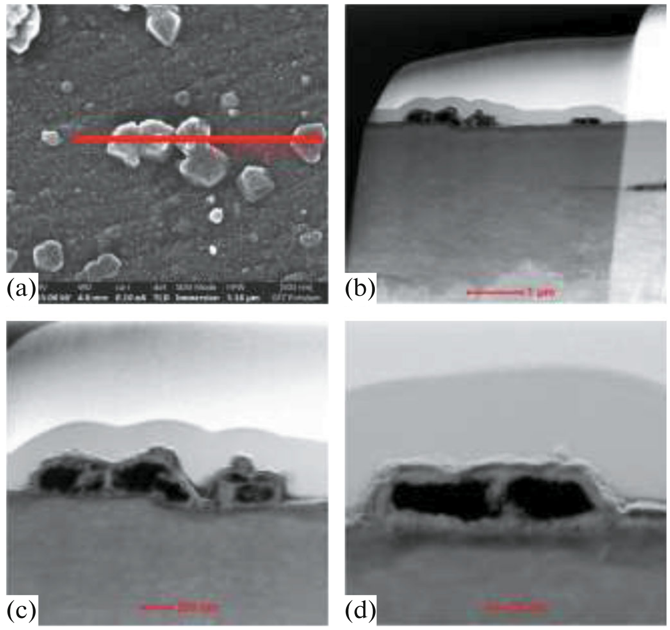

Fig. 4. Cross section of overgrowth structures ((a) trace of the FIB cut foil (red line)) and the internal structure of the FIB foils (b–d). (a) SEM image, (b–d) HAADF TEM images, foil # 7135.

In another foil # 7117 (Fig. 3d), sub-parallel cracks of the crystal matrix in the plane $(1.1.\overline{2}.15)$, are filled with various nanophases.

Most of the studied crystal-overgrowths are hollow-body skeletal structures—shaped like octahedrons (Fig. 4), rarely cubes. The red line in Fig. 4a indicates the location where the FIB foil # 7135 has been cut out. The HAADF TEM images in Figs. 4b–4d show exactly the cross section through these 4 overgrowth structures. They are composed of a solid crust, which is usually amorphous and chemically composed of Fe, C, O, Ni, Al, Si, Ba, Ca, Mg, S, Cl. The major volume of the overgrowth structures is now empty space. It was most likely filled with a fluid phase. Figure 5 shows details of the features of some typical overgrowth structures. In other overgrowth structures the internal material is different with respect to chemical composition (Fig. 6). In general, the structure of the overgrowths is such that the outermost layer forms a crust of amorphous material composed of Fe as major component plus C, S, O, Al, Mg, Si, K, Ca and in some cases Ba. As seen in Fig. 4 this outermost layer forms a complete crust at the contact with diamond, at both sides and at the outermost surface. The inner part of this structure is partially filled with amorphous material or it is empty now. It was originally filled with a fluid that escaped during FIB sample preparation.

In some cases inside the overgrowth structures we observed a crust of poorly crystallized graphite, and below it an almost amorphous inner part of varying thickness, which includes poorly crystallized nanophases of $BaSO_4$, Fe–Ni compound or Fe–Ni oxide (magnetite) together with amorphous carbon (Figs. 7, 8). The elemental composition of the inner part filling is: Fe, C, O, Ni, Al, Si, Ba, Ca, Mg, S, Cl. The nanometer-sized phases observed or the amorphous material also fill crystallographically oriented cracks of probable impact origin in the impact diamond crystal (Fig. 9), which were apparently impregnated by fluids.

We found that the overgrowths structures on the (0001) surface of the impact apographitic diamond are not diamonds, nor can they be attributed to typical graphite paramorphoses on diamond, since the carbon substance is only poorly crystallized. The mechanism of the formation of the overgrowth structures is concluded from the images in Fig. 10.

In Fig. 10a it is obvious that a fluid has partially dissolved the original impact diamond. The surface of diamond has a very irregular structure, which is due to the high dislocation density in the original diamond. Dislocations facilitate dissolution. During or after corrosion a mixture of amorphous carbon plus numerous elements supplied by a fluid such as predominantly Fe, C, O, Ni, Al, Si, Ba, Ca, Mg, S and Cl are precipitated thus forming the amorphous crust. The presence of sulfur and chlorine in EDS spectra from the quench material suggests that the fluid contained S and Cl. Dissolution of the impact diamond results in the formation of so called "negative crystals" after diamond—such as octahedrons or rarely cubes. The crust formation follows the outline of the "negative crystals" stabilizing them and thus result-

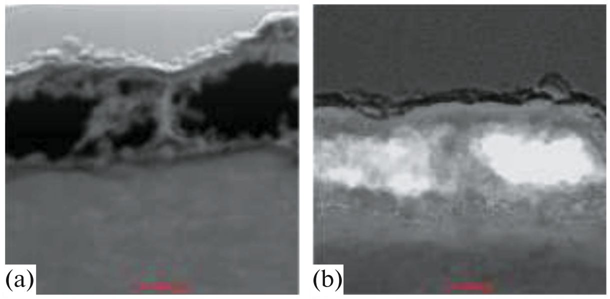

Fig. 5. Details of overgrowth structures. HAADF (left) and TEM bright field (right) images, foils # 7134 and # 7135. Note the crust of amorphous material surrounding the overgrowth structure and the empty space.

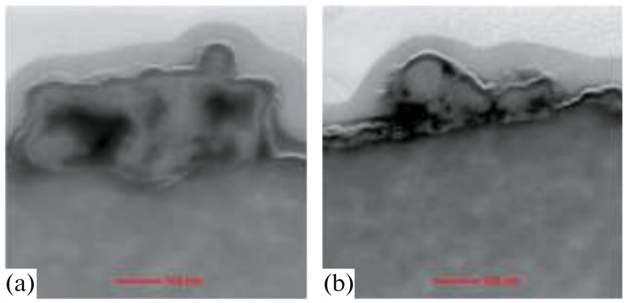

Fig. 6. Less common types of overgrowth structures. HAADF TEM images, foil # 7134.

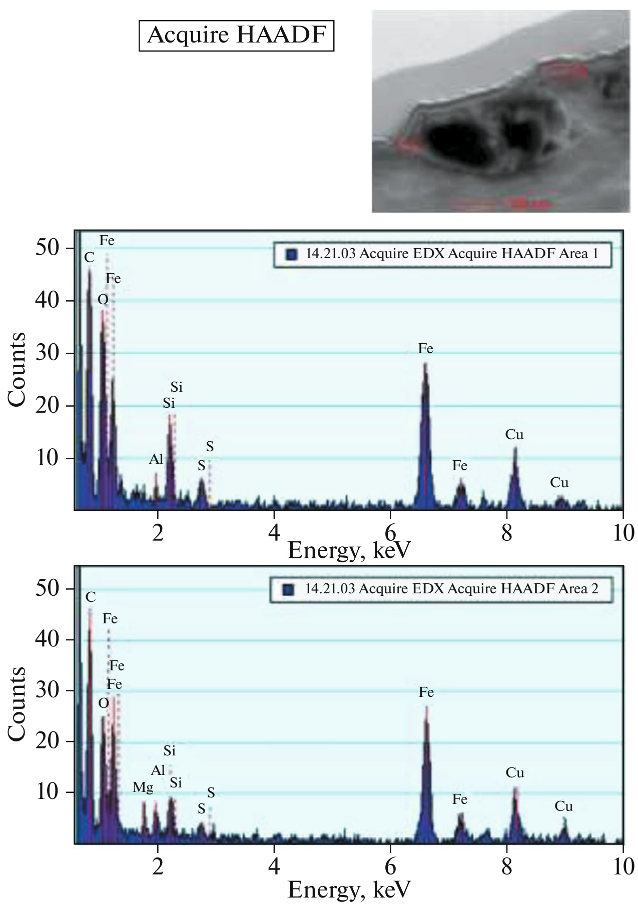

Fig. 7. HAADF TEM image of overgrowth structures (foil # 7261) and the corresponding EDS spectra.

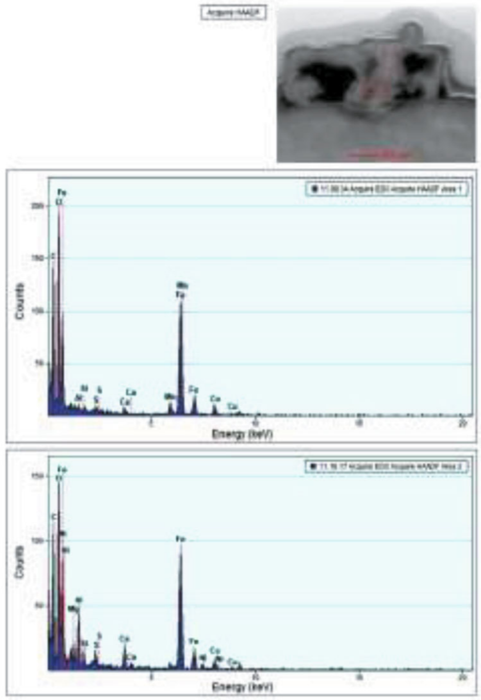

Fig. 8. HAADF TEM image of overgrowth structures (foil # 7134) and the corresponding EDS spectra.

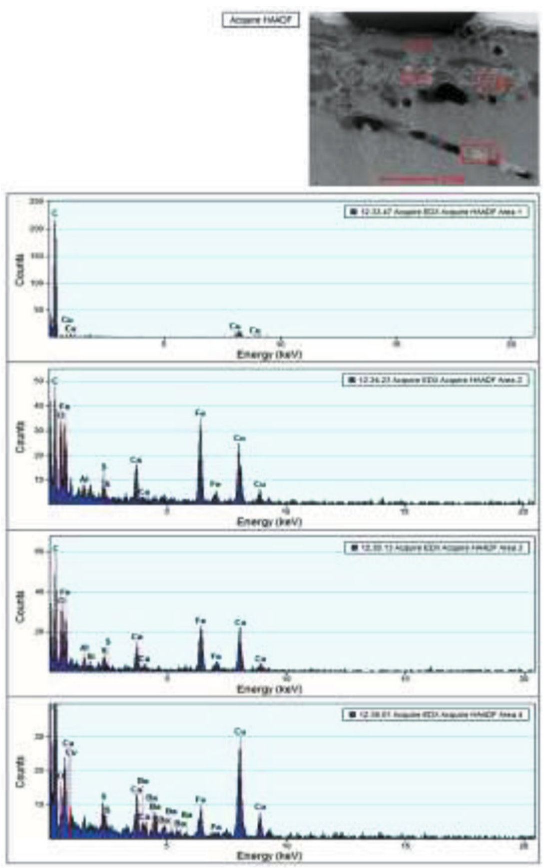

Fig. 9. HAADF TEM image of foil # 7117 and the corresponding EDS spectra of corroded structures inside diamond.

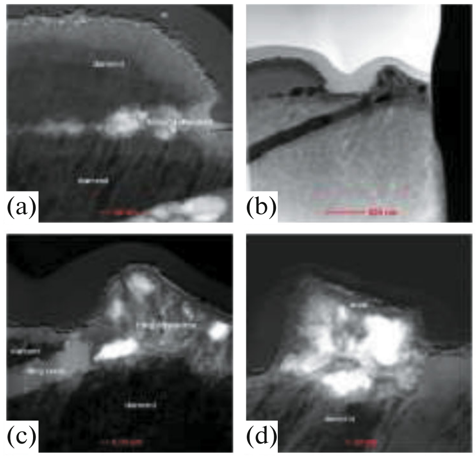

Fig. 10. Dissolution of the impact diamond crystal forming “negative crystals.” TEM bright field image showing the initial state of diamond dissolution (a); HAADF image showing the partially dissolved diamond from (a) and overgrowth structure (b, c); TEM bright-field images of the overgrowth structure (b, c) and another overgrowth with pronounced crust formation and internally deposited mostly amorphous material (d), foil # 7259.

ing in the formation of the observed octahedrons. In Fig 10a the beginning of the dissolution process of diamond and the initial stage of the crust formation is documented. In Fig. 10d another outgrowth close to the one in Figs. 10b, 10c but more developed is displayed. Here the crust formation is more developed with the remains of a fluid present as holes partially filled with amorphous quench material composed of Fe, C, O, Ni, Al, Si, Ba, Ca, Mg, S and Cl. That crust represents the shape of the original diamond crystal (octahedra or cubes). The octahedral or cube-shaped overgrowths are considered as unusual paramorphoses on the impact diamond. They might have formed by gas phase condensation of carbon on the surface in the context of the impact.

CONCLUSIONS

It was found that overgrowths on the (0001) surface of impact apographitic diamond in their current state are not diamonds and cannot be attributed to typical paramorphoses of graphite on diamond, since their carbonaceous matter is only poorly crystallized. The obtained results allow us to reject the previously published conclusions about the globular structure of the overgrowths and their block growth mechanism.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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