

TEM observations of microscopic inclusions in synthetic diamond

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Nowadays, diamonds are synthesized by various dynamic and static high-pressure techniques and by chemical vapor deposition (CVD) [1]. The conventional technique for diamond synthesis at high pressure and temperature employs metallic solvent-catalysts such as molten iron, nickel, cobalt, manganese, or mixtures of these transition metals. Despite the widespread use of this technique, the growth mechanisms of diamond and the catalytic effect of the metal are still a matter of discussion [2–4]. To gain insight into the growth of diamond, we designed multi-anvil high-pressure experiments, which allowed trapping of the solvent-catalyst at synthesis conditions as microscopic inclusions in diamond (see also [5]). These inclusions were small enough to be studied by transmission electron microscopy (TEM). The TEM observations also cast light on the deformation of diamond, induced by the inclusions.

Two high-pressure experiments were carried out using the HYMAG MA-6/8 1000 ton multi-anvil apparatus of the Bayerisches Geoinstitut, University of Bayreuth, Germany [6]. Pure iron and an iron/cobalt mixture were used as metallic solvent-catalysts and were well mixed with graphite powder. The powder was placed into a graphite sleeve, which in turn was encapsulated in a rhenium foil. This complex capsule was finally put into an octahedral MgO cell and then compressed between eight tungsten carbide cubes separated by pyrophyllite gaskets. Run conditions of the

two experiments were: 13 GPa and 2200 °C for iron + graphite; 15 GPa and 2050 °C for iron + cobalt + graphite. These pressures and temperatures are relatively high for diamond synthesis and were chosen to enhance the nucleation and growth rates of diamond, thereby improving the chances of trapping inclusions.

For TEM study, recovered run products were crushed and then loaded on holey carbon grids; a few larger pieces were also thinned by argon ion beam bombardment. The diamonds in both runs contained abundant microscopic inclusions with cubooctahedral shape (Fig. 1). The diameter of most inclusions was smaller than 60 nm and in many cases it was as small as 2 or 3 nm. In inclusion-rich areas, we observed a high density (10^{14} m^{-2}) of dislocations as well as numerous stacking faults and microtwins on (111) planes (Fig. 2). The dislocations were clearly glissile, as indicated by their curvatures, and had the usual Burgers vector $\langle 110 \rangle$. Stacking faults and microtwins were tangentially connected to octahedral faces of inclusions. These defects were absent in inclusion-free areas, which suggests that the inclusions can be regarded as the cause for the observed plastic deformation.

Qualitative energy-dispersive X-ray microanalyses on the TEM revealed that the inclusions in the experiment with an iron/cobalt/graphite mixture were mostly composed of metallic cobalt. In the experiment with pure iron we observed either metallic iron or iron carbide inclusions, suggesting that the carbon

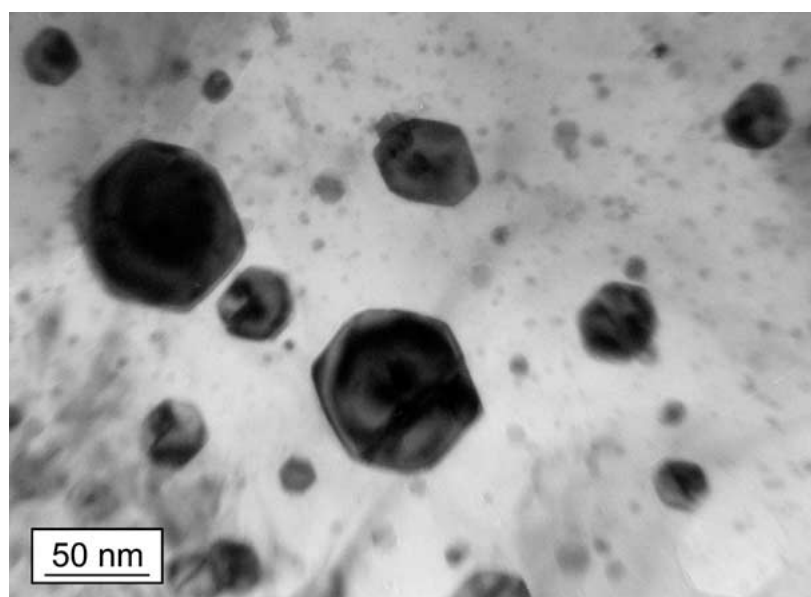


Figure 1 Bright-field TEM image of numerous tiny Co inclusions in diamond synthesized at 15 GPa and 2050 °C.

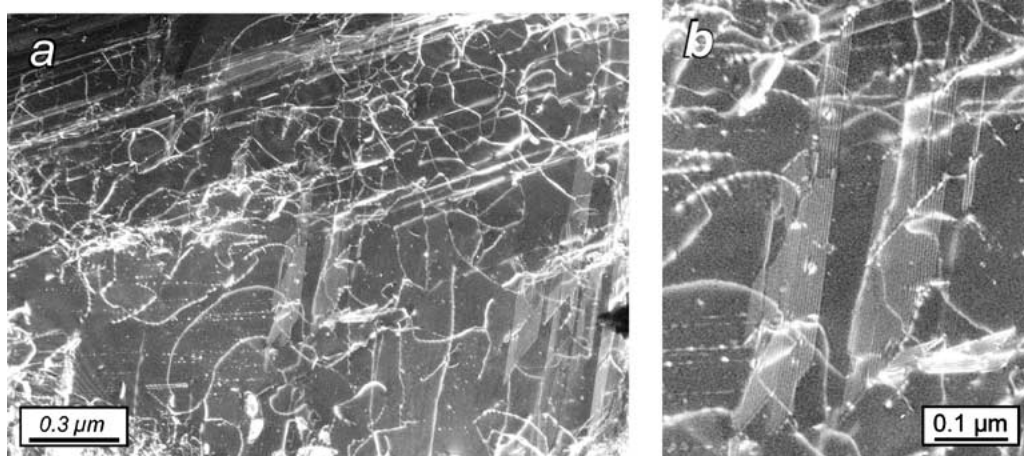


Figure 2 (a) Weak-beam TEM image of numerous tangled dislocations and stacking faults in diamond synthesized at 13 GPa and 2200°C. (b) A close-up view of the stacking faults on (111) in the synthetic diamond.

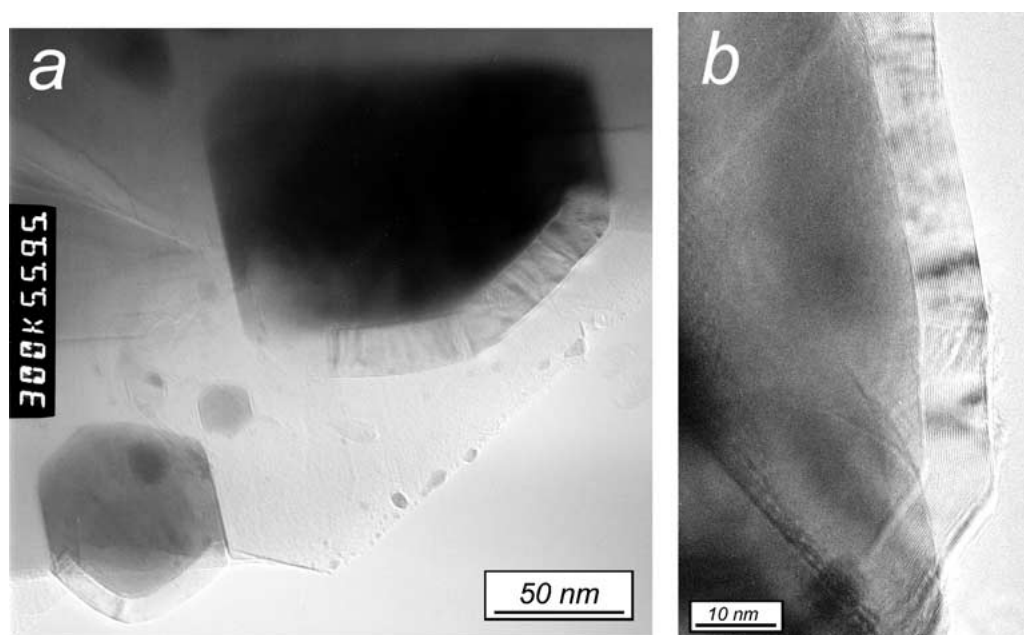


Figure 3 (a) Bright-field TEM image of Co inclusions in synthetic diamond rimmed by graphite. (b) HRTEM image of a shell of graphite around a Co inclusion, showing the (0001) lattice fringes in graphite.

concentration in iron was not uniform. Cobalt and iron carbide crystals inside the inclusions were sometimes wrapped in a shell of layers of graphite (Fig. 3). It is noteworthy that the metal and carbide inclusions were always monocrystalline and were in topotactic relationship to the host diamond. The metallic cobalt inclusions had the hcp structure (ϵ -Co) and were in the following orientation relationship with diamond: $[111]_{\text{Dia}} // [10\bar{1}0]_{\text{Co}}$ and $[220]_{\text{Dia}} // [11\bar{2}0]_{\text{Co}}$. The metallic iron inclusions had the fcc structure (γ -Fe), like diamond, which explains the observed coincidence of a axes of diamond and γ -Fe. The iron carbide could not be clearly identified and its interplanar spacings do not fit to any of the known iron carbides [7]. It seems to possess a hexagonal superstructure, also in topotactic relationship with diamond. This is compatible with the presence of distinct streaks in the electron diffraction pattern along $[111]$ of diamond (Fig. 4). The streaking points to a disordered stacking sequence of the carbide along the presumed c direction with $[111]_{\text{Dia}} // c\text{Fe}_x\text{C}_y$.

Some interesting thoughts arise from these observations concerning the deformation behavior of diamond in the presence of inclusions and the role of the solvent-catalyst in diamond growth. The observations become understandable when the pressure-temperature path in the experiments and the different compressibilities and thermal expansivities of inclusions and diamond are taken into account. Deformation of diamond is apparently first induced, when the samples are quenched to ambient temperature at high pressure. As a consequence of the different thermal expansivities, the inclusions then shrink more than the host diamond and the pressure drops in the inclusions. This causes pure shear stresses in the diamond, which, while temperature is still high, can be relaxed by emission of dislocations and plastic deformation.

An order of magnitude estimate of the pressure drop in the inclusions and the shear stresses in the diamond, during cooling under 15 GPa pressure, can be obtained by solving the elastic problem of a spherical inclusion

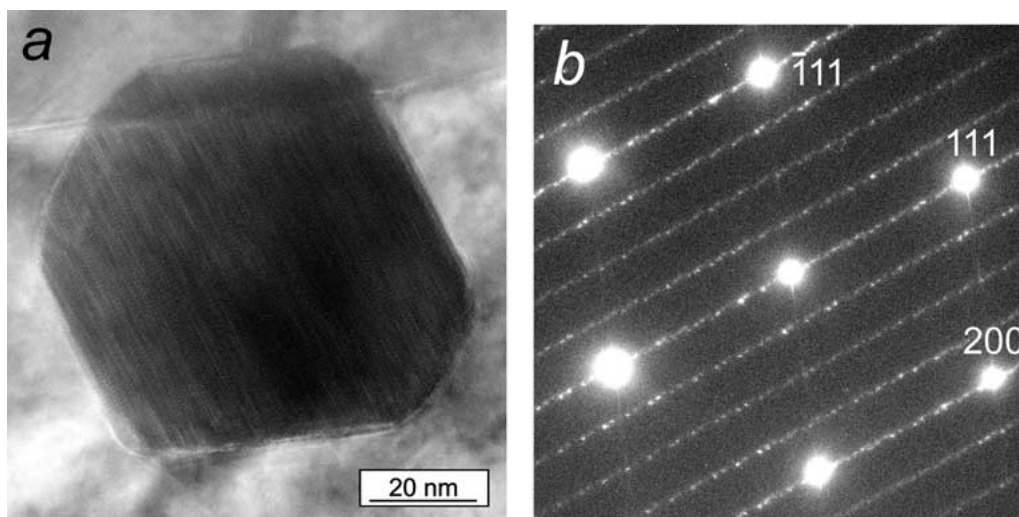


Figure 4 (a) Bright-field TEM image and (b) corresponding selected area electron diffraction pattern of an iron carbide inclusion in synthetic diamond viewed along the $[0\bar{1}1]$ zone axis. Miller indices refer to the main reflections of diamond.

in a hole at the center of a bigger sphere, when the thermal expansivities of the sphere and the inclusion differ [8]. The thermal expansivities of carbides and diamond are $3.35 \times 10^{-5} \text{ K}^{-1}$ and $1.5 \times 10^{-5} \text{ K}^{-1}$, respectively [9, 10], so during cooling, the inclusion diameter tends to decrease more than that of the hole in diamond, thus putting the inclusion in extension. For a 500 K temperature drop, the “size factor” of a carbide inclusion would then be $\eta \approx -0.013$ and the residual pressure in the inclusion would be $P_i \approx 1 \text{ GPa}$, much lower than the pressure of formation of diamond. The diamond around the inclusion is put in a state of pure shear stress. The principal stresses, at a distance of the center of the inclusion equal to twice its radius, are then found to be quite high, of the order of 6 GPa.

The TEM observations suggest that diamond is deformed in a second stage, when it is decompressed to ambient pressure, after it has cooled down. Upon decompression, pressure increases again in the inclusions due to the fact that the compressibility of diamond is lower than that of the inclusion. Since the diamond is now cold and cannot deform by dislocations, the resulting shear stresses are relaxed by the formation of stacking faults and mechanical microtwins on (111).

The decrease in internal pressure during quenching provides also an explanation for the association of the cobalt and iron carbide inclusions with graphite. For example, in the Fe-C system with 8–10 wt% C, a molten solution of iron and carbon crystallizes at high pressure as $\text{Fe}_x\text{C}_y + \text{carbon}$ [9]. Since quenching leads to a drop in pressure, carbon precipitates as graphite and not as diamond. The fact that the metal and carbide inclusions crystallize as monocrystals in topotactic relation with diamond may indicate that the melt is structurally related to diamond, resulting in a good wetting of growth

surfaces. It is striking that the interplanar distances between the densest planes in the hcp ($10\bar{1}0$, 0002) or fcc metals known as good catalysts (e.g., Fe, Co, and Ni) are very similar to the (111) spacing of diamond. This might be an important prerequisite for a good catalyst for diamond synthesis.

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