IMPURITY DIFFUSION AND MICROSTRUCTURE IN DIAMONDS DEFORMED AT HIGH PRESSURES AND TEMPERATURES

Shiryaev A.A. (IC RAS; Bayerisches Geoinstitut, Bayreuth, Germany),
Frost D. J. (Bayerisches Geoinstitut, Bayreuth, Germany),
Langenhorst F. (Bayerisches Geoinstitut, Bayreuth, Germany; Institut für Geowissenschaften, Jena, Germany)
shiryaev@ns.crys.ras.ru; Fax: +7(495) 135-10-11

Nitrogen is a principal impurity in diamonds; its concentration may reach several thousands atomic ppm. In synthetic crystals grown using metal catalysts N is incorporated into the diamond lattice as single substitutional atoms (so-called C-defect). It is usually believed that the same is true for natural diamonds, though recently it was shown that nitrogen incorporation as a pair (A-defect) may occur during diamond growth from carbonate melts. Nitrogen diffusion during annealing converts the C-defects into pairs (the A-defect) and then to more complex B-defects, believed to be the complexes 4N+V. Several important investigations of the process kinetics have been performed, but discrepancies between values of activation energy of diffusion and other parameters still exist. In geosciences the degree of nitrogen aggregation is used to investigate the Time-Temperature history of diamond storage in the mantle. Though in general this approach gives reasonable results, the mantle residence time of some diamonds extracted from the N aggregation behaviour is longer than the Earth age. It is clear that some physical processes influence nitrogen diffusion, i.e., either accelerate it or slow it down. The absolute majority of natural diamonds are plastically deformed, which is manifested, for example, in the birefringence patterns. Therefore, understanding the role of plastic deformation on the nitrogen aggregation kinetics is of considerable interest.

Studies of the diffusion of impurities in materials are closely linked to the investigation of material microstructure. The microstructure of deformed diamonds is of considerable scientific and applied interest. Diamond is a perfect example of a brittle material at low temperatures, but with increasing temperature it softens considerably and plastic flow becomes possible.

Diffusion of virtually all chemical impurities in diamond is very slow. The only feasible approach to study influence of deformation on diffusion is to look at the transformation of impurity-related defects in the bulk of the sample. We compare here the degree of nitrogen aggregation in undeformed diamonds annealed under quasi-hydrostatic high-pressure and temperature conditions with heavily deformed diamonds annealed under identical PT conditions. This allows us to investigate the influence of strong deformation on the kinetics of single nitrogen atoms aggregation into pairs (i.e. C→A defects).

High-pressure (HP)-high-temperature (HT) deformation experiments were performed using Kawai-type 6-8 multi-anvil devices in conjunction with 1000 and 1200 ton presses at BGI. The diamond sample was packed together with a pressure-transmitting medium. In this work several different pressure-transmitting media were used to create different sample stress environments. For quasi-hydrostatic conditions diamonds were packed in MgO powder. To produce very high stresses the diamonds were packed with either SiC or diamond powders. To create intermediate stresses experiments were performed with hard silicate powders, such as synthetic olivine or natural garnet, sometimes also mixed with SiC. The diamonds were annealed at a temperature of 1600 °C and a pressure of 6.5 GPa for 4 hours.

Results

Microstructure: Prior to the HPHT experiments the synthetic diamonds were of high crystalline quality: TEM and X-ray topography investigation showed very low densities of dislocations. The microstructure of deformed diamonds strongly depends on the pressure-transmitting medium. With a MgO transmitting medium HPHT annealing or cold compression does not alter the crystalline lattice quality significantly. Annealing in SiC or diamond powder induced extremely high residual stresses in the recovered diamonds. Transmission electron microscopy study shows a very high density of dislocations (2×10^{14} m^{-2}) in the deformed diamonds. These dislocations are in glide configuration and have the common Burger vector b = <110>. It is very important to note that the dislocation distribution in the sample is very heterogeneous on micron scale. Some of the analysed diamond chips are indeed very rich in dislocations, whereas other diamond pieces from the same copper grid are relatively pristine.

Annealing in a mixture of hard silicates (i.e., Ol+Gt) lead to the creation of a very different microstructure: the density of dislocations is relatively low, but extended defects such as mechanical twins and stacking faults on the (111) plane are formed. The X-ray topography shows that rotational plasticity took place and the samples mosaicity increased very significantly.

Nitrogen defects: The nitrogen aggregation state was inferred from IR microspectroscopy. For every diamond specimen a comparison of the aggregation states in the chip annealed in MgO with that deformed in harder pressure transmitting media was performed. The percentage of nitrogen in the A-defects in the annealed samples was below 30% for the majority of the samples. Despite the clear influence of the pressure-transmitting medium on the diamond microstructure the aggregation behavior is more complicated. Whereas for some samples the conversion degree was higher in the deformation experiments, for others no clear difference or even adverse effects are observed. In the sample annealed in hard silicates mixed with the SiC powder the conversion degree was consistently higher than in the non-deformed counterpart, especially keeping in mind the different growth sectors analyzed.

In some of the annealed diamonds strong bands between 800 and 1000 cm^{-1} appeared. These bands may represent vibrations of metal-carbon bonds (MeC_4 complexes). A very interesting feature was observed in IR spectra in some regions of heavily deformed diamonds. The one-phonon part is dominated by a very strong band at around 1200-1220 cm^{-1}. The band shape resembles spectra of natural londsdaleite-containing diamonds. The origin of this band is yet uncertain but most likely it is related to deformation-related violation of the diamond lattice symmetry. Some support for the formation of impurity (metal?) precipitates and/or londsdaleite lamellae is provided by Small-Angle Neutron and X-ray Scattering studies of deformed diamond performed at ILL and ESRF. Scattering patterns may be explained by the formation of either planar (in (100) planes) or three-dimensional ((100) bounded) extended defects. Note that these precipitates are not related to common (100) platelets detected in some natural diamonds.

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