Time-temperature reconstruction of diamond growth conditions on FTIR basis

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Zonal distribution of A and B1 crystal structure defects, revealed by FTIR, is observed in the majority of natural diamonds. Change of concentration ratio of A and B1 defects (nitrogen aggregation stage) inside diamonds points to the change of temperature or duration of their annealing. However separate determinations of duration and annealing temperature are still impossible on the base of nitrogen aggregation measurements. There are other defects of crystal structure - "platelets", basing on the research of which it is also possible to perform temperature-kinetic reconstructions.

Introduction

"Platelets" are large planar {100} defects, with linear dimensions from first nanometers up to several micrometers, with the thickness of some atomic layers (Barry, 1991). They are diagnosed on an absorption band with a maximum in 1358 - 1378 sm[-1] range. The position of maximum is defined by linear dimensions of defects (Clackson, 1990). Interstitial carbon atoms I, appearing during formation of B1 defects, are the structural basis of defects B2 - "platelets" (Goss J.P., 2003):

$$2N_2 (A) - B1 (N_4V) + I$$
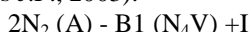
We offer to consider "platelets" formation on the basis of the theory of oversaturated solid solution decomposition. The main idea is the assumption that concentration of defects B2 is defined by initial oversaturation on interstitial atoms of carbon. In the basic model of such concept (Volmer, 1936) the platelets concentration is a function of super-saturation by the interstitial carbon atoms C_I and the temperature at the initial stage of annealing:

$$N_{B2} = C_I \exp (-E_{B2}/kT)$$

where E_{B2} – energy of formation of the B2 center of critical size. The subsequent annealing does not influence the platelets concentration but it causes the increase of their linear dimensions. The equilibrium concentration of interstitial carbon atoms is negligibly low, and their mobility is very high. That is why interstitials concentration is proportional to the B1 defects forming rate, having second order kinetics (Taylor W. R., 1990):

$$C_I \approx dC_I/dt = -\tfrac{1}{4} \, dC_{N(A)}/dt \approx C_N^2 \exp(-E_{B1}/kT)$$

It is important to note the differences between the concentration of "platelets" and the amount of atoms in these defects. The ratio for estimation of temperature change of crystals' growth has been received after transformation of previous equations

$$T/T_{max} = \ln (C_N^2/N_{B2})_{max} / \ln (C_N^2/N_{B2})$$

T - temperature of diamonds' growth, C_N – total nitrogen concentration, N_{B2} - concentration of B2 defects. The index "max" corresponds to the area in the specimen with maximum ratio C_N^2/N_{B2}. Concentration of B2 defects is defined on absorption spectra: $N_{B2} = K\int \alpha_{B2}(v)R_{B2}^{-2}(v)dv$. Where $\alpha_{B2}(v)$ - contour of absorption band B2 with compensation of the base line, K - the factor considering cross-section of B2 defects absorption and concentration of interstitial atoms in it, $R_{B2}(v)$ is dependence between the absorption band frequency and the size of defects, received by interpolation of literary data (Clackson, 1990; Sumida N., 1988; Kiflawi I.,1998 et al). Integration was performed in 1350 – 1380 sm[-1] limits. This approach allows to assess the change of temperature, which took place during the growth of diamond. Having the change of temperature, it is not difficult to assess the change of growth rate of diamonds, on kinetic equation of B1 defects formation. The approach is applicable only to investigation of nitrogen-bearing diamonds in which destruction of "platelets" has not begun. Conformity of "regular" spectra to type (Woods, 1986), or availability of absorption bands with maxima about 1425, 1450 sm[-1] may be criterion of diamonds' fitness to interpretation with such approach (Vasilyev E. A., 2005). These bands point to incompleteness of "platelets" formation.

Methods and specimens

For revealing of the A, B1 and B2 centers' distribution three plates of diamonds of about 3×4×0,4мм size, cut out of octahedrons of kimberlite pipe "Mir" in plane (100), have been investigated. Figure 1 contains photos of the investigated specimens in crossed polarizers.

Specimens 1 and 3 represent a quarter of a crystal cross-section, the growth center is in the right bottom angle. The growth center of the specimen 5 crystal is located in the right part of the photo. Determination of nitrogen concentration in the form of A and B1 defects, and position of the maximum of B2

band, is performed across the plates. Absorption spectra in IR range were recorded on FTIR spectrometer FSM-1201 with an attachment - microscope MIK15 with 4 sm^{-1} resolution. The spectra were recorded from sections of 0.3 mm diameter at overlapping of analyzed areas. Concentration of nitrogen in the form of A and B1 defects were computed by known way (Boyd et. al., 1994, 1995). The root-mean-square deviation at determination of nitrogen concentration in the form of A and B1 defects constituted 6 and 13 % correspondingly, of the integral absorbance of B2 band is 5 %.

Results of research

As it is seen from figure 1, selected specimens have zonal structure. There are no zones and sectors with normal mechanism of growth, boundary lines of dissolution in specimens.
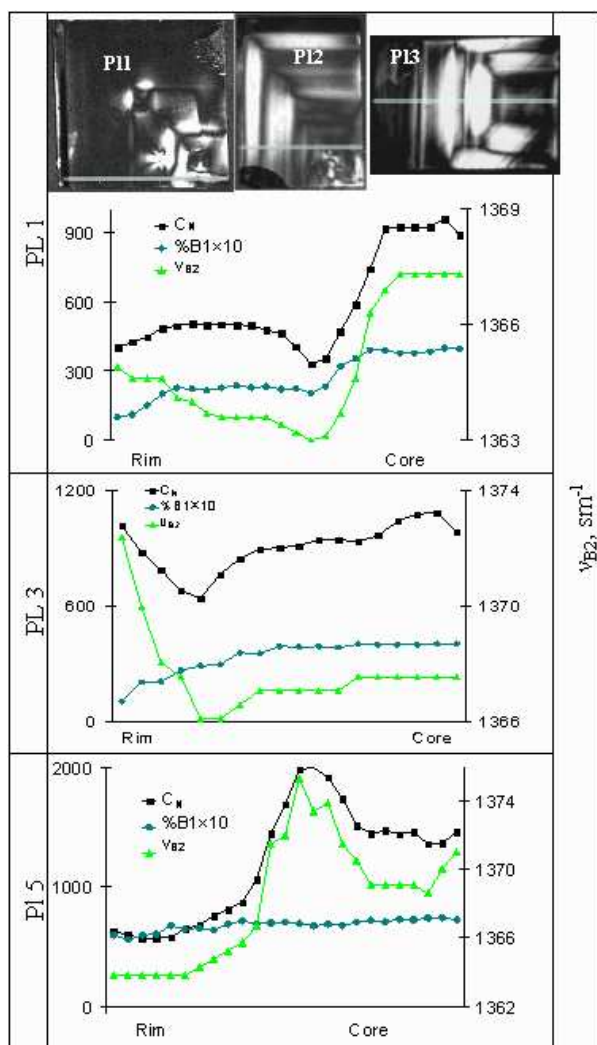

Fig. 1. Photos of diamond plates in cross polarizers and core-rim traverses of total nitrogen (■), nitrogen in B1 defects(●) and B2 absorption band maximum position(▲).

Figure 1 contains profiles of distribution in volume of the investigated specimens of total concentration of nitrogen in defects A and B1 (C_N),

degree of aggregation - share of nitrogen in the form of B1 defects ($C_{N(B1)}/C_N$ 100 %), and positions of B2 band maximum.

For demonstration on one diagram nitrogen aggregation degree is increased ten times. As it is seen from Fig. 1, greater values of temperature or time of annealing correspond to the central areas of the crystals. Deviations from this regularity are within the limits of the lapse of definition of aggregation degree for all specimens. Decrease of aggregation degree of nitrogen from the center of crystals to periphery testifies, that formation from 15 up to 75 % of B1 defects in the investigated specimens occurred during growth of crystals the temperature which provides sufficient speed of the process. Thus, one can judge about temperature and duration of post-growth annealing only by degree of aggregation of nitrogen in near-surface area of the crystals.

Alteration diagrams of T/T_{max} by volume of investigated specimens are given in figure 2. Minimal value of C_{N2}/N_{B2} corresponds to high-nitrogen part of specimen PL5. Having accepted the maximum temperature of diamond growth as 1700 K, according to the results of investigation of impurities in diamonds of kimberlite pipe "Mir" (Bulanova G. P., 1993), it is possible to assess absolute changes of temperature at growth of crystals.
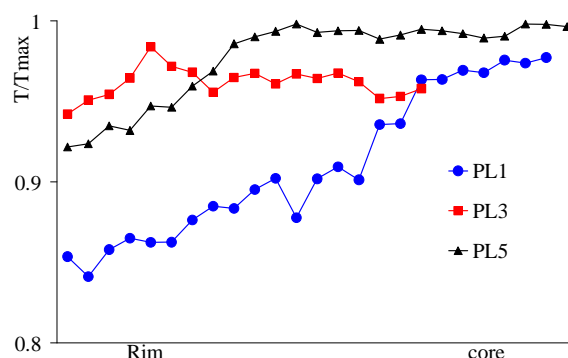

Fig. 2. Core-rim traverses of relative grows temperatures for diamond plates.

Lets temperature 1700 K corresponds to the growth center in specimen PL5, and therefore the minimal temperature corresponding to periphery is 1560 K. Specimen PL3 grew at temperature about 1630 K, and its variations did not exceed 20 K. Gradual decrease of growth temperature from 1660 up to 1440 K is noted in specimen PL1. It is noticeable that the change of nitrogen concentration on the investigated plates is not accompanied by the change of growth temperature, as it is seen on example PL5. As follows from figure 2, decrease of temperature is not the basic reason of diamonds growth termination, as temperatures of growth of peripheral areas in various specimens differ, but more detailed investigations of near-surface layers of diamonds are necessary for verifying this assumption.

Having assessed values of growth temperature of diamonds, it is possible to restore duration of annealing of each investigated area of diamonds from periphery to growth center, using parameters of kinetic

equation found by Taylor (Taylor W. R., 1990). Grows time for plates of diamond, reconstructed as time, needed to achieve nitrogen aggregation stage at temperatures is shown on diagram of figure 3. Some experimental points are not shown on fig.3 due to their negative value. It is take place because of local "anomalous" nitrogen aggregation stage decrease (see fig. 1). We assume it to experimental error end some overlapping of analyzed areas. Certainly, calculated time and temperature values are not true, they show only a possible range of temperature changing and dynamics of diamond grows.
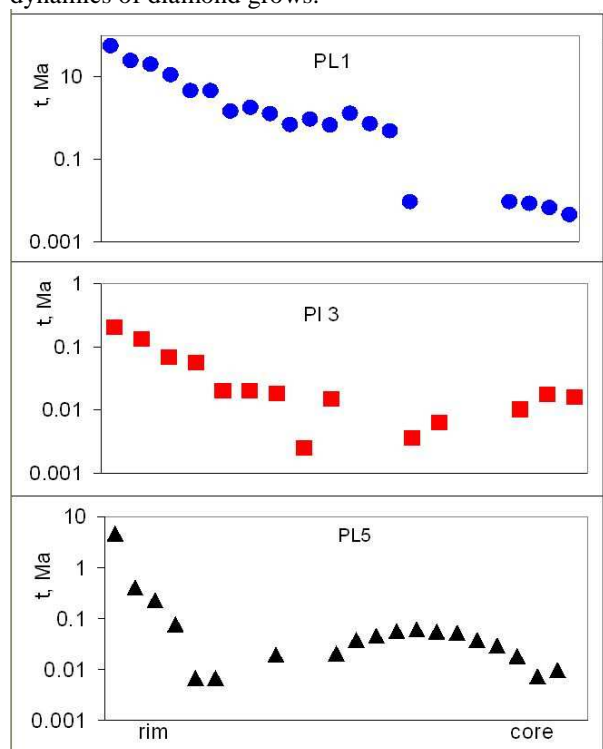

Fig 3. Grows time diagrams for plates of diamond, reconstructed as time, needed to achieve nitrogen aggregation stage at temperatures of fig2.

Estimated grows time of shown diamonds is about ten Ma, and dramatically increase with increasing of crystal dimensions. But for diamonds of 2-3 mm in size the grows rate is not vary significantly. For sample PL1 we can see a delay of grows without any significant temperature changing in fig2. This fact also confirms the suggestion that temperature is not only one main parameter, controlling carbon oversaturation and diamond grows rate.

Conclusion

Investigation of volume distribution of A, B1 defects and B2 in of crystals of octahedral habit from kimberlite pipe "Mir" allowed to state, that formation of B1 defects from A defects occurred at annealing during growth of these diamonds. We assume, that the amount of "platelets" is defined by concentration of nitrogen in diamond and initial temperature of annealing. The received results indicate that distribution of size of B2 defects from the growth

center to periphery of crystals can be considered as the sensitive indicator of temperature alteration of diamond formation environment. That is why further investigation directed on the development of mineralogical geothermometer on the basis of FTIR data: "platelets" characteristics, A and B1 defects concentrations is considered perspective.

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