Twinning formation in nanodiamonds after treatment in a planetary mill: HRTEM studies

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Abstract. The structure of a powder obtained as a result of processing a mixture of silicon and nano-diamond (1:4 weight ratio) in a planetary mill was studied by transmission electron microscopy. It was found that the obtained material includes diamond nanoparticles with an average grain size of 10 nm, having twins and lonsdaleite interlayers. In the present work, the plastic deformation of the diamond was detected at a temperature below 420 K by the mechanism of mechanical twinning, and the maximum stress in the diamond under the experimental conditions was found to not exceed 6 GPa, which is below the critical shear stresses for diamonds (55 GPa).

1. Introduction
Plastic deformation of a diamond at temperatures below ~1200 K is of particular scientific interest, since diamond is a brittle material, and practically any mechanical effect leads to the formation of cracks [1]. Diamond is unique in that its strength is equal to theoretical yield limit (55 GPa) [2,3], which coincides with the experimental value of yield limit [3]. Yield limit is a shear stress, at which a diamond lattice loses its stability and begins a phase transition [4] to the intermediate carbon phase. In addition, the theoretical yield limit is equal to the stress, at which the dislocation movement begins [2].

Plastic deformations in diamond are associated with dislocation plasticity [2]; therefore, it is usually observed at temperatures above 1200-1400 K [1]. At room temperature, the plastic deformations of the diamond were observed earlier in a high-pressure diamond anvil cell with a high nitrogen content at a pressure of 170 GPa [5], as well as during indentation [6,7] (the average contact pressure under the indenter for diamond was ~ 150 GPa [6]). Moreover, in contact with the material, the pressure of which is lower than the hardness of the diamond, in the general case, only the formation of cracks in the diamond is possible [8]. However, questions remain about the mechanism of plastic deformation.

One of the possible mechanisms of the diamond plastic deformations at low (below the Debye temperature) temperatures is twinning [9,10]. Recently, researchers have suggested that it is the twinning process that causes enhanced mechanical properties of the so called “nanotwinned diamond”
Plastic deformations through mechanical twinning are described in the works [15,16]. However, this mechanism was earlier observed only at high (1300 K) temperatures [17]. Despite the fact that the diamond plastic deformations at “low” temperatures are observed, this mechanism has not been studied experimentally, except in the case of a phase transition [14]. In this regard, the issue of the mechanism of the diamond plastic deformations at temperatures below 1200K needs to be clarified.

The objective of this research was to study the structural features of diamond nanoparticles deformation after processing in a planetary mill. In the present work, the unconventional method of obtaining nanopowder – mechanical grinding in a planetary mill – was used. In the grinding process, the powder particles experience a high mechanical load, which leads to phase transformations.

2. Experimental part
A powder-like mixture containing plastically deformed diamond was obtained by processing in a Micro Mill PULVERISSETTE 7 Premium Line planetary mill (FRITSCH, Idar-Oberstein, Germany) with a steel drum and steel milling balls. The processing time in the experiments was 2 h (the processing cycle was 1 min of grinding and 3 min of cooling). After that, the powder obtained after processing in the mill, was subjected to processing in a mixture of HNO₃ and HF acids (EKOS-1, Moscow, Russia) to partially dissolve silicon. The remaining diamond powder was examined by high resolution transition electron microscopy (HRTEM) methods on a JEM-2010 instrument equipped with EDS attachment (JEOL, Tokyo, Japan).

In [18], it was shown that the maximum temperature of the sample during the processing cycle used by us in a planetary mill does not exceed 420 K, therefore, we can assume that under the experimental conditions, the sample is certainly not heated above the Debye temperature $T_\vartheta = 2100$ K. In [19], it was shown that the mechanical stresses arising from the collision of steel balls during processing in a planetary mill do not exceed 6GPa. It can also be considered that the contact pressure at the impact of the balls does not exceed the value of their hardness (7 GPa), since no traces of plastic deformation were found on steel balls when the mill worked without a sample. Using the general theory of elasticity in the case of a short rod striking a drummer with a much larger mass [20], it is possible to describe the stress state of a sample when struck with grinding balls. While the impactor speed has not significantly decreased and the stress is high, the front edge of the wave will go from one end to the other. Meanwhile, in the opposite direction from the second end of the rod, the reflected wave will go. The imposition of these waves will lead to large shear stresses. Thus, plastic deformations are possible already at relatively low impact speeds.

For several reasons, we used a detonation diamond powder with an average size of 10 nm produced by the SINTA company (Minsk, Republic of Belarus). First, this size allows you to directly explore a diamond particle in TEM without additional processing. Second, the average particle size is twice the value at which the quantum confinement effect begins to manifest itself [21]. Third, detonation nanodiamonds have a small concentration of defects [22].

3. Results and discussion
According to our estimates, the initial diamond powder (figure 1a) comprised no more than 3-4 % of particles containing planar lattice defects, namely, stacking faults and twins. To prevent iron from interacting with diamond, the diamond powder was mixed with silicon in a 1:4 weight ratio.
Figure 1. Diamond particles before (a) and after (b) grinding in the mill. In (b) – a diamond particle is shown surrounded by silicon particles. The arrows indicate twinning planes \{111\}.

According to the results of the TEM analysis, at least 30 % of the diamond particles after processing in the mill contain twins. Figure 1b shows a diamond particle surrounded by undissolved silicon, which encompasses the most common twin boundary in diamond. Such twin boundaries of the \( \Sigma = 3 \) type were observed in natural, artificial and thin film diamond layers [23], as well as in other materials that have the diamond lattice [24].

Figure 2. A diamond particle surrounded by silicon, after processing in a planetary mill. The asterisks indicate the incoherent part of the boundary.

In this work, we observed both coherent twin boundary and incoherent boundaries in different particles. In the case of the coherent boundaries, the lattices of twin components are mated along the boundaries, without causing macroscopic stresses in the crystal. The incoherent boundaries can be flat, stepped and curvilinear. Figure 2 shows the traditional twins of the first and second order (\( \Sigma = 3, 9 \)).
similar twin (figure 2) structure of diamond films, grown by plasma-assisted CVD, was introduced and examined in [25].

Twins in diamond are shown in figure 3. The twinning plane \{111\} in this case is also the contact plane – i.e., the lattices forming a twin have one common atomic layer located above the interface (in figure 3, the interfaces are indicated by arrows). Thus, when twinning of diamond crystals occurs along the \{111\} plane in the region of the lattice junction, the initial structure is not disturbed.

It was also found that the obtained material contains some relatively large (up to several nanometers) lonsdaleite fragments. Hexagonal diamond or lonsdaleite (2H) is a form of carbon found in meteorites in 1967. Lonsdaleite has a hexagonal crystal lattice \((a=2.52, c=4.12A)\). The main difference of hexagonal from cubic (3C) diamond is in the packing of layers. The 3C crystal lattice in diamond is represented by the ABCABC sequence, whereas in lonsdaleite the 2H crystal lattice is represented by the ABAB sequence. Hence, a sequence of planes in diamond contains a lonsdaleite grid.

Some of the nanoparticles comprise lonsdaleite layers. Figure 4 shows a high-resolution image of a nanoparticle containing various defects that form such layers. In this figure, to the left, the sequence is ABCABCABC, whereas to the right, the monatomic layer A removed from the sequence of ABCABCABC layers, which contains the mirror plane of symmetry, is demonstrated, thereby indicating the formation of a double structure in the lattice.

It is known that with increasing temperature, the lattice rearrangement is facilitated, which can lead to twinning. On the one hand, for twinning at an elevated temperature, less effort is required and larger residual twins can be obtained. But on the other hand, with increasing temperature, slip deformation begins to prevail, which impedes the twinning process [9]. Twin nucleation is not a heat-activated process, but it occurs in places with high stress concentration [10].
Figure 4. Diamond nanoparticle structure. Packing defects form lonsdaleite layers. To the left - the packaging layer ABCABCBA. The stacking sequence is mirrored, which indicates the formation of a twin structure. To the right - one atomic layer A removed from the sequence of ABC ABCABC layers.

This can be explained by several reasons: blocking by the low mobility of atoms of partial or twin dislocations (in contrast to lattice dislocations); internal structure of the nucleus structure; or strain hardening. In general, the twinning process is more ordered than the slipping one. In the Pirouz model, the transition to twinning is due to the high Peierls force \( i.e., \) the force required to move dislocations in the plane of the atoms in the unit cell). This, in turn, leads to a very low mobility of lattice dislocations at low temperatures together with a large difference in the mobility of various partial dislocations. Therefore, the mechanism of twinning simultaneously with the concept of theoretical yield limit during machining was expected for diamond at a temperature \( (T<T_\vartheta \approx 1200 \text{ K}) \). The results obtained are important for understanding the mechanisms of plastic deformation of diamond and other covalent materials at room temperature.

4. Conclusions
The experiments considered herein demonstrated that in the diamond, the plastic deformation by mechanical twinning is possible under cyclic loads and stresses, as well as below the critical shear stresses of 55 GPa when the theoretical yield limit is achieved. Indeed, the maximum stresses in the diamond under the experimental conditions are limited by the hardness of steel balls (7 GPa). Various estimates also show that when machining in planetary mills, the mechanical stresses arising from the ball collision do not exceed 6GPa.

Thus, it was experimentally shown that for diamond at temperatures below 420 K (which is significantly below the Debye temperature) with cyclic stresses below 7 GPa, plastic deformation by mechanical twinning takes place.

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