

Mechanical properties of different types of diamond

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Abstract

The mechanical properties of different types of diamond (synthetic diamonds with different nitrogen impurity concentrations 0.3 and 200 ppm) have been investigated by sclerometry hardness and wear resistance measurements. Diamond (111) and (100) faces in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions were tested. It was found the synthetic diamond with nitrogen impurity concentration of 0.3 ppm exceeds other diamond types with respect to hardness and wear resistance, and reveals anisotropy of the mechanical properties, different from other diamond types. The hardness measured on the (111) face for synthetic diamond was 175 ± 5 GPa for 0.3 ppm of nitrogen impurities and 151 ± 5 GPa for 200 ppm of nitrogen impurities. The hardness measurements were performed using an ultrahard fullerite indenter exceeding diamond in hardness and the diamond faces were deformed plastically under scratching conditions. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Hardness and wear resistance are important mechanical properties of diamond that permit comparison between diamonds of different type. Numerous papers have reported hardness measurements of diamond [1-8]. The range of hardness values reported, from 56 GPa to 257 GPa, has been shown depend on the indenter load. This disagreement was discussed in detail in previous publications [1,2]: the main problem in the hardness measurements is that the indenter and the specimen are of equal hardness. The recent discovery of new, ultra-hard fullerite (a three-dimensional polymer of C₆₀ molecules) exceeding diamond in hardness, wear [1,2] and elastic modulus [9] has opened up fresh opportunities for hardness measurements on diamond.

The hardness of diamond depends strongly on both the concentration nitrogen impurities and the orientation of the indenter with respect to the crystallographic orientation of the specimen [3-8]. The Knoop hardness on (100) faces in the $\langle 100 \rangle$ direction is higher than in the $\langle 110 \rangle$ direction for natural diamond, but synthetic diamond of type I la, with impurity concentration of less than 0.1 ppm, is characterized by reverse hardness

anisotropy [6]. That is, the hardness in the (100) $\langle 110 \rangle$ direction exceeds that in the (100) $\langle 100 \rangle$ direction and, as reported [6], the Knoop indenter does not produce distinct indentations in the $\langle 110 \rangle$ direction.

The goal of the present study was to investigate the hardness and wear of different types of diamond (synthetic diamonds with different nitrogen impurity concentrations of 0.3 and 200 ppm) where the hardness of the indenter material (ultrahard fullerite) exceeds that of the specimen (diamond).

2. Experimental details

2.7. Preparation of samples

Synthetic diamond with a nitrogen impurity concentration of 0.3 ppm was synthesized at the Large Diamond Crystal Growth Laboratory of the Research Center for Superhard Materials, Troitsk, Moscow Region. Synthesis was performed in a "toroid"-type tungsten carbide chamber by the method of temperature gradient using an Fe-Al system solvent metal at a growth rate of 1 mg h^{-1} .

Diamond with a nitrogen impurity concentration of 200 ppm was synthesized at ALMAZOT Company, Republic Belarus. Synthesis was performed in the 'split sphere'-type

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chamber ('Bars') by the method of temperature gradient using an Fe-Ni system solvent metal at a growth rate of 3 mg h^{-1} .

The synthesis conditions and structure of ultrahard fullerite used as indenter material have been described elsewhere [10-12]. Specimens were synthesized in the "toroid"-type tungsten carbide chamber at the Research Center for Superhard Materials, Troitsk. Synthesis was performed under a pressure of 13 GPa and a temperature of 1800 K.

The diamond samples for hardness and wear testing were prepared according to the demands listed by Grigorovich [13].

2.2. Hardness and wear resistance measurements

Hardness and wear resistance measurement procedures have been described in detail by Blank et al. [1,2]. Measurements of hardness by the method of sclerometry (scratching at a constant indenter load) were performed on a submicrometre length scale with a NanoScan (NS) measurement system, which is based upon the principles of the scanning force microscopy. A detailed comparison of the indentation and sclerometry methods is given by Grigorovich [13]. These methods conform well to each other. Blank et al. [1,2] showed that the results of hardness measurements on hard and superhard materials by means of the sclerometry procedure, using the NS, are in good conformity with hardness measured by the Vickers indentation procedure, using the micro-hardness tester, and agree with the literature data. The hardness measurement procedure using the NS system was used successfully by Blank et al. [1,2] for hardness measurements of diamond and super- and ultrahard fullerite.

The shape of the indenter is a very important parameter for submicrometre hardness tests, but in practice it is difficult to make indenters having a repeatable geometry. A special procedure described earlier [1,2] was used in this study to calibrate the indenter. In accordance with that, the tip calibration is made by reference to a primary standard with known hardness. Fig. 1 shows the calibration scratch on the sapphire face.

The indenter for the sclerometry measurements of hardness is simultaneously the tip for surface scanning in the NS system. Ultrahard fullerite C_{60} was used as material for the tip.

The scratch was made by the 'indenter edge forward' method. The time of the indenter loading was 10 s, the scratching time was 2 s, the scratch width was in the range $0.6\text{-}1 \text{ }\mu\text{m}$ and the scratch length was about $3 \text{ }\mu\text{m}$ in all experiments. The maximum load on the indenter was 0.1 N . Fig. 2 shows the NS image of the scratch made during the sclerometry test on the diamond face.

The wear resistance was determined from cuts made with a rotating disk [2]. The brass disk

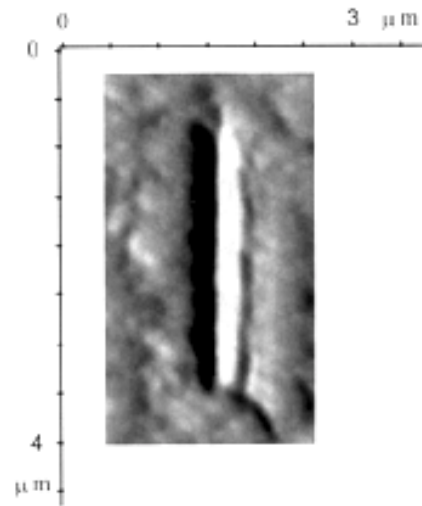


Fig. 1. The calibration scratch on the sapphire face. Vertical scale is 30 nm .

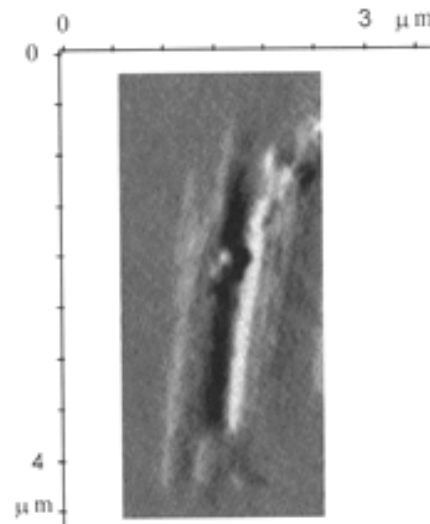


Fig. 2. Image of the scratch from the sclerometry test on the diamond (200 ppm) (100) face in the $\langle 110 \rangle$ direction. Vertical scale is 15 nm .

($\varnothing 9.25 \text{ mm} \times 0.13 \text{ mm}$ size) slid on a test surface in a drop of olive oil which contained 16 wt% of diamond particles. The size of the particles was $10\text{ to }14 \text{ }\mu\text{m}$. The disk was spun at 250 revmin^{-1} , the load on the disk was 0.1 N .

The value $J = \pi D n / h$ was chosen for evaluation of the wear resistance. In this equation n is the number of disk rotations, D is the diameter of the disk and h is the depth of the scar.

The length of the scar was constant and was equal to 1.15 mm to avoid uncertainties connected with variation in the pressure distribution in the scar under the disk as the depth of the scar increased. The standard error of the measurements of J was within 10%

2.3. *Material of indenter for hardness measurements*

For correct hardness measurements, the hardness of the indenter must exceed that of the test material. Furthermore, the indenter must be considered as a rigid body with respect to the specimen for calculations of strength properties [14]. A diamond indenter does meet to these demands when a diamond specimen is tested at room temperature.

As shown by Blank et al. [1,2], ultrahard fullerite is a suitable material for hardness measurements on diamond. The hardness of ultrahard fullerite is 310±40GPa while that of a type IIa diamond face (111) measured under the same conditions is 167±5 GPa [2].

Ultrahard fullerite also has superior elastic properties to diamond. An acoustic microscope study of ultrahard fullerite [9] gives the following findings (data for polycrystalline diamond are given in parentheses for comparison): velocities of sound (km s⁻¹) — compressional 26±2 (16±0.5) and transverse 9.7±1 (9.6±0.3); bulk modulus (GPa) — 1700±400 (500±90); shear modulus (GPa) — 300 ± 60 (340±20); Young's modulus (GPa) — 840±300 (840±190); Poisson's ratio — 0.42±0.16(0.22±0.09).

3. Results and discussion

3.1. *Hardness and wear resistance of diamond*

Results of the hardness and wear resistance measurements of different types of diamond on the (111) face, averaged for various directions, and the (100) face, in <100> and <110> directions, are listed in Table 1. Hardness data for natural diamond type IIa obtained by use of the same equipment were reported earlier [1,2]: 137±6 for the (100) diamond face (averaged over directions), and 167 ± 5 GPa for the (111) diamond face. These results correspond qualitatively to those of Sumiya et al. [6]: an increase of the nitrogen impurity concentration leads to a decrease in hardness, and synthetic nitrogen-free diamond reveals different anisotropy, on the (100) face, from other diamond types.

The wear resistance data correspond to the hardness data: increased nitrogen impurity concentration led to a decrease of the wear resistance. Our effort to study the anisotropy of wear was not successful because the error of wear measurements covered the effect of anisotropy on the

(100) diamond face, but the difference between (111) and (100) faces is distinct.

As mentioned above, it is not correct to compare quantitative data obtained in the present study, with use of the ultrahard fullerite indenter, with data obtained using a diamond indenter because of inaccuracies in hardness measurements in the latter case. Nevertheless, the present data fall in the range of hardness values from 56 GPa to 257 GPa described earlier [1-8].

In our previous publications [1,2] we have reported that the size-dependent hardness effect (the hardness increases as the indentation size decreases) is excluded at the scale of 1 μm in the hardness measurement procedure used (the tip calibration by reference to a primary standard with known hardness). Thus, we conclude that the results of diamond hardness measurements presented in this paper correspond to the true hardness of diamond.

3.2. *Features of plastic deformation of diamond*

An interesting phenomenon was revealed when scratched diamond faces were studied. In some experiments the indented part of a diamond surface heaved after scratching instead of forming a groove. Typical examples of different scratches are shown in Figs. 2 and 3. In Fig. 2 an image of a 'normal' scratch is shown (compare with Fig. 1 showing the scratch of the tip calibration on a sapphire surface). Figs. 3c and d show the cavity formed in the swelled surface. Fig. 3a reveals the heaving formed in the bottom of the scratch and Fig. 3b presents the intermediate result.

A possible effect of contamination as a result of activation of the surface after scratching is excluded because the features of the NS system [1] permit observation of the surface under a viscous layer (for example, under a contamination layer). This possibility was checked against a sample with known structure that was covered by a layer of oil.

An analogous phenomenon was described by Andoh and Kaneko [15]. Silicon and diamond-like carbon film surfaces scratched with a light load heaved immediately. One of the possible explanations of this phenomenon, according to [15], is plastic deformation.

In the present study the phenomenon of surface heaving was revealed on all faces and shown to depend

Table 1
Results of the hardness and wear resistance measurements of different types of diamond

Nitrogen impurity concentration (ppm)	Hardness (GPa)/wear resistance (dimensionless)		
	(111) averaged over directions	(100)<100>	(100)<110>
200	151±5/(1.4±0.2) x 10 ⁷	131±2/(1.1±0.2) x 10 ⁷	115±10/(1.1±0.2) x 10 ⁷
0.3	175±5/(1.9±0.2) x 10 ⁷	139±7/(1.4±0.2) x 10 ⁷	160±3/(1.1±0.2) x 10 ⁷

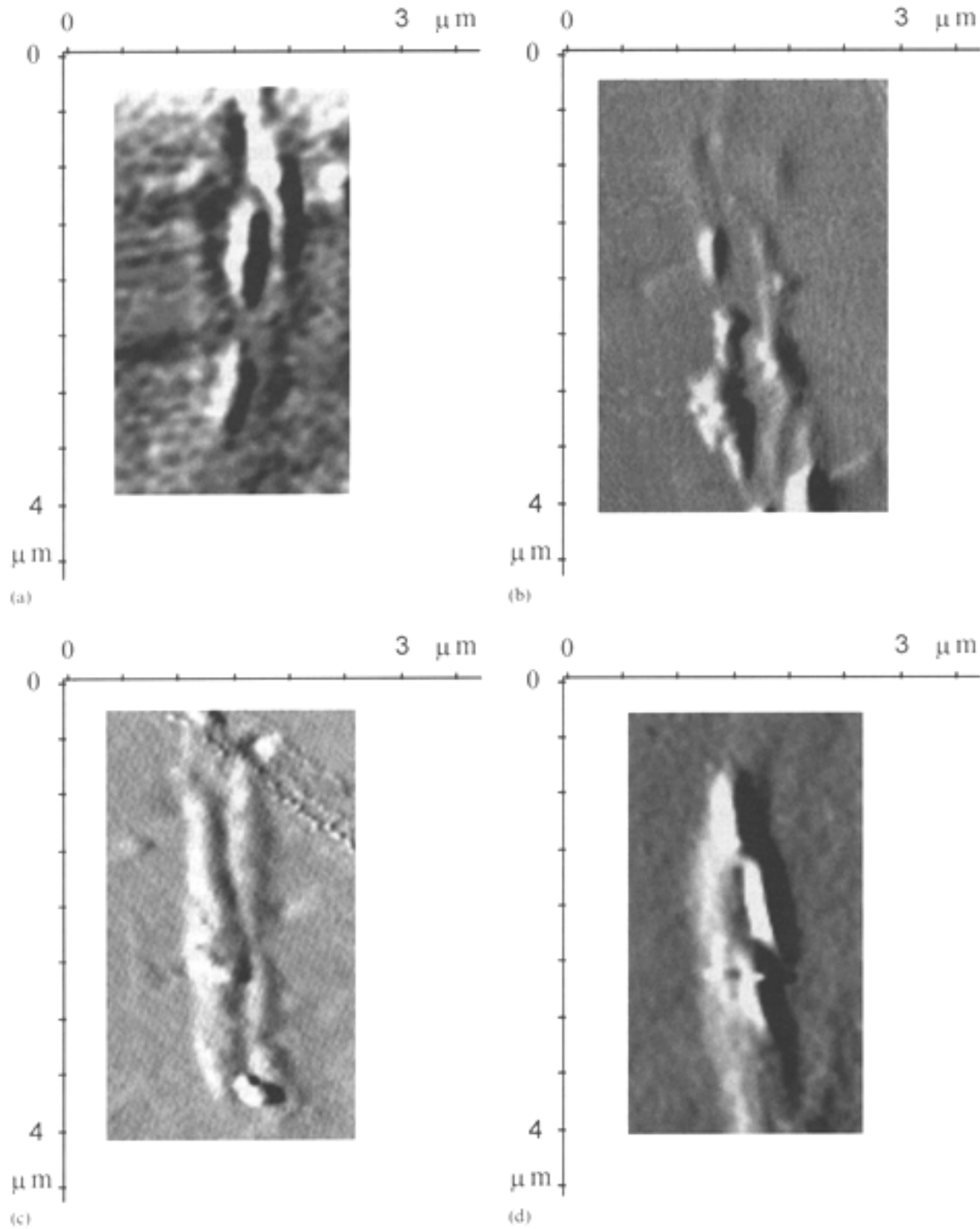


Fig. 3. The effect of heaving of a diamond surface after scratching. Vertical scale is 10 nm in all figures, (a) The heaving is formed in the bottom of the scratch; (b) the intermediate result; (c) and (d) a cavity is formed in the swelled material.

on load on the indenter and indenter shape. A decrease in load leads to a relative increase of the heaving. We suggest that plastic deformation causes the heaving.

4. Summary

The hardness and wear of different types of diamond (synthetic diamonds with nitrogen impurity concentrations of

0.3 and 200 ppm) have been investigated by sclerometry hardness and wear resistance measurements. Diamond (111) faces, in various directions, and (100) faces, in $\langle 100 \rangle$ and $\langle 110 \rangle$ directions, were tested. It was found that the synthetic diamond with the nitrogen concentration of 0.3 ppm exceeds other diamond types in hardness and wear resistance, and reveals an anisotropy of the hardness that is different from other diamond types.

The hardness measurements on all diamond faces were performed under controlled conditions with an ultrahard fullerite indenter, which exceeds diamond in hardness. Consequently, the results of the hardness measurements presented in this paper correspond to reproducible values of the hardness of diamond.

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