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Superior Wear Resistance of Aggregated Diamond Nanorods

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ABSTRACT

The hardness of single-crystal diamond is superior to all other known materials, but its performance as a superabrasive is limited because of its low wear resistance. This is the consequence of diamond's low thermal stability (it graphitizes at elevated temperature), low fracture toughness (it tends to cleave preferentially along the octahedral (111) crystal plains), and large directional effect in polishing (some directions appear to be "soft", i.e., easy to abrade, because diamond is anisotropic in many of its physical properties). Here we report the results of measurements of mechanical properties (hardness, fracture toughness, and Young’s modulus) of aggregated diamond nanorods (ADNRs) synthesized as a bulk sample.1-3 Our investigation has shown that this nanocrystalline material has the fracture toughness 11.1 ± 1.2 MPa m0.5 , which exceeds that of natural and synthetic diamond (that varies from 3.4 to 5.0 MPa m0.5 ) by 2–3 times. At the same time, having a hardness and Young’s modulus comparable to that of natural diamond and suppressed because of the random orientation of nanorods “soft” directions, ADNR samples show the enhancement of wear resistance up to 300% in comparison with commercially available polycrystalline diamonds (PCDs). This makes ADNRs extremely prospective materials for applications as superabrasives.

Fracture toughness and hardness are the two most important properties of solids for material applications. Both of these properties contribute to the wear resistance of a hard material, which is a measure of its suitability as an abrasive. The increase of either toughness or hardness (or both) improves the material’s wear resistance. Fracture toughness characterizes the resistance of a material to crack propagation. The low fracture toughness of single-crystal diamond is enhanced by 2–3 times its magnitude in PCDs, which are manufactured mainly by the sintering of diamond powders using metallic (Co, for example) and nonmetallic (SiC and other carbides) binders. Although they win in toughness, PCDs lose in hardness. Thus, currently commercially available hard materials are not capable of some challenging tasks of very deep drilling in the oil and mining industry, high speed and precision machining of hard alloys and ceramics, and so forth. The design of ideal cutting and drilling tool materials, which should be hard and tough at the same time, is still an impelling and actual goal of materials science.

High-purity polycrystalline diamond has unique potential for industrial applications as an abrasion-resistant material because of its extremely high hardness, no cleavage feature, and high thermal stability. Natural polycrystalline diamond (carbonado) is rather rare. Recently there have been reports on the synthesis of superhard polycrystalline diamonds, nanodiamonds, and ADNRs1-7 from various precursors. Nanodiamonds (polycrystalline diamonds with nanosized grains) show extremely high hardness ranging from 70 to 145 GPa depending on the synthesis conditions.1-7

We synthesized a bulk sample of ADNRs using a multianvil press at 20 GPa and 2500 K as described elsewhere.1-3 Our previous attempts to measure the microhardness of unpolished samples1 failed because a diamond tip of a Vickers-type indenter did not make indentations on the surfaces of the tested material. The roughness of the unpolished surface was crucial for the nanoindentation measurements as well.1 A piece of an ADNR sample was welded into a copper cylinder and polished for hours to overcome this problem in the present study. In the polishing process, a porous cast-iron lap was impregnated with diamond dust and this was rubbed against the diamond specimen at a speed of rotation of 2800 min⁻¹.

Hardness tests on the polished surface were carried out using a PMT-3 microhardness tester (LOMO, Russia) under a load of 500 g (4.91 N). Both Vickers and Knoop indenters were used. At each test, 5 impressions at a distance about 150 micrometers from each other were made. It has been shown that the shape of the Vickers indenter is not proper for measurements of hardness of superhard materials,5-10 and
in the best case one can estimate only the lowest value of hardness. For ADNRs it turned to be 75.5 ± 2.9 GPa. The Knoop hardness of ADNRs was found to be 105 ± 12 GPa. As a rule the values of Vickers hardness are higher than the values of Knoop hardness for the same hard material. The fact that for our sample the measured Knoop hardness exceeds the Vickers hardness confirms our proposal that with the Vickers indenter we obtained only the estimation of the minimal value.

Nanoindentation experiments were performed using a Nano Indentor II (MTS Systems Inc., Oak Ridge, TN). A diamond Berkovich indenter with a tip radius of about 407 nm was used in experiments conducted with a maximum load of 5 mN. The loading and unloading phases of indentation were carried out under load control (nominal rate of 0.2 mN/s). At maximum load, a dwell period of 20 s was imposed before unloading, and another dwell period of 50 s at 80% of unloading, to correct for the thermal drift in the system. The adjacent indents were separated by 20 μm. Pure elastic behavior was observed for natural diamond and ADNRs during nanoindentation. Figure 1 shows the loading curves of a Berkovich indenter for natural diamond and ADNRs. The lower part of the loading curves (in the range of 7–22 nm) was used to determine the Young’s modulus because at greater depths the shape of the tip of the Berkovich indenter starts to deviate from the shape of a sphere, and the Hertz equation becomes inapplicable for the analysis of the results.

![Figure 1. Loading curves of a Berkovich indenter for natural diamond and ADNRs. At loads up to 5 mN, a load-displacement curve for diamond is pure elastic, and loading (arrow direction) and unloading (opposite direction) curves coincide. The lower part of the loading curve (in the range of 7 to 22 nm) was used to determine the Young’s modulus because at greater depths the shape of the tip of the Berkovich indenter starts to deviate from the shape of a sphere, and the Hertz equation becomes inapplicable for the analysis of the results.](image)

Table 1. Properties of Various Element Six (Pty) Ltd. PCD Products\(^{18}\) in Comparison with Natural Diamond\(^{8-10,18}\) and ADNRs

<table>
<thead>
<tr>
<th>property</th>
<th>syndrill(^{18})</th>
<th>syndite(^{18})</th>
<th>syndax(^{18})</th>
<th>natural diamond</th>
<th>ADNRs</th>
</tr>
</thead>
<tbody>
<tr>
<td>fracture toughness</td>
<td>9.8</td>
<td>8.8</td>
<td>6.9</td>
<td>3.40–5.0</td>
<td>11.1(1.2)</td>
</tr>
<tr>
<td>(MPa·m(^{1/2}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Knoop hardness</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>57–104</td>
<td>105(12)</td>
</tr>
<tr>
<td>(GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>810</td>
<td>776</td>
<td>925</td>
<td>1140</td>
<td>1070(54)</td>
</tr>
<tr>
<td>(GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>wear coefficient</td>
<td>3.97</td>
<td>3.89</td>
<td>2.99</td>
<td>2.14–5.49</td>
<td>10(2)</td>
</tr>
</tbody>
</table>

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function of the applied load, hardness, and fracture toughness of the material. The harder and tougher the material, the better is its wear resistance and the higher its wear coefficient, for which there are a number of empirical formulas. To compare ADNRs with natural diamonds and commercially available polycrystalline diamonds we used the same formula that was used by one of the world largest PCD manufacturers (Element Six (Pty) Ltd.):\(^{18}\)

\[
W_H = K_{IC}^{0.5} \cdot E^{-0.8} \cdot H^{1.43}
\]

As seen from Table 1, ADNR material, with its extremely high fracture toughness combined with extremely high hardness and suppressed directional effect in polishing due to nanocrystallinity, has a wear coefficient, \(W_H\), 2–3 times higher than that of natural diamond and 3 times higher than that of one of the best PCDs (Syndrill).

To check the performance of ADNRs as a grinding piece, we conducted a series of mechanical tests, which showed that nanodiamond did not react with iron, forming carbides, when used for machining ferrous steels (what normally happens with single-crystal diamond, which etches very quickly because of this reaction, and is not employed for machining iron-containing alloys). Figure 2 shows two grinding pieces after a test at the same conditions. Although natural diamond clearly etched, there was no apparent sign of damage to ADNRs. This suggested that under the same conditions the ADNR material is a more effective grinding piece than natural or synthetic diamond. Thus, ADNRs show outstanding properties useful for designing new kinds of structural ceramics with extremely high wear resistance and thermal stability\(^1{–}^3\) for use as superabrasives, reinforcements in nanocomposites, and for high speed and precision machining.

References


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