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Ultrahard and superhard phases of fullerite C_{60}: comparison with diamond on hardness and wear

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Abstract

Hardness and wear of ultra-and superhard fullerites and diamond were measured. The measured hardness was revealed 137 ± 6 and 167 ± 5 GPa for the diamond faces (100) and (111) respectively and that for the ultrahard fullerites was 290 ± 30 and 310 ± 40 GPa depending on synthesis conditions. The method of sclerometry (scratch at a constant indenter load) was used for the hardness measurements. The diamond surface (111) was deformed as a plastic material under the scratching with the ultrahard fullerite C_{60} indenter at room temperature. A wear resistance of ultrahard fullerite ceramic in order exceeds that of polycrystal (carbonado-type) diamond. The results of hardness and wear measurements of ultra- and superhard fullerites show a good opportunity for processing of hard and superhard materials. © 1998 Elsevier Science S.A.

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1. Introduction

The resent discovery of new superhard and ultrahard fullerite (3D polymer of C_{60} molecules) [1–3] has opened up fresh opportunities for mechanical processing of hard and superhard materials, especially diamond. The synthesis conditions of these materials and investigation of their structure by X-ray powder diffractometry and Raman scattering were described in Ref. [1–3]. The theoretical prediction of anomalously high mechanical properties of the fullerite C_{60} phase, that is characterized by the intermolecular distances matching the intramolecular distances of C–C bonds is given in Ref. [4].

The term "ultrahard fullerite" was introduced in Ref. [1–3] to distinguish the new carbon state in hardness from diamond. In Ref. [2] was reported, that diamond indenter did not produce an indentation on the ultrahard fullerite specimen. In contrast, the ultrahard fullerite indenter makes an indentation on a (111) diamond face. The other superhard fullerite states were related to the hardness range 55 GPa (cubic BN) to 170 GPa (diamond face (111)) by their possibility to produce an indentation on cubic BN and diamond face (100).

The goal of the present study is investigation of hardness and wear of ultra- and superhard fullerites and comparison of that with diamond and other hard materials.

2. Experimental details

2.1. Preparation of sample

The synthesis conditions of bulk fullerite samples were described in Ref. [1–3]. Specimens were synthesized in the "toroid"-type tungsten carbide chamber. Synthesis was performed at pressures 9.5 and 13 GPa in the temperature range 600–1800 K. The structure of the samples was described in Ref. [1–3].

The hard and superhard samples for hardness and wear tests were prepared accordingly the demands listed in the Ref. [5]. The tests of ultrahard specimens were performed on smooth split surfaces.

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2.2. Hardness measurements

Hardness measurements were performed on the sub-micron length scale using the NanoScan (NS) measurement system based upon the principles of the scanning force microscopy (SFM). NS was developed by the HTE company (Zelenograd) in partnership with the Moscow Engineering and Physics Institute. Performing of the direct hardness measurements using the SFM is possible without any additional equipment [6].

The hardness measurements at a sub-micron scale may be accompanied by the specific kind of errors [7–9]. To avoid it, the new procedure for the hardness measurement is developed in the present study.

The method of sclerometry (scratching at a constant indenter load) was used for the hardness measurements using the NS.

A detailed comparison of the indentation and sclerometry methods is described in Ref. [5]. These methods conforms well to each other.

According to the sclerometry method the hardness value H is calculated as

$$H = kP/b^2. \quad (1)$$

In this equation k is a coefficient of the tip shape, P is the indenter load, b is a scratch width.

The shape of the indenter is very important parameter for the sub-micron hardness tests [9], but in practice it is difficult to make the indenters with a repeatable geometry. A special procedure was used in this study to perform the indenter calibration.

In accordance with the standard method of the sclerometry, at designated P the scratch width b is measured. During the proposed procedure b is a constant (in this study it was 0.6 μm), P_m is measured, and the hardness H_m is proportional to P_m according to Eq. (1). Thus, it is necessary to perform the tip calibration by reference to a primary standard with the known hardness H_s (to determine the load, P_s under that the scratch with $b=$ 0.6 μm is created) to measure the hardness of other materials. According to Eq. (1) if b^2 and k are constant, we have:

$$H_m/H_s = P_m/P_s \text{ and } H_m = H_s(P_m/P_s) \quad (2)$$

Sapphire was used as the standard in this study.

The scratch was made by the method "indenter edge forward". The indenter loading time was 10 s, the scratching time was 2 s, the scratch width was in the range 0.5–0.7 μm, the scratch length was approx. 2.5 μm in all the experiments. In Fig. 1 the NS image of the scratch of the sclerometry test on the topaz face is represented.

To avoid possible mistakes the hardness measurements were performed at the same specimens (quartz, topaz, garnet, sapphire, cubic ZrO_2, cubic BN), both using the NS via the new procedure and a standard microhardness tester, PMT-3, by the Vickers indenter test. Single crystals were used for the hardness measurements. The results of the two hardness measurement procedures conform well to each other, within the experimental error (7%).

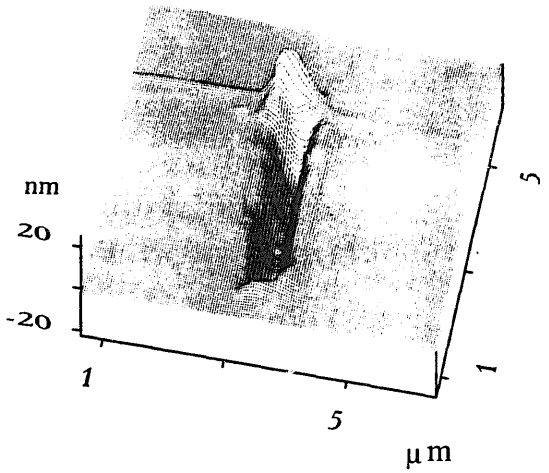

Fig. 1. The NanoScan image of the scratch of the sclerometry test obtained with the ultrahard fullerite tip on the topaz face.

The indenter for the sclerometry measurements of hardness is simultaneously the tip for surface scanning in the NS. Ultrahard fullerite C_{60} and natural diamond were used as materials for the tip.

2.3. Wear resistance measurements

Wear resistance was determined by cuts made with a rotating disk [10,11]. The brass disk (∅9.25 × 0.13 mm^3 size) in a bearing was mounted in the standard microhardness tester PMT-3 instead of an indenter. The disk slid on a tested surface in a drop of olive oil contained 16% wt of diamond particles. The size of particles was 10–14 μm. The disk was spun at 250 rev/min^{-1}. An load on the disk was 0.1 N.

The value $J = \pi Dn/h$ was chosen for evaluation of the wear resistance. In the equation, n is a number of disk rotations, D is the diameter of the disk, h is the depth of 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 scar increased. The standard error of the measurements of J was within 8%.

3. Results and discussion

3.1. Methods of sclerometry and indentation for hardness measurements

The sclerometry method implies a larger plastic deformation in comparison with the indentation method [5]

(that is a value $e_e/(e_e + e_p)$ for the method of indentation exceeds that for the method of sclerometry; here e_e is the elastic and e_p the plastic deformations in the volume deformed under the scratching or indentation). A detailed comparison of the indentation and sclerometry methods is described in Ref. [5]. These methods conform well with each other.

Thus, the sclerometry procedure decreases the uncertainty of the hardness measurements concerned with the problem of the elastic recovery hardness.

The results of the hardness tests are listed in Table 1. The hardness measured by the sclerometry procedure using the NS ("NS hardness" in Table 1) are in good conformity with the hardness measured by the indentation procedure using the micro-hardness tester ("Vickers hardness") and appropriate to the literature data [5,12].

Some disagreement may occur in the comparison of the measured hardness using the NS at the scale 0.6 μm and using the PMT-3 tester at the scale 10 μm because of the size-dependent hardness effect (the hardness increasing with an indentation size decreasing). That is seen at the deformed volume less 1 μm in size [13,14]. The following potential reasons may explain the absence of the size effect in the present study:

(1) The width of the scratch (0.5–0.7 μm) is not small enough to display the size effect.
(2) The tip calibration for the NS tests was performed by reference to sapphire. Its hardness was measured using the micro-hardness tester at the scale 10 μm. Thus, it is impossible to observe the size effect in this procedure, at least for sapphire. If the remaining materials tested have the same (or close to that) function of the size effect as sapphire, it makes it impossible to observe the size effect for these materials too.

Table 1
The results of the hardness tests

Material	Vickers hardness (GPa)	σ	NS hardness (GPa)	σ
Quartz	11	±1	11	±1
Topaz	17	±1	19	±1
Garnet	19	±1	19	±1
Sapphire	23	±1	23	±1
Cubic ZrO_2	24	±2	27	±1
Cubic BN	—	—	60	±3
Type IIa diamond (100)	—	—	137	±6
Type IIa diamond (111)	—	—	167	±5
Ultrahard fullerite	—	—	310	±40

The hardness measured by the sclerometry procedure using the NS ("NS hardness" in the table) are in good conformity with the hardness measured by the indentation procedure using the micro-hardness tester ("Vickers hardness"). σ is the standard error.

3.2. Hardness of diamond and ultrahard fullerite

In Fig. 2 the NS images of the scratches of the sclerometry tests obtained with the ultrahard fullerite tip on the (111) diamond face (Fig. 2a), and with the diamond tip on the (111) diamond face (Fig. 2b) are represented. The scratching of the (111) diamond face with the diamond tip is accompanied by the appearance of numerous cracks, whereas the scratching of that with the ultrahard fullerite tip causes the plastic deformation of diamond without fracture. This depends upon the fact that the hardness of ultrahard fullerite is enough to create a sufficient pressure in the contact point for the plastic flow of diamond at room temperature and the hardness of ultrahard fullerite exceeds the hardness of diamond. Thus, the results of this experiment prove the opportunity for the correct diamond hardness measurements with the ultrahard fullerite indenter.

The measured hardness of diamond using the ultra-

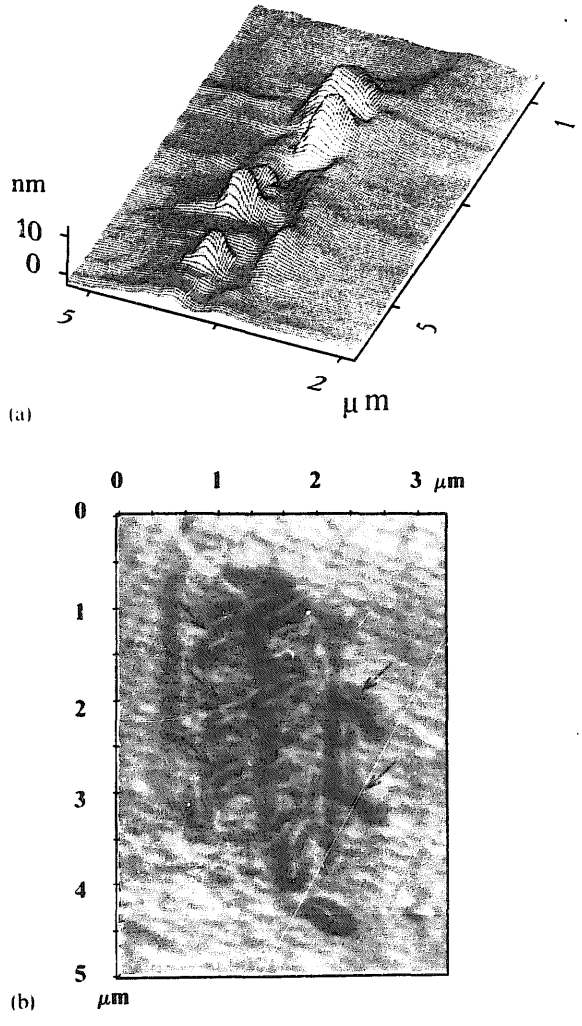

Fig. 2. The NanoScan images of the scratches of the sclerometry tests obtained with the ultrahard fullerite tip on the (111) diamond face (a); and with the diamond tip on the (111) diamond face (b). Cracks are marked by arrows, vertical scale is 2 nm for (b).

hard fullerite tip is 137±6 and 167±5 GPa for the diamond faces (100) and (111), respectively. That using the diamond tip is 231±6 GPa for the diamond face (111).

The disagreement between the measured hardnesses of the diamond face (111) obtained with the ultrahard fullerite and diamond tips (167 and 231 GPa, respectively) displays the difference between the conditions of indentation with ultrahard fullerite (that hardness exceeds diamond) and diamond tips: crack-free indentation for the first and effect of cracking for the last.

The measured hardness of the ultrahard fullerites is 290±30 and 310±40 GPa for the specimens synthesized at pressure 13 GPa and temperature 1473 and 1773 K, respectively (Fig. 3). The qualitative result of the hardness test of the ultrahard fullerite using the ultrahard fullerite tip is analogous to that of diamond using the diamond tip: scratching is accompanied by the appearance of cracks. Consequently, by analogy with diamond (231 GPa is the measured hardness using diamond tip and 167 GPa is the real hardness) the measured value for the ultrahard fullerite may be less.

In Ref. [2] it was reported that the diamond indenter did not produce an indentation on the ultrahard fullerite specimen. This is supplementary evidence for the high degree of hardness of ultrahard fullerite.

3.3. Hardness of superhard fullerites

The results of the hardness tests of the known hard and superhard materials described above enable us to perform correct hardness measurements of superhard fullerites in the new hardness measurements procedure using the NanoScan measurement system with the ultrahard fullerite tip.

The results of the hardness tests of fullerite specimens are represented in Fig. 3. The hardness values depending on the temperature of synthesis are plotted. The specimens were synthesized at pressures of 9.5 and 13 GPa. Hardness levels of sapphire, cubic BN and diamond are plotted for comparison in Fig. 3.

An additional check of the hardness was carried out via Mohs's method. This test confirmed the results obtained: the data plotted in Fig. 3 belong to the ranges of hardness (cubic BN–diamond face (100)–diamond face (111)) as indicated in the figure.

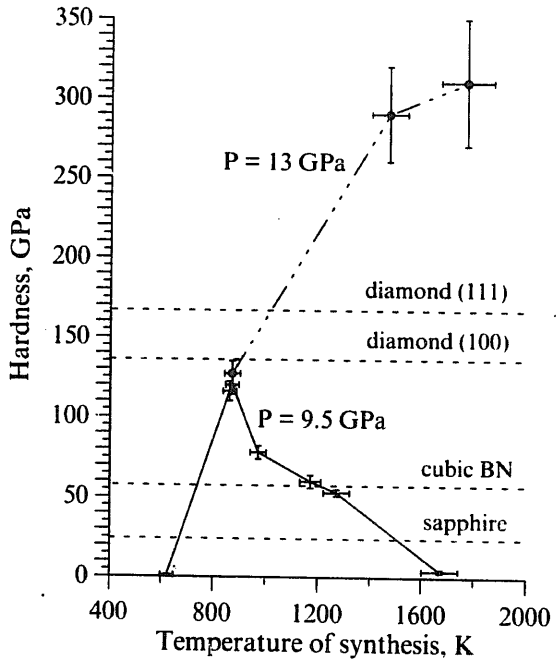

Fig. 3. Results of the hardness tests of fullerite specimens. The hardness values are plotted vs temperature of synthesis. The specimens were synthesized at pressure 9.5 and 13 GPa. Hardness levels of sapphire, cubic BN and diamond are plotted for comparison.

3.4. Wear of fullerite and diamond

The results of the wear tests of the specimens of hard alloy WC+6%Co, sapphire, carbonado-type diamond, super- and ultrahard fullerites are represented in Fig. 4 (synthesis conditions are mentioned on the figure).

A large number of cracks are present in the ultrahard fullerite specimens. A net of cracks is observed at 120× magnification, both on the split surfaces and in the scar. This is confirmed by the fact that the specimens under a load are split into plate-like particles varying in size from 15 to 100 μm. Consequently, the measured wear resistance characterizes the compacted ceramics of ultrahard fullerite, and we believe that a correct comparison between wear resistance of ultrahard fullerite ceramic and diamond may be performed using specimens of polycrystal (carbonado-type) diamond. We studied three samples of carbonado-type diamonds; each was tested in a different locations on the sample section. The value of J encompasses the interval from 3×10^6 to 5×10^6;

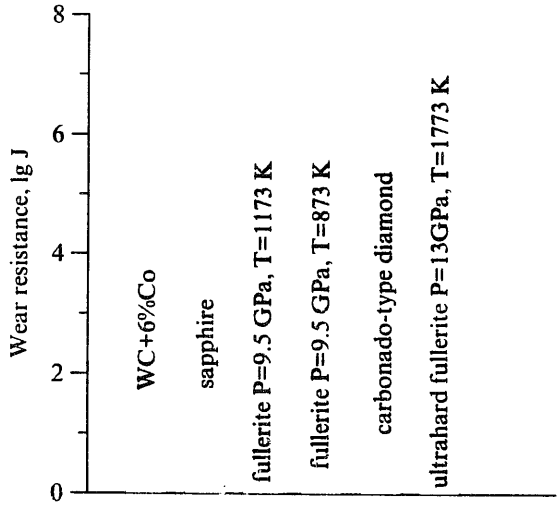

Fig. 4. Results of the wear tests of specimens of hard alloy WC+6%Co, sapphire, carbonado-type diamond, super- and ultrahard fullerites (synthesis conditions are mentioned in the figure).

the mean value 4.4×10^6 is presented in Fig. 4. The mean value of J for ultrahard fullerite ceramic was determined $(1.3 \pm 0.3) \times 10^7$. Thus, ultrahard fullerite ceramic displays the greatest wear resistance.

4. Summary

Hardness and wear of ultra- and superhard fullerites and diamond were measured in the present study. The diamond surface (111) was deformed as a plastic material under the scratching with the ultrahard fullerite C_{60} indenter. This indicates that the hardness of ultrahard fullerite is sufficient to create a high pressure in the contact point for the plastic flow of diamond at room temperature and it exceeds the hardness of diamond. This provides the opportunity for correct measurements of diamond hardness with the ultrahard fullerite indenter. The measured hardness is 137 ± 6 and 167 ± 5 GPa for the diamond faces (100) and (111), respectively. The measured hardness of the ultrahard fullerites is 290 ± 30 and 310 ± 40 GPa for the specimens synthesized at pressure 13 GPa and temperature 1473 and 1773 K, respectively.

The results of hardness and wear measurements of ultra- and superhard fullerites present a good opportunity for processing of hard and superhard materials. The class of superhard materials is increased substantially by the new fullerite states and a new class of ultrahard materials is introduced in the hardness scale.

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