

# Получение, структура, свойства

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**A. Kurio** (Yokohama, Matsuyama, Japan)

**Y. Tanaka** (Yokohama, Japan)

**H. Sumiya** (Itami, Japan)

**T. Irifune, T. Shinmei, H. Ohfuji** (Matsuyama, Japan)

**H. Kagi** (Tokyo, Japan)

## **Wear resistance of nano-polycrystalline diamond with various hexagonal diamond contents**

*Wear resistance of nano-polycrystalline diamond (NPD) rods containing various amounts of hexagonal diamond has been tested with a new method for practical evaluation of the wear-resistance rate of superhard ceramics, in addition to the measurements of their Knoop hardness. The wear resistance of NPD has been found to increase with increasing synthesis temperature and accordingly decreasing proportion of hexagonal diamond. A slight increase in Knoop hardness with the synthesis temperature also has been observed for these samples, consistent with the results of the wear-resistance measurements. These results suggest that the presence of hexagonal diamond would not yield any observable increase in both hardness and wear resistance of NPD, contradictory to a recent prediction suggesting that hexagonal diamond is harder than cubic diamond. It is also demonstrated that NPD is superior to single crystal diamond in terms of relatively homogeneous wearing without any significant chipping/cracking.*

**Keywords:** *nano-polycrystalline diamond (NPD), hexagonal diamond, hardness and wear resistance of NPD.*

### **INTRODUCTION**

Diamond is the hardest material and useful for industrial applications such as cutting tools, but the hardness of single-crystal diamond largely depends on crystallographic planes and directions. Moreover, single crystal diamond is rather fragile relative to natural polycrystalline diamonds, such as ballas or carbonado, because of the development of cleavages in the single crystals. Nano-polycrystalline diamond (NPD) recently synthesized by direct conversion of graphite at high pressure and high temperature has peculiar nano-textures with lamellar and granular grains and possesses very high hardness and toughness, even exceeding those of natural single crystal diamonds [1–3]. Since NPD is a well-

sintered aggregate of randomly oriented nano-diamonds, it also has homogeneous hardness with virtually no anisotropy throughout the sample. Thus, NPD should be potentially important as an ultrahard material for various industrial applications, as demonstrated by a recent cutting performance test [4].

Although studying mechanical properties of NPD is important for its applications to industrial use, quantitative evaluation of its hardness is sometimes difficult due to the extreme hardness. Careful measurements are required by choosing the right shape and material for the Knoop indenter, examining dependency of the applied loads, etc. [2]. Because one of the potential applications of NPD is as a wear-resistant hard material, reliable evaluation of the mechanical properties of this novel material is indispensable taking actual wearing processes into account.

On the other hand, it has been suggested that another high-pressure form of diamond, hexagonal diamond or lonsdaleite [5, 6], which is metastably formed at pressures exceeding  $\sim 18$  GPa at room temperature [7], is harder than cubic diamond on the basis of a numerical simulation [8]. Although a bulk sample of pure hexagonal diamond has not been successfully recovered at the ambient pressure both in nature and experimentally [5–7, 9], it is of great interest to evaluate its hardness and wear resistance to prove this prediction.

We have developed a new method to practically evaluate the wear resistance of NPD, by introducing a polishing system using an NC milling machine combined with a newly designed sample holder, where the sample is loaded at a constant pressure and polished on a rotating hard ceramics plate with circular movements over a long distance. Although the conventional method of loading the sample on a rotating diamond grinding wheel [3] needs to dress the wheel frequently, we can continue the present test over long durations without interrupting the test for maintenance of the ceramics plate in the present method. Moreover, only the wear resistance on one direction of the sample surface is measured in the conventional method, while ours can evaluate the wear resistance of the sample surface averaged on all directions.

The wear resistances of some NPD samples synthesized at different temperatures at high pressure, which contain various amounts of hexagonal diamond, have been tested using the present system, in addition to the Knoop hardness measurements on the same samples. The possibility of ultra-hard nature of hexagonal diamond is examined on the basis of the present wear-resistance and Knoop hardness measurements on these NPD samples.

## EXPERIMENTAL

High purity graphite ( $> 99.99\%$ ) is used as the starting material, which was machined to a rod shape 3.0 mm in diameter and 3.0 mm in length. The graphite rod was enclosed in a Ta foil tube, which is surrounded by a magnesia sleeve, a Re tube heater, and a  $\text{LaCrO}_3$  thermal insulator, and was inserted in a Co-doped magnesia pressure medium, as described in [10]. Four NPD rod samples without any visible cracks were synthesized at temperatures of 1900, 2200, 2300, and 2400°C at a same pressure of 20 GPa for 20 minutes (60 min for the run at 1900 °C) by the direct conversion method using a Kawai-type multianvil apparatus. As the synthesis temperature was estimated by a relationship between temperature and the input electric power to the heater, uncertainty of the order of  $\sim \pm 50$  °C may exist in these temperatures. The pressure was evaluated based on the covalent-metallic transitions in ZnS, GaAs, and GaP at room temperature, which may suffer uncertainty of  $\sim \pm 1$  GPa.

The recovered samples were inspected with an optical microscope, and analyzed using X-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM). An X-ray diffractometer equipped with a Mo-K $\alpha$  source and an imaging plate detector was used for the XRD measurements, while the Raman spectra were obtained using argon ion laser with a wavelength of 514.5 nm. Thin foils of some of the NPD samples were prepared with a focused iron beam (FIB) system, and their fine textures and grain sizes were examined by TEM. Hardness of the obtained NPD samples were measured under a load of 4.9 N at room temperature using Knoop indenters made of a synthetic type IIa single-crystal diamond [11]. The tip orientation of the indenter was a superhard (001) <110> direction [12], and the hardness of the (001) <100> of high purity synthetic type IIa single crystal was used as a reference for the hardness measurements [2].

After these measurements, the NPD rod sample was processed using a pulsed laser to form a regular-shaped rod with a diameter of 2.0 mm and a length of 1.5 mm. One end of the rod was further processed to a cone–shape with a tapered angle of 120 degrees with a flat-top culet surface of 300  $\mu\text{m}$  in diameter by mechanical polishing on a diamond polishing wheel.

A testing device was designed and assembled, which was used for the evaluation of the wear resistance of the NPD samples. A newly designed sample holder was attached to the Z-axis of a NC milling machine (Fig. 1, a), which push the sample on a hard polycrystalline ceramic ( $\text{Al}_2\text{O}_3$ ) plate at a constant loading pressure of 0.3 MPa by a piston operated with controlled air pressure (Fig. 1, b). The  $\text{Al}_2\text{O}_3$  plate was placed on the horizontal stage of the machining center, which was rotated at 5 m/min for about 34 hours with changing the rotation diameter so that the trace of the running sample would not overlap (Fig. 1, c). In this way, the top surface of the NPD sample is polished from all directions without changing the polishing conditions (e.g. applied load, surface conditions of the polished ceramics, temperature of the sample surface, etc.) for a very long total running distance of about 10 km.

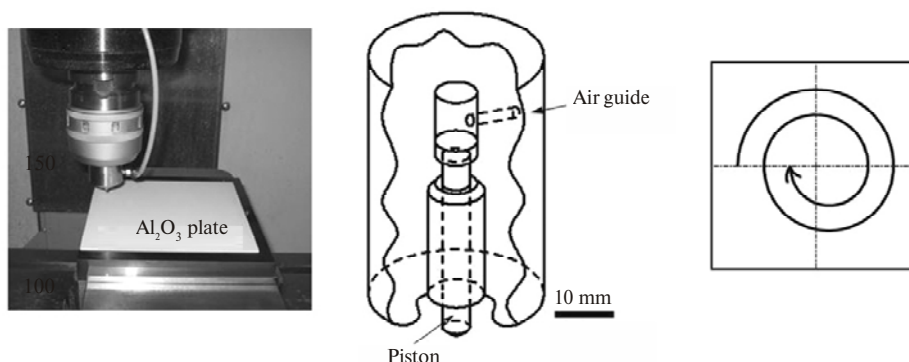


Fig. 1. The machining system used for the present wear–resistance test. A photograph of the sample attachment and the alumina ( $\text{Al}_2\text{O}_3$ ) plate (a), and a schematic illustration of the sample attachment (b). The trajectory of the sample running on the alumina is illustrated in (c).

The removed volume of the sample after the wearing run was evaluated from the changes in the surface areas measured with a microscope. The polished surface was also inspected with optical and laser scanning microscopes. The (100) plane of synthetic Ib diamond was used for the wear–resistance test for comparison, in addition to the NPD samples.

## RESULTS AND DISCUSSION

Table lists the conditions of synthesis of NPD performed at a fixed pressure of 20 GPa and the results of some measurements on the obtained samples. X-ray diffraction measurements show that the NPD samples synthesized at 1900, 2200, and 2300 °C are made of a mixture of cubic diamond and small amounts of hexagonal diamond, as shown in Table and Fig. 2, *a*, while the sample obtained at 2400 °C is of pure cubic diamond. The presence of graphite was not confirmed in any of the NPD samples, consistent with our earlier study [10]. The proportions of hexagonal diamond in these samples were estimated by intensity ratios of the (100) diffraction peak of hexagonal diamond relative to the (111) peak of cubic diamond based on a fitting with two Gaussian peaks. As shown in Fig. 2, *b*, the proportion of hexagonal diamond monotonously decreases from ~ 20% at 1900 °C to zero at 2400 °C. Note that the proportions of hexagonal diamond evaluated in the present analysis are relative values.

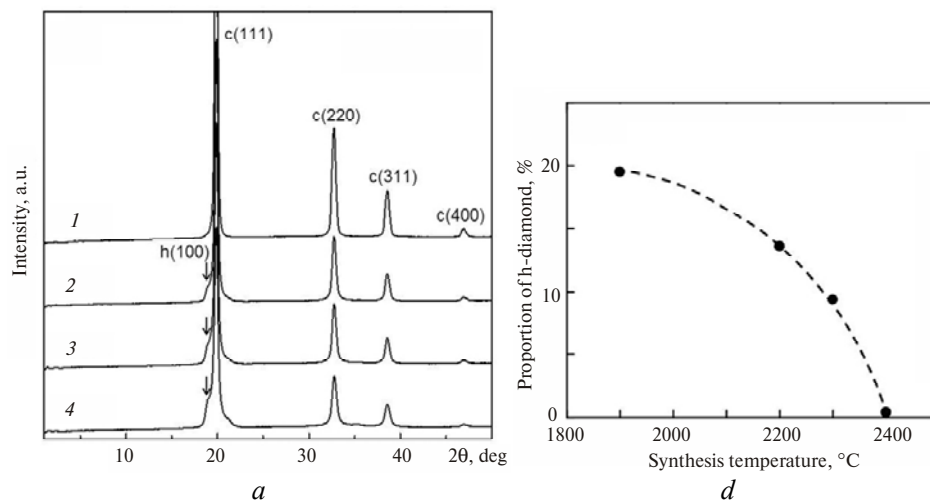


Fig. 2. (a) XRD profiles of the NPD samples used for the wear-resistant test, synthesized at various temperatures (2400 (1), 2300 (2), 2200 (3), 1900 (4) °C) at 20 GPa: c – cubic diamond, h – hexagonal diamond. No graphite was found to exist in all of these samples, while the amount of coexisting hexagonal diamond decreases with increasing temperature as indicated by the changes in the intensity of the (100) diffraction peak of hexagonal diamond. (b) Changes in proportions of hexagonal diamond in the NPD samples with increasing synthesis temperature, estimated based on the intensity ratios of h(100) and c(111) in the XRD profiles of (a).

Figure 3, *a* shows a Raman peak near  $1332\text{ cm}^{-1}$  characteristic of cubic diamond ( $T_{2g}$  mode) observed in the NPD samples. The Raman peak at  $1324\text{ cm}^{-1}$  of hexagonal diamond is not well resolved in the present measurements because of its small relative intensity and broadness [13]. These peaks are broad and possess relatively small signal to noise levels due to the strong fluorescence from NPD, consistent with our earlier results [10]. Figure 3, *b* shows the change of the full width at half-maximum (FWHM) in the Raman peak, which clearly demonstrates that the FWHM decreases with increasing synthesis temperature. However, the FWHM value for the sample synthesized even at the highest temperature of 2400 °C ( $10.8\text{ cm}^{-1}$ ) is substantially larger than the value ( $\sim 3\text{--}4\text{ cm}^{-1}$ ) for type IIa diamond single crystal used as a reference. The Raman peak sharpening at the higher temperature can be attributed to grain growth of diamond [10, 14], and we

performed TEM observations of the samples synthesized at the lowest and the highest temperatures (Fig. 4). It is rather difficult to precisely measure the grain size of diamond in these samples because of the coexistence of lamellar crystals with granular grains, but the averaged grain sizes of the granular parts of these samples are about 30 nm (1900 °C) and 60 nm (2400 °C), respectively, showing a slight grain growth over the temperature range of ~ 500 °C.

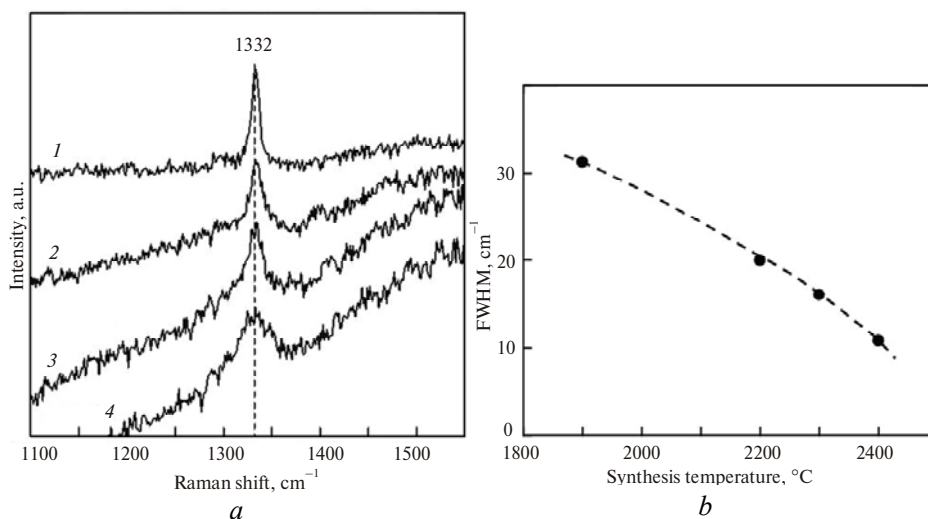


Fig. 3. Raman spectra of the NPD samples synthesized at various temperatures (2400 (1), 2300 (2), 2200 (3), 1900 °C (4)) at 20 GPa (a). Variation of the full widths at half maximum (FWHM) of the Raman spectra of the NPD samples with synthesis temperature (b).

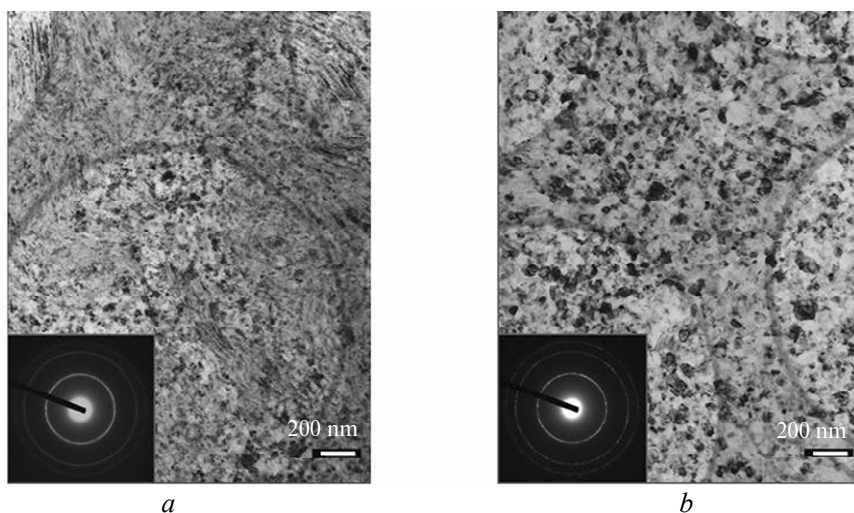


Fig. 4. TEM images of the NPD samples synthesized at 1900 (a), and 2400 (b) °C. Averaged grain sizes in the granular regions of these samples increase from ~ 30 to ~ 60 nm, respectively. Inlets are the electron diffractions of the samples with TEM.

Figure 5 shows the variation of Knoop hardness of the NPD samples as a function of synthesis temperature. The hardness ranges in 125–142 GPa consistent with the results of earlier studies (130–145 GPa [1, 2]). No clear dependence of the hardness on synthesis temperature is observed for these samples, although a

tendency of a slight increase with synthesis temperature is seen in Fig. 5. It is demonstrated that the presence of larger amounts of hexagonal diamond in the NPD samples synthesized at lower temperatures does not result in any notable increase in hardness of diamond. This is contradictory to the prediction that suggests hexagonal diamond is harder than cubic diamond based on an ab initio calculation [8]. Nevertheless, other factors such as the slight difference in grain size of diamond and the plausible higher inter-grain cohesion in the samples synthesized at higher temperatures need to be considered for the decisive conclusion.

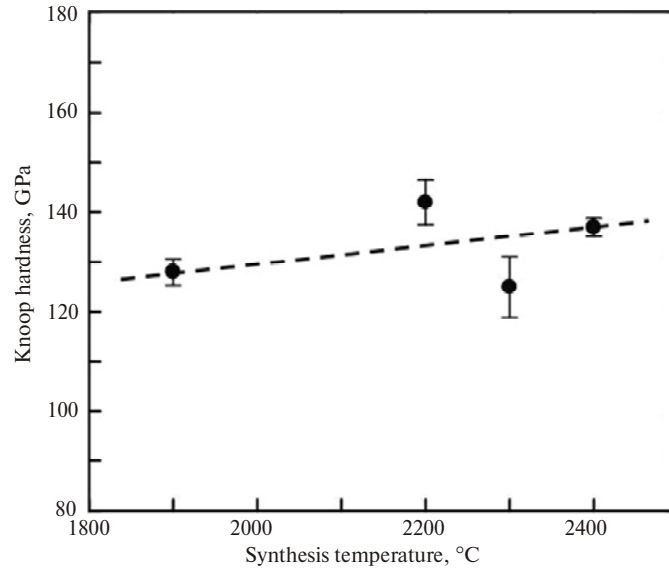


Fig. 5. Knoop hardness of the NPD samples synthesized at various temperatures.

Figure 6 shows the wear rate of the polished NPD surface, defined as the reduced volume per minute on the basis of the enlargement of the top surface area measured after the wear resistance test. It is seen that the wear rate of the NPD samples decreases with increasing synthesis temperature; i.e. those synthesized at higher temperatures have higher wear resistance, consistent with the slight increase in the hardness of the NPDs with temperature as shown in Fig. 5. Although the measured Knoop hardness has some significant errors and is rather scattered, the wear rates determined by the present wear-resistance test systematically vary with the synthesis temperature. This indicates that the present method is a promising way of evaluating the effective wear resistance of superhard materials. It should be noted that the presence of larger fractions of hexagonal diamond reduces the wear resistance of the NPD samples, suggesting that hexagonal diamond is less harder than cubic diamond and/or the lower heat resistance of the metastably formed hexagonal diamond.

Figure 7 demonstrates optical and laser microscope images of the polished surface of the NPD samples after the wear resistance test. It is seen that the samples synthesized at lower temperatures exhibit significantly rougher surfaces, while those synthesized at the highest temperature show relatively smooth surfaces, suggesting that the wearing of the NPD sample proceeds by a heterogeneous dropping of small fragments of the nano-diamond grains. However, it is not clear whether the apparently more substantial peeling of the fragments at lower

temperature is caused by the presence of hexagonal diamond or the lower inter-grain cohesion of individual diamond grains.

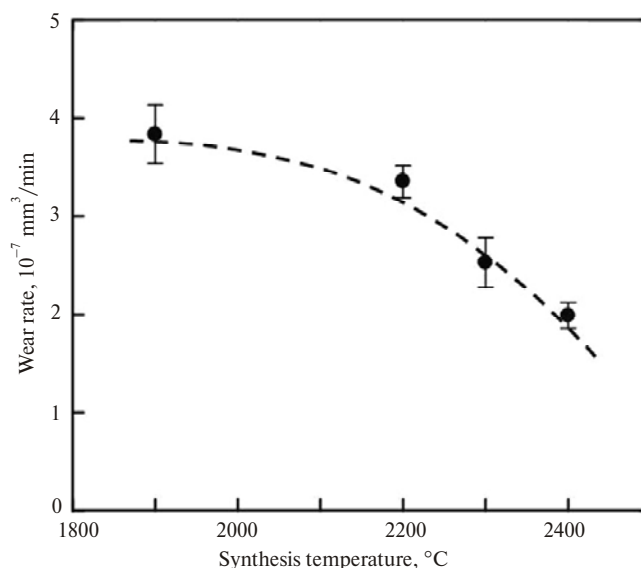


Fig. 6. Wear rates of the NPD samples synthesized at various temperatures.

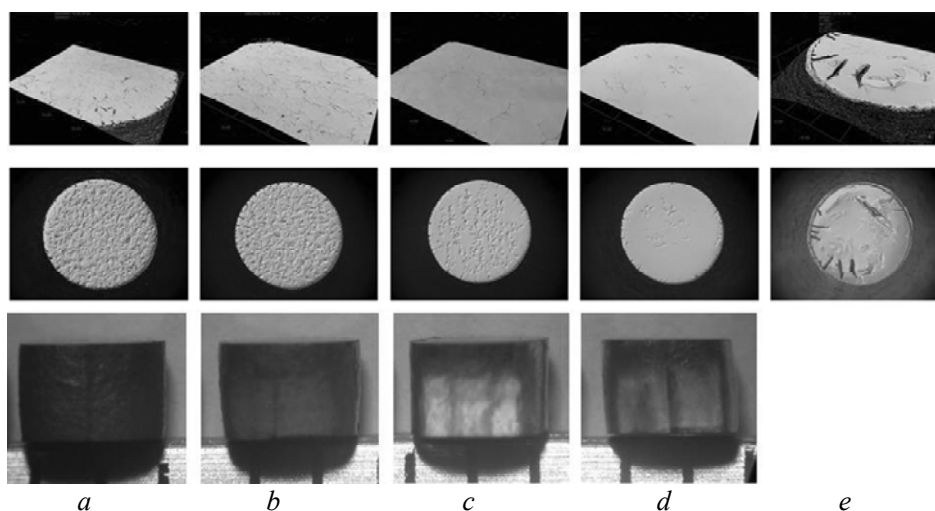


Fig. 7. Laser microscope (upper) and optical microscope (middle) images of the polished surface of the NPD samples (*a–d*). The corresponding optical and laser microscope images for synthetic single crystals of type Ib diamond are also shown for comparison (*e*). The lower pictures are the side views of the NPD rods recovered after synthesis experiments, which are opaque (*a*), translucent (*b*), and highly transparent (*c*, *d*). Synthesis temperatures are 1900 (*a*), 2200 (*b*), 2300 (*c*), 2400 (*d*) °C.

On the other hand, it is interesting to note that the present wear–resistance test shows that the (100) plane of synthetic type Ib single crystal diamond, possessing the maximum Knoop hardness of only 80–90 GPa [3], yields a wear rate similar to those of the NPD samples (see the table). As the volume reduction in NPD seems to proceed by the peeling of the fragments of diamond grains in the present test, polycrystalline materials are relatively easily polished due to heterogeneous stress

concentrations on the grain boundaries that would help the peeling of fragments. Nevertheless, it should be noted that although the enlargement of the surface area is lower in the single crystal type *Ib* diamond than those of most of the NPD samples, a number of relatively large cracks are recognized on the polished surface (Fig. 7, *e*), particularly in the peripheral parts, of the single crystal. This is most likely due to the operation of cleavage in the single crystal [15], developed from the edge of the sample surface, suggesting that the wear rate of the single crystal evaluated from the surface area change should be biased and regarded as the minimum estimation. In contrast, the present wear-resistance test shows the absence of major chipping/crack on the polished surfaces in any of the NPD samples, suggesting outstanding characteristics of NPD for industrial applications such as cutting/polishing tools.

### Characterization of NPD samples and experimental results

Sample	Synthesis temperature, °C	Phases present	Proportion of h-diamond, %	FWHM of Raman peak, cm <sup>-1</sup>	Knoop hardness, GPa	Wear rate, ×10 <sup>-7</sup> mm <sup>-3</sup> /min
NPD	1900	c + h	19.5	31.2	128 (3)	3.84 (30)
	2200 (16)	c + h	13.6	19.9	142 (5)	3.35
	2300	c + h	9.4	16.1	125 (6)	2.53 (25)
	2400	c	0	10.8	137 (2)	1.99 (13)
<i>Ib</i> (100)	–	–	–	–	90–100	2.18 (43)

Note. c is cubic diamond, h is hexagonal diamond.

In conclusion, our measurements on NPD samples containing various amounts of hexagonal diamond suggest that the latter form of carbon is less hard than cubic diamond, consistent with a recent theoretical study [16], although further study is needed to measure the hardness of a bulk sample of pure hexagonal diamond to prove it. It has been proposed that there may be other carbon allotropes with densities higher than that of cubic diamond [17]. However, these forms of carbon are predicted to be less hard than cubic diamond, and NPD remains the hardest polycrystalline bulk sample ever synthesized.

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*Зносостійкість нано-полікристалічних алмазних (НПА) стрижнів, з різним вмістом гексагонального алмазу, була протестована новим методом практичної оцінки швидкості зносу надтвердої кераміки, додатково до вимірювання їх твердості по Кнупу. Було виявлено, що зносостійкість НПА збільшується зі зростанням температури синтезу і, відповідно, зі зменшенням частки гексагональних алмазів. Також, відповідно до результатів вимірювань зносостійкості, для цих зразків спостерігалось невелике збільшення твердості по Кнупу з температурою синтезу. Ці результати дозволяють припустити, що присутність гексагональних алмазів не приводить до будь-якого помітного збільшення як твердості, так і зносостійкості НПА, що суперечить недавньому припущенню про те, що гексагональний алмаз твердіший, ніж кубічний. Також показано, що НПА перевершує монокристал алмазу з точки зору відносно однорідного зношування без значних відколів/тріщин.*

**Ключові слова:** нано-полікристалічні алмази (НПА), гексагональний алмаз, твердість і зносостійкість НПА.



*Износостойкость нано-поликристаллических алмазных (НПА) стержней, с различным содержанием гексагонального алмаза, была протестирована новым методом практической оценки скорости износа сверхтвердой керамики, в дополнение к измерениям их твердости по Кнуну. Было обнаружено, что износостойкость НПА увеличивается с ростом температуры синтеза и, соответственно, с уменьшением доли гексагональных алмазов. Также, в соответствии с результатами измерений износостойкости, для этих образцов наблюдалось небольшое увеличение твердости по Кнуну с температурой синтеза. Эти результаты позволяют предположить, что присутствие гексагональных алмазов не приводит к какому-либо заметному увеличению как твердости, так и износостойкости НПА, что противоречит недавнему предположению о том, что гексагональный алмаз тверже, чем кубический. Также показано, что НПА превосходит монокристалл алмаза с точки зрения относительно однородного изнашивания без значительных сколов/трещин.*

**Ключевые слова:** нано-поликристаллические алмазы (НПА), гексагональный алмаз, твердость и износостойкость НПА.

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Geodynamics Research Center, Ehime University

Advanced Materials R&D Laboratories, Sumitomo Electric Industries, LTD

Geochemical Research Center, the University of Tokyo