Large-volume static compression using nano-polycrystalline diamond for opposed anvils in compact cells

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Abstract. In order to extend the pressure regime of intrinsically low-sensitivity methods of measurement, such as neutron scattering and NMR, sample volume to be compressed in compact opposed-anvil cells is desired to be significantly increased. We hereby conducted a series of experiments using two types of compact cells equipped with enforced loading mechanisms. Super-hard nano-polycrystalline diamond (NPD) anvils were carefully prepared for large-volume compression in these cells. These anvils are harder, larger and stronger than single crystal diamond anvils, so that they could play an ideal role to accept the larger forces. Supported and unsupported anvil geometries were separately tested to evaluate this expectation. In spite of insufficient support to the anvils, pressures to 14 GPa were generated for the sample volume of > 0.1 mm³, without damaging the NPD anvils. These results demonstrate a large future potential of compact cells equipped with NPD anvils and enforced loading mechanism.

1. Introduction

Diamond anvil cells (DAC) are now playing essential roles in high pressure science and technology for their simple design, wide pressure range, and straightforward accessibility to the sample by optical, spectroscopic, and electromagnetic methods [1, 2]. However, we must always compromise with an essential problem of the DAC to appreciate its versatility; DAC can compress very limited sample volume of ~0.01 mm³ even at pressures to 10 GPa, which further decreases with increasing pressure. Although the majority of DAC applications such as synchrotron x-ray diffraction do not critically conflict with this problem, some potential applications involving intrinsic low sensitivity methods of measurement, such as neutron scattering [3] or NMR [4, 5], are seriously hindered by low signal-to-background or signal-to-noise ratio from the tiny sample. To extend the pressure regime of these methods of significant future importance, we need to take substantial effort to increase the sample volume of DAC or other types of compact opposed-anvil cells.
The tiny sample volume of the DAC is due to the limited size of single crystal diamond (SCD) anvils. To enlarge the anvils, natural moissanite (SiC) single crystal and chemical-vapor deposited diamond single crystal have been utilized [6, 7]. In addition to them, we hereby report our preliminary results of larger-volume compression experiments than the conventional DAC. We used the super-hard nano-polycrystalline diamond (NPD) as opposed anvils. The NPD is made of diamond particles of several tens nanometers, which is synthesized by direct conversion of graphite at pressures of 15-20 GPa and at temperature of 2300 °C [8]. The NPD contains neither binder materials nor secondary phases [9]. The NPD has no anisotropy of hardness and free from cleavage features, making it even stronger than SCD (and of course than moissanite). Furthermore, the size of single NPD piece currently reaches to 5 millimeters, which has exceeded the size of single crystal diamond anvils [10]. Considering these unique features of NPD, it is promising to develop harder, larger and stronger anvils than those made of the SCD. Thus the NPD anvils may play an ideal role for large-volume static compression experiments using the compact cell.

2. Experimental

2.1. Preparation of NPD anvils

To increase the sample volume while keeping the wide pressure range of opposed-anvil cells, not only anvil size but also applied load must be simultaneously increased. The previous work with moissanite anvils reported that a cone-cut anvil coupled with a supporting ring was significantly strengthened by confined force [6]. To evaluate the difference, we prepared both supported and unsupported geometries of the NPD anvils (see Table 1 for their dimensions). We recently developed an efficient laser micromachining method for the NPD to give them precise shape as desired [11]. Two pieces of supported anvils were laser-cut from as-sintered cylindrical NPD test pieces with 3.8 mm in diameter and 2.8 mm in thickness. A piece of unsupported anvil was laser-cut out from another NPD test piece with 5.2 mm in diameter and 4.3 mm in thickness. These test pieces were supplied from Sumitomo Electric Industries, LTD (Itami, Osaka, Japan). Figures 1 and 2 respectively show schematic drawings and photographs of the supported and unsupported NPD anvils in conjunction with their supporting base or height adjustor. To improve optical transparency, the culet and table (or top and bottom) surfaces of these NPD anvils were mechanically flat-polished after the surfaces were cut out by the laser beam. The pavilion (slope surrounding the culet) was laser-cut to sixteen or higher number of symmetric pyramidal faces around the culet. These faces were not mechanically polished because their quality does not matter for pressure generation. The pavilion angle was set at 18º, which is significantly smaller than that of the conventional SCD anvils. This is because NPD does not cleave like SCD does; then the shallower pavilion angle is the more effective to increase massive support [12]. The girdle (side surfaces) of the supported-type anvils has a precise cone-shape with 30º inclination; it was laser-cut as a combination of numerous flat surfaces, and then mechanically polished to further improve the fitting with the surrounding support. The side surface of the unsupported-type anvil was not processed at all, because this surface does not matter in pressure generation. All these NPD anvils were finally furnaced at 600 °C in air to remove carbon condensates from the laser-cut surfaces.

2.2. Opposed-anvil cell designs

Two different designs of compact cells are separately tested to compress the two different geometries of NPD anvils. The couple of supported NPD anvils were compressed with a newly designed DAC equipped with an enforced loading mechanism by two M12 loading bolts, which sustains the loading force up to 10 tons (Fig. 3; Sasaki et al., in preparation). The unsupported NPD anvil was compressed with a hybrid-anvil high-pressure device, equipped with a clamping mechanism by six M6 set-screws, which sustains the loading force to at least 5 tons (Fig. 4). These limits of the applicable loads are higher than those of the conventional DAC (ca. 1 ton); thus larger sample volume is effectively compressed to the desired pressure regime. The hybrid anvil device was originally developed for single crystal neutron diffraction at high pressures [13]; it was designed to enlarge the sample volume.
especially sample height) while keeping the pressure range of compact cells, which is of course consistent with our current motivation. The current hybrid anvil system was the combination of the unsupported NPD anvil with flat culet, and a tungsten carbide anvil with a center-dimpled culet. The former enables optical access to the sample while the latter is effective to increase the sample volume. The NPD anvil was with 4.2 mm in height, which was much smaller than the standard anvil size of the hybrid device; single crystal sapphire with 10 mm height had been originally used as the transparent anvil. To compensate the smaller height of the NPD anvil, a beryllium-copper adjustor was prepared and equipped. The dimpled tungsten carbide anvil was made of SF25 and with 14 mm in diameter, 10 mm in height, 2.68 mm in culet diameter, 1.6 mm in dimple diameter, and 0.22 mm in dimple depth.

| Table 1. Experimental conditions. |
|-----------------------------------|
| **Type of NPD anvils** | **Supported** | **Unsupported** |
| Anvil | | |
| Dimension [mm] | $\phi 2.8 \times t \ 2.7$ | $\phi 5.2 \times t \ 4.2$ |
| Culet diameter [mm] | $\phi 1.25$ | $\phi 2.6$ |
| Girdle geometry | $30^\circ$ conical, cut and polished | straight, as sintered |
| Anvil base | | |
| Material | SUS420J2 | beryllium-copper |
| Geometry | supporting ring | flat, height adjusted |
| Sample size | | |
| Initial dimensions [mm] | $\phi 0.50 \times t \ 0.50$ | $\phi 1.10 \times t \ 0.38^a$ |
| Initial volume [mm$^3$] | 0.1 | 0.3 |
| Final dimensions [mm] | $\phi 0.68 \times t \ 0.11$ | $\phi 1.00 \times t \ 0.32^a$ |
| Final volume [mm$^3$] | 0.04 | 0.2 |
| Gasket | | |
| Material | SUS304 | A2017 |
| Thickness [mm] | 0.25 | 0.28 |
| Preindentation | yes | yes |
| Sample chamber | | |
| Pressure medium | water | glycerine |
| Size of enclosed ruby chip [µm] | $35 \times 1 \ chip$ | $100 \sim 150 \times 3 \ chips$ |
| Excitation laser conditions | | |
| Wavelength [nm] | 514.5 | 632.8 |
| Power [mW] | 0.05 | 2 |
| Type of cells used for compression | enforced-DAC type | hybrid anvil device |
| Maximum generated pressure [GPa] | 14 | 8 |
| Anvil damage | none | none |

$^a$Including the dimple depth (0.22 mm) on the counterpart anvil
Figure 1. Supported-type geometry of the NPD anvil. The lower photo shows the anvil fixed into the supporting ring.

Figure 2. Unsupported-type geometry of the NPD anvil. The lower photo shows the anvil equipped with the height adjustor.
2.3. Measurement of pressure

NPD is made of nanometre-sized grains which induce large absorption and fluorescence for visible to ultraviolet wavelengths, as demonstrated by high background in its Raman spectra [14] and by its enhanced absorption to laser beams [11]. Therefore, for pressure measurement through NPD anvils, in situ x-ray diffraction of an established calibrant [15] has been rather preferred than the popular ruby fluorescence scale [16]. However, we cannot always use a synchrotron for our expected applications of NPD anvils, so that the ruby scale should be available with practical accuracy. Its accuracy may vary with excitation laser properties, because absorption and fluorescence intensities of NPD increase at shorter wavelength and at higher power, while the ruby fluorescence intensity also changes with these conditions. We therefore tested a series of fluorescence excitation conditions; a ruby chip with 10 µm in size at ambient pressure was irradiated through a 5 mm-thick NPD test piece. Four laser wavelengths from 410 nm to 633 nm were tested to determine the applicable wavelength range. Figure 5 shows the results, which demonstrate that laser wavelengths between 488 (blue) and 633 nm (red) are all suitable to excite the ruby through NPD, as long as sufficient (but not too large) power was supplied. For longer excitation wavelength, the minimum power to find a good spectrum decreases. This is because absorption and background fluorescence of NPD decrease with increasing laser wavelength [14]. The excitation efficiency of ruby fluorescence also decreases, while this latter effect was not obvious in these results. Excitation at 410 nm (violet) did not work because the background was too intense to find a spectrum (results not shown). Considering these results, it was concluded that we can accurately determine the pressure by the ruby scale even through the thick NPD anvil, as long as the qualified excitation laser conditions were applied. We followed these conditions in our pressure generation experiments to measure the pressure with sufficiently accuracy (see Table 1 and Figure 5d).
Figure 5. Ruby fluorescence spectra taken through NPD. (a-c) Fluorescence of 10 µm-sized ruby chips at ambient pressure measured through a double-polished NPD window with 5 mm in thickness. Focused laser beams with various wavelengths and powers were applied for the excitation (see these parameters within the figures). At longer wavelength, the minimum laser power to find a good spectrum decreases. (d) Representative spectra measured at high pressure through the supported NPD anvil with 2.7 mm in the thickness.
2.4. Sample size, gasket, and pressure medium
Table 1 also shows sample sizes and other sampling parameters for pressure generation using the supported and unsupported NPD anvils, respectively. Both types of the anvils are compatible with the initial sample volume of \( > 0.1 \text{ mm}^3 \), which is at least one order of magnitude larger than that of the DAC. For accuracy of the ruby scale, we used soft and compressible pressure media. Therefore the final sample volume at the maximum pressures was reduced to about half of the initial.

3. Results and discussion
Figures 6 and 7 respectively show the results of pressure generation experiments using the supported and unsupported NPD anvil geometries. Pressures to 14 GPa were generated with the supported NPD anvils for 0.1 mm\(^3\) initial volume, while pressures to 8 GPa were generated with the unsupported NPD anvil for 0.3 mm\(^3\) initial volume. In the latter experiment we directly measured the loading forces with increasing and decreasing them. By increasing the load the pressure acceleratively increased, and finally the cell became unstable when the load reached at 3.3 tons. This value is significantly larger than the maximum load applicable to the SCD anvils. It is rather comparable to the load applicable to the twice-larger moissanite with similar culet size to our anvil; it was reported that a moissanite anvil with 8 mm in diameter and 2.8 mm in culet size was failed at \( \sim 4 \) tons [6]. After reaching the highest pressure in the latter experiment, a pressure hysterisis was observed by decreasing the load (Fig. 7). In future use of the device at low temperature, a resin sheet will be situated between the anvil and the piston. This sheet has larger thermal contraction than that of the cell jacket, and the difference of the contraction between the anvil and the jacket will be compensated. This will prevent the undesired increase of pressure during cooling. We expect that the observed hysteresis will also work to stabilize the pressure when extra thermal contraction of the sheet will occur.

It was remarkable that both types of the NPD anvils were not damaged even after applying the strong loading forces. The supported anvils could not be loaded beyond that shown in Fig. 6, because friction of the loading bolts against the DAC body (Fig. 3) became too tight for further fastening. The unsupported anvils could not be loaded beyond the load shown in Fig. 7, because the beryllium-copper height adjustor (Fig. 2) had been critically deformed and the cell became unstable. These results suggested a great potential of the combination of large NPD anvils and compact cells equipped with enforced loading mechanism. We are improving the loading mechanism and the anvil supporting or adjusting geometries which have used for the current study, in order to securely apply even larger forces into the NPD anvils. As for the hybrid device, the beryllium-copper height adjustor can be replaced with the harder tungsten carbide which has a factor 3 to 5 larger compressive strength. Then the loading force can be further increased, as long as the force is sustainable by the NPD and dimpled tungsten carbide anvils, and also by the hybrid device. The dimpled tungsten carbide is presumably the weakest to set the next limit of pressure, which will be at 10 to 15 GPa, as suggested by previous results where larger force was applied to the carbide anvils by Paris-Edinburgh press [17]. Beyond that limit, the pressure of the hybrid device could be further increased by using sintered diamond as the dimpled anvil.

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Figure 6. Pressure generation with a couple of supported NPD anvils and an enforced DAC. The horizontal axis is the rotation angle of the two loading bolts. Different symbols indicate the results of different pressure cycles, which were conducted with the same sample shown in Table 1.

Figure 7. Pressure generation using an unsupported NPD anvil and a hybrid-anvil device. Filled circles show the observed pressures with increasing load, while open circles show the observed pressures with decreasing load (the left scale). Diameter of the sample chamber is shown with the thick solid line at the top of the figure (the right scale).
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