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High pressure generation using double-stage diamond anvil technique: problems and equations of state of rhenium

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ABSTRACT

We have developed a double stage diamond anvil cell (ds-DAC) technique for reproducible pressure by precisely fabricating 2nd stage anvils using a focused ion beam system. We used 2nd stage micro-anvils made of ultra-fine (< 10 nm) nano-polycrystalline diamond with various shapes and dimensions synthesized from glassy carbon at high pressure and temperature. The X-ray diffraction patterns from the rhenium sample always showed very broad peaks due to large pressure gradients in the culet of the micro-anvils. Deconvolution of the broad 101 diffraction peak results in compression of rhenium to $V/V_0 = 0.633$ for the smallest d-spacing. The calculated pressure for this minimum volume varies from 430 to 630 GPa, depending on the choice of the equation of state of rhenium. We conclude that the most likely pressure achieved for the minimum volume of rhenium is in a range of 430–460 GPa based on a calibration using the platinum pressure scale to 280 GPa and the latter value of 630 GPa is unreasonably high, suggesting that the pressures in an earlier study for the equation of state of rhenium would have been significantly overestimated.

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KEYWORDS
ds-DAC; equation of state of rhenium; nano-polycrystalline diamond (NPD)

1. Introduction

Double stage diamond anvil cell (ds-DAC) technique invented by Dubrovinsky et al. [1] is a promising technique to generate static ultra-high pressures beyond the limit of conventional diamond anvils. In their paper, the authors claim that pressures of above 600 GPa were generated based on the unit-cell volumes of gold and rhenium. Since then, many researchers have attempted high-pressure generation using various ds-DAC techniques (*e.g.* [2–4]). However, no other groups have succeeded in generating pressures comparable to those by Dubrovinsky et al. [1], although this same group has reported generation of even higher pressures reaching the TPa regime [5,6]: Dubrovinsky et al. [5] reported the

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result of compression study of osmium up to 774 GPa using the ds-DAC technique. They used equations of state (EoSs) of platinum and osmium up to about 500 GPa, which were calibrated based on the gold pressure scale by Yokoo et al. [7] for pressure evaluations. The same gold pressure scale was used in their subsequent study [6] reporting the achievement of the maximum pressure of 1065 GPa.

Dubrovinskaia et al. [6] pointed out that material of the 2nd stage anvil is one of the key points for higher pressure generation in the ds-DAC experiments. They claim that the use of their 'Nano-Crystalline Diamond' with grain sizes smaller than 10 nm (hereafter referred to as 'NCD' to avoid confusion with our nano-polycrystalline diamond, NPD [8]) synthesized from glassy carbon (GC) ball is essentially important, because 'NCD' is mechanically superior to our NPD synthesized from graphite in terms of both compressional strength and elastic stiffness.

We have made 13 additional experiments by changing various parameters such as material, size, and shape of micro-anvils, after we reported the results of our attempt to use precisely fabricated 2nd stage anvils based on the very first four experiments [2]. Although we succeeded in generation of over 100 GPa pressures for all these runs, the highest pressure we confirmed has been limited to about 430–460 GPa, which is significantly lower than those reported in earlier studies [1,5,6]. In this paper, we summarize our experimental results so far obtained and discuss the problems associated with the ds-DAC technique for further development of this potentially important new technique.

2. Experimental method

We synthesized NPD with a grain size smaller than 10 nm (hereafter called as ultra-fine NPD), identical to the 'NCD' by Dubrovinskaia et al. [6], at 19–20 GPa by keeping the temperature at 1900°C for 20 min in a multi anvil apparatus. The GC powder having a spherical shape with diameters greater than 25 μm (Tokai carbon Ltd.) was used as starting material, which was mixed with an MgO powder as the pressure medium (MgO:GC = 3:1 in volume).

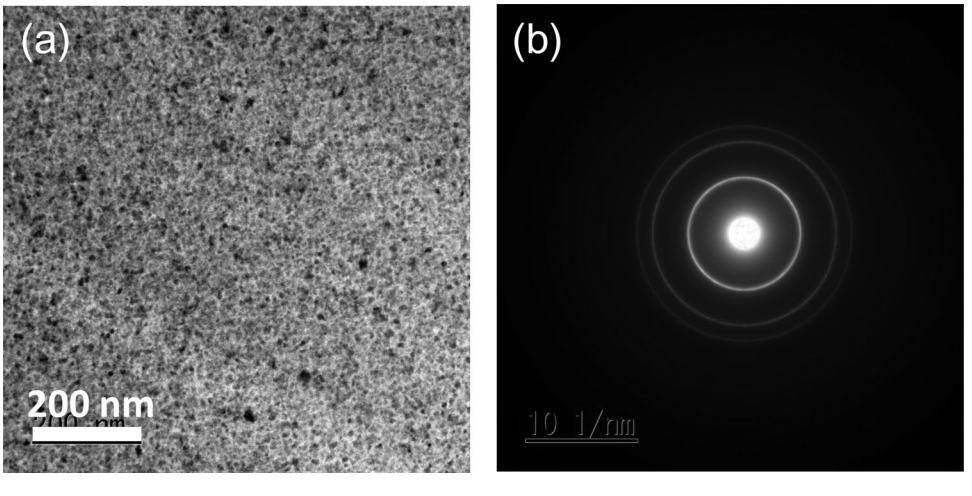

Figure 1. (a) TEM image and (b) the electron diffraction image of the ultra-fine NPD synthesized from GC balls.

Thus synthesized NPD was highly transparent and had grain sizes less than 10 nm, which was confirmed by transmission electron microscopic (TEM) observations as shown in Figure 1(a). The electron diffraction pattern shows a smooth Debye ring (Figure 1(b)) and the Raman spectrum does not show any clear peak at about 1330 cm^{-1} (Figure 2). Both of these features are the results of the ultra-fine nature of the present NPD, consistent with the TEM observations, as reported in Dubrovinskaia et al. [6].

Micro-anvils were fabricated by using a focused ion beam (FIB) system (Scios, FEI Ltd.) at Geodynamics Research Center, Ehime University, and the one (Versa3D, FEI Ltd.) at Earth-Life Science Institute, Tokyo Institute of Technology. At the initial stage of our study, we made paired anvils from a single block of single crystal diamond or NPD [2], but subsequently we made two micro-anvils separately and unified them into one paired anvils as shown in Figure 3, which makes the fabrication much easier. The two micro-anvils were connected with GC rods using the FIB deposition technique. We first used single crystal silicon as the rod material but we found that silicon transforms to a hexagonal-close-packed (hcp) structure above about 40 GPa via several intermediate phases ([9] and references therein). The unit-cell volume of this hcp silicon is very close to that of hcp rhenium above about 220 GPa, which lead to a misidentification of the X-ray diffraction (XRD) from the sample. Thus, we avoided using silicon as the connecting rod and replaced it by GC. A small disk-shaped rhenium sample (3 μm in diameter and 1 μm in thickness, which is the same size as that of the sample used in Dubrovinskaia et al. [6]), was prepared from a thicker foil with FIB and was placed on one of the culet of the micro-anvils as shown in Figure 3 (Run Micro16). The culet size and the material of micro-anvils for each run are listed in Table 1.

Powder XRD experiments were performed at BL10XU, SPring-8. We directed an X-ray beam (λ = 0.41425(7)–0.41532(14) Å) to the sample minimizing the beam size by a combination of a single pinhole as a virtual point source of light and a tandem Compound refractive lenses. The full width at half maximum (FWHM) of the intensity profile of the X-ray

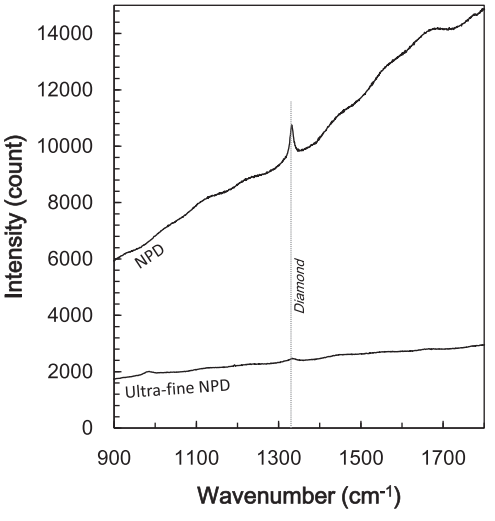

Figure 2. Raman spectrum of the ultra-fine NPD synthesized from GC balls and the 'normal' NPD. Dashed line indicates the location of the 1st order Raman peak of diamond at 1332 cm^{-1}.

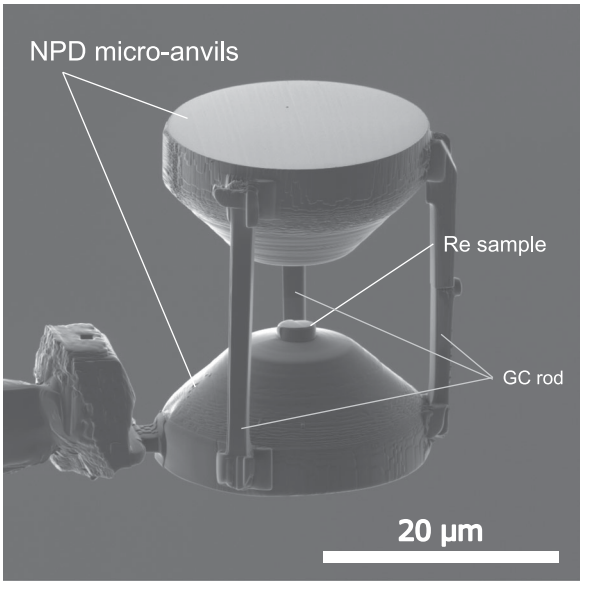

Figure 3. Scanning ion microscopic image of the micro-anvils (Run Micro16). The size of rhenium sample is $^{\Phi}$3 μm and ^{t}1 μm. NPD, the ultra-fine NPD. GC, glassy carbon.

micro-beam was about 3 μm at the sample position. Pressure was determined from the unit-cell volume of rhenium using the EoS reported by Anzellini et al. [10]. Further details of the experimental setup can be found in Sakai et al. [2].

In order to explore the consistency of the EoSs of rhenium and those of platinum, we performed an additional experiment (Run Micro17) in which both rhenium and platinum were used as samples. We used a larger culet (5 μm in diameter) without bevel for 2nd stage micro-anvils, and two disk-shaped samples were stuck together and compressed by the micro-anvils. We have also performed a conventional DAC experiment using a pair of single crystal diamond anvils with a 40 μm double beveled culet (Run RP01). Rhenium and platinum samples were compressed up to 280 GPa with a silica glass as a pressure medium using a tungsten gasket.

3. Results

Typical XRD patterns we obtained in run Micro16 are shown in Figure 4. Before the 2nd stage anvils started to compress the rhenium sample, we observed only several strong

Table 1. Anvil and sample informations of the experiments.

	2nd stage					
Run	culet (μm)	bevel (μm)	material	type		Sample
Micro08	3	10	Single crystal diamond	paired	Re	$^{\square}$10 μm, ^{t}2.5 μm
Micro13	3	10	Single crystal diamond	unified	Re	$^{\square}$11 μm, ^{t}1.4 μm
Micro16	3	10	Ultra-fine NPD	unified	Re	$^{\Phi}$3.0 μm, ^{t}1.0 μm
Micro17	5	–	Single crystal diamond	separated	Re + Pt	$^{\Phi}$5.3 μm, ^{t}1.1–1.4 μm
RP01*	40*	250/450	Single crystal diamond	double beveled	Re + Pt	$^{\Phi}$3.0 μm, ^{t}1.0 μm

*Not the double stage, but the single stage (a conventional DAC experiment).

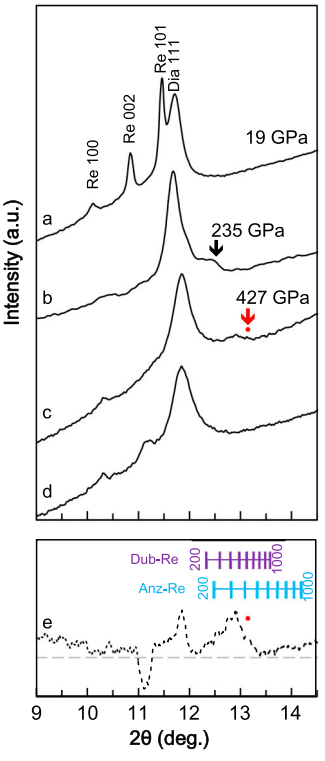

Figure 4. Powder XRD profiles (Run Micro16) at (a) 19 GPa, (b) 235 GPa, (c) 427 GPa, (d) 48 GPa, respectively. The confining pressures were (a) 17 GPa, (b) 33 GPa, (c) and (d) 48 GPa, respectively. (c) and (d) are XRD patterns just before and after the 2nd stage anvils' fracture. Re 002 peak was re-appeared after the fracture in (d) at around 11.2 degree. (e) is the profile subtracted (d) from (c). Dub-Re and Anz-Re indicate the diffraction line position of Re 101 corresponding to each pressure based on Re-EoSs by Dubrovinsky et al. [1] and by Anzellini et al. [10], respectively. X-ray wavelength was 0.41532(14) Å.

diffraction spots of rhenium in 2D pattern, because the grain size of the rhenium starting sample is larger than that of the X-ray beam. By integrating this spotty pattern, we obtained sharp peaks (FWHM = 0.10–0.15) from the rhenium sample and relatively broad peaks (FWHM = ~0.3) from the NPD due to its ultra-fine grain size in the 1D XRD profile (Figure 4(a)). After starting compression by the 2nd stage anvils, the spotty pattern in the 2D space gradually changed to a continuous Debye ring and shoulders appeared on the higher-pressure side, which correspond to the diffractions from the sample compressed between two culets of the micro-anvils (Figure 4(b)). Further compression resulted in a rapid shift of shoulders to higher angles, indicating rapid pressure increase on the tips of the micro-anvils.

At the highest pressure, the diffraction of Re 101 peak was observed in a broad range from about 11.7 to 13.1 degree (Figure 4(c)). The peak at around 11.7 degree corresponds to the diffraction from the sample under confining pressure, although it also overlaps with the broad diffraction of diamond 111. The broad peak on the higher angle side indicates the existence of a large pressure gradient within the rhenium sample irradiated by the X-ray beam with a diameter of ~3 μm. Although we carefully moved the sample to find the

best position, it was impossible to identify the XRD from the sample compressed between two micro-anvils alone. This is reasonable if we take into account the volume of the sample remained between two culets of the 2nd stage anvils and that squeezed out around the culets. The former part of the sample is only about 100 nm thick while the latter part is more than ten times thicker from an electron microscope image of the recovered sample as described later. As a result, even though the intensity of the tail of the incident X-ray beam is only a few % of the peak intensity, the diffraction from the sample squeezed outside the culet would become quite strong. The simultaneous appearance of XRD patterns from the samples under different pressure conditions was also reported in previous studies [2,3] but not in Dubrovinsky et al. [1,5] and Dubrovinskaia et al. [6], although the spatial dimensions of the incident X-ray beam profiles are similar to each other among these studies.

The shoulder in the XRD profile completely disappeared when the pressure was released upon the fracture of the 2nd stage anvil (Figure 4(d)). By subtracting this profile (Figure 4(d)) from the one just before the fracture (Figure 4(c)), we could extract the diffraction peak coming only from the sample compressed between two culets of the micro-anvils (Figure 4(e)). Thus extracted broad peak spreads over a range from 12.2 to 13.3 degree due to the large pressure gradient within the sample. Accordingly, a peak deconvolution is necessary to determine the highest pressure generated in the central part of the culet. The results of the peak deconvolution are shown in Figure 5. As described above, typical FWHM values of the XRD peaks before the compression are 0.10–0.15. In the case of 5-peak fit (Figure 5(a)), the FWHM value of each peak is in a range of 016–0.25. The 4-peak fit and the 3-peak fit in Figure 5(b,c) respectively show twice or larger FWHM values compared to those of the 5-peak fit. Based on any feasible assumptions on the FWHM, however, the maximum pressure did not change significantly and was around 420–430 GPa, where the pressure was evaluated using only Re101 line assuming $c/a = 1.61$. It should be noted that the uncertainty of this axial ratio, for example ±0.05, results in the pressure uncertainty of about ±20 GPa.

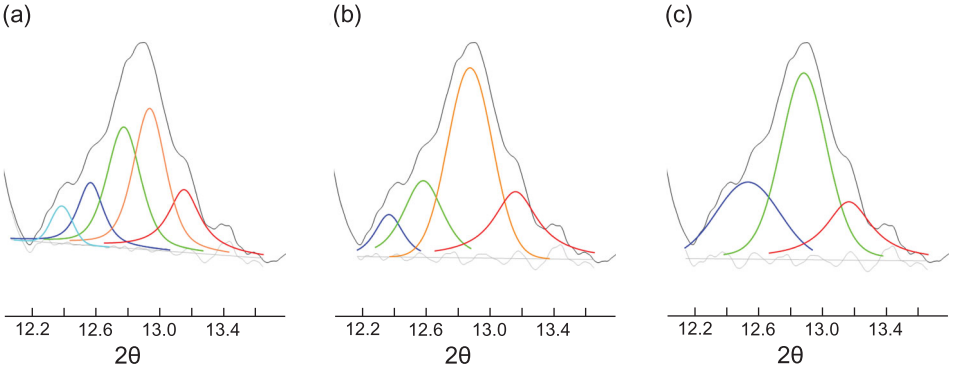

Figure 5. Peak deconvolutions for Re 101 diffraction line. (a) 5-peak fit, (b) 4-peak fit, (c) 3-peak fit. The maximum pressures of each fitting are (a) 422 GPa, (b) 423 GPa and (c) 427 GPa. The FWHM values of each fitting are 0.16–0.25, 0.30–0.37, and 0.34–0.47, respectively. If we calculate the pressure error assuming FWHM value equal 1σ, the pressure error is $1\sigma = 51$–79 GPa.

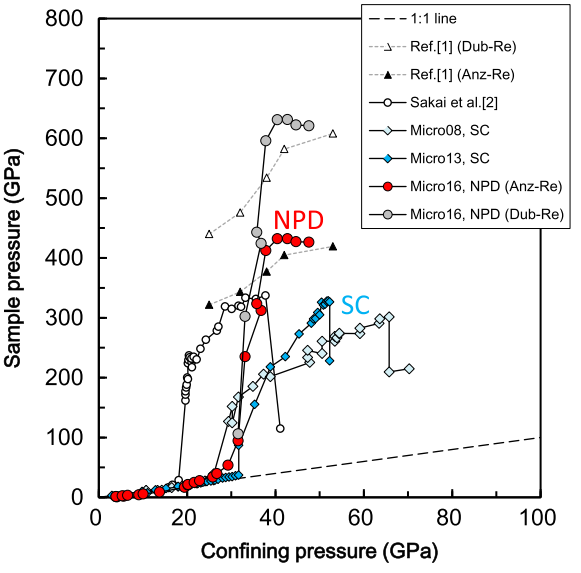

Figure 6. Sample pressure with respect to the confining pressure. SC, single crystal diamond. NPD, the ultra-fine NPD. Anz-Re and Dub-Re are the data based on Re-EoSs reported by Anzellini et al. [10] and by Dubrovinsky et al. [1], respectively.

Figure 6 shows the sample pressure with respect to the confining pressure. The sample pressures were almost equal to the confining pressure before the compression by the 2nd stage anvils became effective. When the sample is pinched by the micro-anvils, the sample pressure increased promptly. Upon further compression, the sample pressure dropped suddenly when the micro-anvils fractured, but the pressure did not drop down to the confining pressure and some additional pressure was still retained. This is because the pressure transmitting medium, glycerin, solidified under such high pressure conditions, which kept the bulk shape of the fractured micro-anvils and thereby sustained the extra pressure. In Figure 6, all the pressure values are calculated based on the unit cell volume of rhenium using the EoS by Anzellini et al. [10]. For Run Micro16, additional plots are made using the EoS by Dubrovinsky et al. [1].

When we used NPD as the material of micro-anvils, broad diffraction peaks from NPD were always observed, which allows us to evaluate the unit-cell volume changes of NPD itself. Figure 7 shows a compression curve of the ultra-fine NPD as a function of the confining pressure, which was determined from the unit-cell volumes of rhenium sample and/or those of the inside wall of the sample chamber of the rhenium gasket in the run Micro16. The ultra-fine NPD for the micro-anvils shows a monotonous unit-cell volume decrease along the compression curve based on the EoS of diamond [11], while it appears to become incompressible once the compression by the 2nd stage micro-anvils started.

Figure 8 shows scanning electron microscopic (SEM) and chemical mapping images of a cross section of the recovered micro-anvils and sample in the run Micro16, which was prepared using FIB. The lower anvil has a lot of cracks, while the upper anvil is basically intact. We also found a misalignment of culet positions by about 1 μm between upper and lower

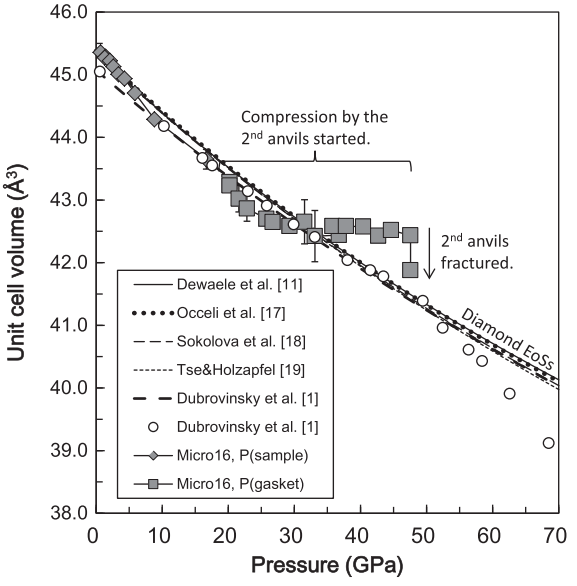

Figure 7. Compression data of the ultra-fine NPD 2nd stage anvils (Run Micro16). Diamonds and squares; the pressures were determined from the unit-cell volumes of rhenium sample itself and those of the inside wall of the sample chamber of the rhenium gasket, respectively. Solid, dotted, long-dashed, short-dashed curves are the compression curves calculated from EoSs of diamond by Dewaele et al. [11], Occeli et al. [12], Sokolova et al. [13], Tse and Holzapfel [14], respectively. Thick-dashed curve is the compression curve calculated from the EoS of 'NCD' by Dubrovinsky et al. [1].

anvils, although it is difficult to specify when this shift occurred, *i.e.* whether during compression/decompression or when the anvils fractured. The initial rhenium sample was about 1 μm thick and 3 μm in diameter, but the thickness of the recovered sample was only about 100 nm on the culet and bevel positions. As shown in the chemical

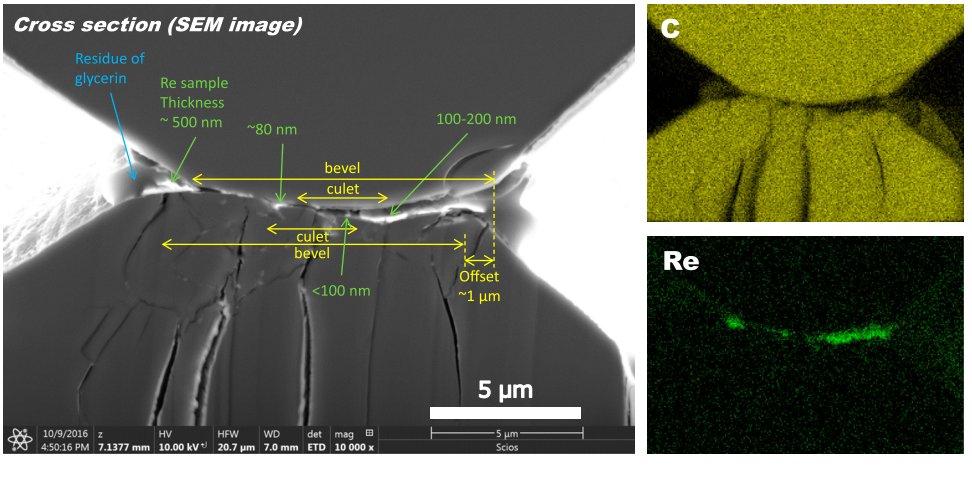

Figure 8. SEM image and the chemical mapping of a cross section of the recovered 2nd stage anvils (Run Micro16).

mapping image of rhenium, the sample exists from the culet to out of bevel almost continuously as a very thin film. The continuous sample distribution is consistent with the broad XRD peak that we observed under the very high pressure.

In the run Micro17, the micro-anvils fractured when the pressure reached about 164 GPa. We observed relatively sharp XRD peaks (FWHM = ~0.2) due to larger culet and lower pressure conditions compared to those of our earlier runs stated in the above (Figure 9(a)). The XRD patterns were measured at the center of the culet, and the volumes of rhenium and platinum samples were determined simultaneously. The samples were compressed directly by two micro-anvils in glycerin pressure medium, and we confirmed that both samples stay between two culets by the chemical mapping of the recovered samples, which are clearly shown to have been directly compressed by the culets of the 2nd stage anvils. It is seen that the pressures calculated from the unit-cell volume of platinum using the EoS by Yokoo et al. [7] agree well with those calculated from that of rhenium using the EoS by Anzellini et al. [10] at pressures around 150 GPa, where we obtained the XRD data. On the other hand, if the pressure values are calculated using the EoS of rhenium by Dubrovinsky et al. [1] which is calibrated by Yokoo et al.'s gold pressure scale [7], they become systematically much higher (~30 GPa) than those derived using the EoS of platinum by Yokoo et al. [7], although both rhenium and platinum are subjected to similar stress conditions.

The XRD pattern observed in run RP01 at the highest pressure is shown in Figure 9(b). The compression curves of rhenium based on platinum pressure scales reported by Dewaele et al. [15] and Yokoo et al. [7] are shown in Figure 10. The pressures based on Dewaele et al.'s platinum scale [15] are consistent with the Re-EoS curve by Anzellini et al. [10], while the pressures based on Yokoo et al.'s platinum scale [7] are slightly higher pressures at above 200 GPa. In contrast, there is a large difference between the present results and the Dubrovinsky et al.'s Re-EoS [1] curve as shown in Figure 10.

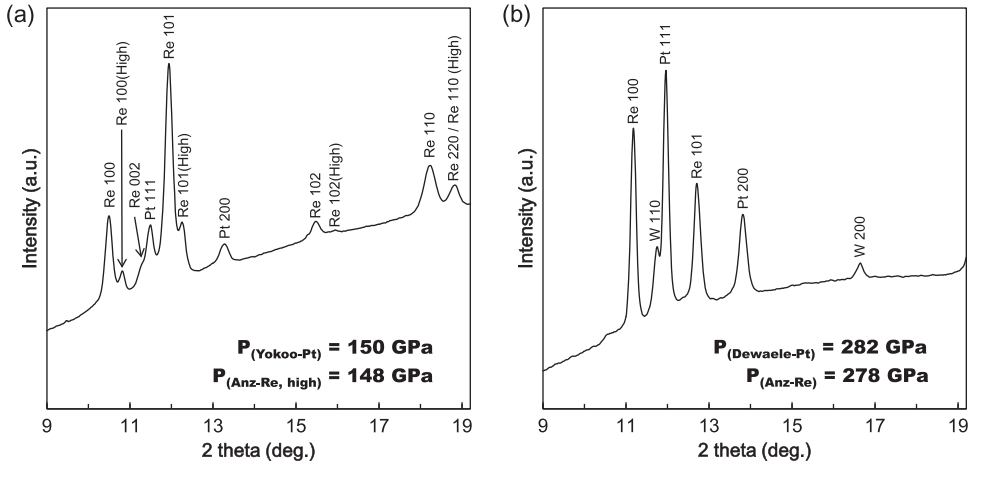

Figure 9. (a) XRD pattern of Run Micro17 performed by the ds-DAC technique with 5 μm culet. X-ray wavelength was 0.41532(14) Å. (b) XRD pattern of Run RP01 performed by the conventional DAC technique with 40 μm culet (double beveled). The silica glass pressure medium and the tungsten gasket were used. X-ray wavelength was 0.41434(13) Å.

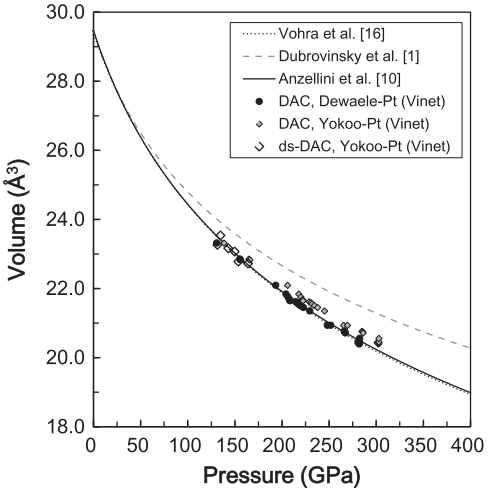

Figure 10. Compression curves of rhenium. Solid circles and gray diamonds are data obtained using a the conventional DAC based on Dewaele et al.'s platinum scale [15] and Yokoo et al.'s platinum scale [7], respectively (Run RP01). Open diamonds are the data using the ds-DAC based on Yokoo et al.'s platinum scale [7] (Run Micro17). The dotted, dashed, solid curves are compression curves of rhenium calculated from EoSs reported by Vohra et al. [16], Dubrovinsky et al. [1], and Anzellini et al. [10], respectively.

In order to see the effect of the use of different pressure scales, the rhenium compression data based on Yokoo et al.'s platinum scale [7] was fitted to Vinet EoS, which yields the EoS parameters $K = 358(10)$ GPa, $K' = 4.8(2)$ with a fixed $V_0 = 29.47$ Å^3. If we use this Re-EoS, the maximum pressure of the present ds-DAC experiment (Run Micro16) is calculated as 464 GPa, which is slightly higher but consistent with those estimated by the platinum pressure scale, while it is far lower than that estimated by Dubrovinsky et al.'s Re-EoS [1], as is seen from Figure 10.

4. Discussion

Although Dubrovinskaia et al. [6] reported generation of pressures up to about 1 TPa, there are several technical points that other groups cannot reproduce. Most difficult point is to obtain the sharp XRD peaks solely from the sample under ultra-high pressure conditions. The only possibility we can think of is that the deformation of the culet of the micro-anvil ('cupping') in early stage of the compression would trap the sample under the highest pressure. This is very difficult to occur, however, because the samples are much softer than the anvils and easily squeezed out before the cupping of the micro-anvils. Even if some amount of sample is trapped in the central region of the culet, much larger volume of the residual sample should be squeezed out to the surrounding area, which yields XRD peaks mixed with those of the sample near the central region, as reported by other researchers [2,3]. The only way to get the XRD from the sample compressed by the 2nd stage anvils alone will be to use the X-ray nano-beam with a diameter far smaller than the culet size. Such thin X-ray beam also allows us to measure the distribution and thickness of the heavy metal sample squeezed by the small culets of the anvils [17]. It

would be quite helpful to make such in situ measurements for ds-DAC experiment to understand various problems associated with this technique.

As shown in Figure 7, NPD became seemingly incompressible once the compression by the 2nd stage micro-anvils started. This phenomenon can be well explained by the effect of uniaxial stress (*e.g.* [18]), leading to the overestimation of the unit-cell volume when the XRD measurement is made parallel to the compression axis. The uniaxial stress that is produced when the micro-anvils started touching the sample should have been released when the 2nd stage micro-anvil fractured, which is observed as a sudden volume decrease as shown in Figure 7. This 'incompressible' feature prior to the anvil failure is totally opposite to the 'compressible' behavior of the 'NCD' ball when it started to touch the anvils as reported in Dubrovinsky et al. [1] and Dubrovinskaia et al. [6], which is hard to be explained by the above effect of uniaxial stress. It should be also noted that the behavior of our NPD is close to or even slightly more compressible as compared to the compression curve of diamond [11]. This is also in contrast to what is reported by these authors, where the 'NCD' ball is claimed to be less compressible until they started touching with the 1st stage anvils. These discrepancies in compression behaviors of the ultra-fine NPD (='NCD') should be further explored under the hydrostatic compression.

Dubrovinskaia et al. [6] emphasizes that the use of 'NCD' with the grain size less than 10 nm, which is synthesized from GC, is a key to achieve pressures beyond 400 GPa in the ds-DAC technique, as they claim 'NCD' is elastically stiffer and also plastically harder than NPD. The high elastic stiffness of 'NCD' is, however, suspicious as discussed in the above.

The synthesis of NPD with grain sizes less than 10 nm from GC, equivalent to 'NCD', was already reported, which was shown to have substantially low Knoop hardness ($Hk = 66$–86 GPa) relative to that of the NPD from graphite ($Hk = 113$–140 GPa [19]). These authors showed that the ultra-hard nature of NPD from graphite is due to its micro-textural feature of a mixture of granular and lamellar diamond nano-crystals. Rather softer nature of the NPD with grain sizes smaller than 10 nm (='NCD') is attributed to the domination of the intergranular fractures or defective regions because of the weaker grain boundary cohesion due to relatively low temperatures required for the synthesis of NPD from GC.

Although Dubrovinskaia et al. [6] suggests that 'NCD' is harder than NPD because the 'NCD' ball can make indention on the anvil made of NPD, this does not necessarily mean that 'NCD' is harder than NPD but instead merely shows that a very high pressure (>> 100 GPa) was produced beyond the yield strength of the NPD anvil around the 'NCD' ball sample. If the pressures far higher than 400 GPa was actually achieved using 'NCD', there is a possibility that a cupping occurred on the top of the 'NCD' semi-ball anvils at the initial stage of compression, as this material is rather softer than single crystal diamond or NPD. Further compression could have resulted in enhancement of mechanical strength of 'NCD' due to high confining pressure. The smaller and homogeneous grain size of 'NCD' may also help in minimizing stress concentration within the 2nd stage anvils. However, all these possibilities, as well as the reported high bulk modulus of 'NCD', should further be explored experimentally.

The observed XRD shows that the rhenium sample was compressed to about $V = 18.65$ Å^3 ($V/V_0 = 0.633$) at the highest pressure in this study. This volume corresponds to about 430 GPa based on both the Re-EoSs proposed by Anzellini et al. [10] and Vohra et al. [16], while it is about 630 GPa according to the Re-EoS reported in Dubrovinsky et al. [1]. We

confirmed the consistency of our pressure value using the Re-EoS by Anzellini et al. [10] with those evaluated based on different pressure scales of platinum as shown in Figures 9 and 10, leading to a conclusion that the highest pressure we achieved in our ds-DAC experiments is most likely in a range between 430 and 460 GPa. We suggest that the Re-EoS of Dubrovinsky et al. [1] would lead to a significant overestimation of pressure in such high pressure regions as studied using ds-DACs. Note that the achievement of a pressure of 1065 GPa itself [6] was claimed from the observed XRD pattern of a gold sample using Yokoo et al.'s gold pressure scale which is calibrated up to 550 GPa [7]. Although it is true that the XRD pattern leads to a pressure of about 1 TPa, such a pressure was derived by an extrapolation of the existing pressure scale for the pressure range far beyond that rationalized by experimental data. Experimental and theoretical studies of the pressure scales for these and higher pressure ranges are very scarce and further efforts to establish an adequate pressure scale are required to confirm the achievement of pressures far higher than 500 GPa.

5. Conclusion

The ds-DAC is a promising technique to generate ultra-high static pressures beyond the limit of conventional DAC. However, this technique has been successfully used for pressures above 500 GPa only by one group in the world, and various technical problems associated with this technique are discussed in this paper. It became clear that the property of nanopolycrystalline aggregates of diamond synthesized by the direct conversion of various carbon materials still have many unknown properties and open discussions are strongly desired in order to make the ds-DAC technique really useful in the ultra-high pressure science community.

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Disclosure statement

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