Stress state of diamond and gold under nonhydrostatic compression to 360 GPa

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Diamond and gold powders were compressed nonhydrostatically in a diamond anvil cell and examined by x-ray diffraction using a radial geometry to evaluate the evolution of stresses and strains in these materials to ultrahigh pressure. We found that near isostrain continuity developed across diamond and gold grains under uniaxial compression. The observed mean pressure of diamond powder reached to 360(40) GPa while it was only 31(1) GPa for the polycrystalline gold under the highest load. Polycrystalline diamond can support a microscopic deviatoric stress of 160(18) GPa at about 360 GPa. Due to the deformation of the diamond anvil culet, the macroscopic differential stress of the diamond sample was limited to about 43(8) GPa. There is no evidence that the diamond grains have yielded in our experimental pressure range. © 2010 American Institute of Physics. [doi:10.1063/1.3485828]

I. INTRODUCTION

The diamond anvil cell (DAC) can generate static pressures in the multimegabar range. Combined with various in situ measurement techniques, such as x-ray diffraction, Raman and Brillouin scattering, etc., the DAC has become a powerful instrument used in modern high-pressure research. Internal pressure standards such as gold, platinum, tungsten, and ruby are commonly used in DAC experiments. For accurate pressure calibration, this requires a strict isostress condition, that is, the stress must be continuous across the interface between crystallites of the pressure standard and the investigated materials which is usually assumed in hydrostatic compression.1 However, the samples in a DAC without a pressure transmitting medium are always subjected to a nonhydrostatic compression. Even if the sample is initially contained within a fluid, a completely hydrostatic environment cannot be sustained above ~15 GPa due to the solidification of all known pressure media at ambient temperature.2 In this situation, the boundary stress condition among the sample grains may become complex. If the sample and pressure marker have different strength and do not yield under nonhydrostatic compression, the stress state between the pressure standard and the investigated sample may not be consistent. The details of mixed sample assemblage can also affect the stress relationships between the pressure standard and the investigated sample.3 Considering that diamond is the hardest known material and gold is frequently used as a pressure standard in static high-pressure experiments, it is interesting to simultaneously look at the stress state of diamond and gold under nonhydrostatic compression.

In addition, the study of the properties of diamond at high pressure and high temperature is also interesting and challenging as diamond has unique properties that make it a key material in high-pressure technology.4,5 However, experimental data on the yield strength of diamond are still incomplete and ambiguous especially at ambient temperature because diamond is difficult to deform under cold compression. In this study, we simultaneously investigated the stress state of polycrystalline diamond and gold in the DAC under nonhydrostatic compression to above 300 GPa. The influence on the observed stress caused by the relative strength difference between diamond and gold is discussed. Our results also give a lower limit value of the yield strength of diamond under high pressure and ambient temperature.

II. EXPERIMENT

The experiment was performed at the X17C beam line of the National Synchrotron Light Source at Brookhaven National Laboratory using energy-dispersive x-ray diffraction techniques. Natural diamond with a grain size of 2–3 μm (Warren Diamond Powder Co.) was loaded into a 90-μm-diameter hole of a Be gasket in a DAC. The gasket was preindented to ~13–15 μm thickness at about 34 GPa. A piece of gold foil (~8 μm in diameter) was placed on top within 3 μm of the sample center and served as a position reference and pressure marker. We used beveled diamond anvils with a culet size of 150 μm to apply uniaxial compression. No pressure-transmitting medium was used. The incident x-ray beam was focused by a pair of Kirkpatrick–Baez mirrors to approximately 11×17 μm² and directed through the Be gasket and the sample in the radial direction. The diffracted intensity was recorded using a Ge solid-state detector with a fixed angle at 2θ=15.002(4)°. Diffraction spectra were collected only after sufficient time (more than 1 h) elapsed after each compression step to allow for stress relaxation. In total, nine elevated pressures were investigated. Diffraction patterns were collected at ψ =0°, 54.7°, 90°(ψ is the angle between DAC loading axis and the normal to the diffraction plane), respectively, at each pressure except the first two steps (only at ψ=0° and 90°). The well-resolved diamond diffraction peaks of (111), (220),...
and (311) were used for data analysis. The lattice parameters of gold were derived from the (111), (200), (220), (311), and (222) diffraction lines.

III. THEORY

A solid polycrystalline sample under nonhydrostatic compression in a DAC is subjected to a macroscopic differential stress, $t$, due to the uniaxial stress field, as well as the microscopic deviatoric stress, $\nu$, caused by grain-to-grain contacts.\(^5\) The two types of stress will be limited by the yield strength of the sample. The differential stress, $t$, can be expressed as the difference between $\sigma_3$ and $\sigma_1$, where $\sigma_3$ (maximum stress) is along the DAC loading axis and $\sigma_1$ (minimum stress) is in the radial direction. And it can be given by $t = 6G\langle Q(hkl) \rangle$ under isostress condition.\(^7\)–\(^12\) $\langle Q(hkl) \rangle$ presents the average $Q(hkl)$ value over all observed reflections, while $G$ is the aggregate shear modulus of the polycrystalline sample. The deviatoric stress $\nu$ is determined by $\nu = e E$, where $e$ is the microscopic deviatoric strain distribution, $E$ is the aggregate Young’s modulus of the sample.\(^6\),\(^13\)–\(^16\) Measuring the differential stress or/and deviatoric stress in a polycrystalline sample under nonhydrostatic compression has been applied to strength determination of many materials.\(^6\),\(^8\),\(^17\)

IV. RESULTS AND DISCUSSION

The radial x-ray diffraction data were obtained at each loading step at room temperature and contained the peaks of diamond, gold as well as Be gasket. At higher pressure, the diffraction peaks of diamond (111), (311) were overlapped with Au (311) and (222) peaks, respectively. To overcome this, we moved the diffraction region $\sim 10 \ \mu m$ along the cell axis direction to obtain a diffraction pattern below the gold foil layer that contains only diamond diffraction peaks. There is no detectable stress gradient along the direction of loading axis. Figure 1 shows the diffraction spectra of diamond

![Diffraction Spectra](Image)

Comparing the observed mean pressure of diamond with gold at the same loading step (Fig. 2), we found that the diamond can support a much larger stress than gold. The maximum mean pressure of diamond achieved was 360(40) GPa while for gold it was just 31(1) GPa at the highest load. The pressure difference between diamond and gold increased with increasing stress. The minimum difference was 17 GPa and the maximum difference reached 330 GPa.

Moreover, the normalized volume changes for diamond and gold under the same loading step at $\psi = 54.7^\circ$ were roughly about the same (Fig. 3), which indicates that the boundary across the diamond and gold grains is under close to isostrain conditions. As diamond is harder and more incompressible than gold, there will be void space between diamond and gold at the same loading step at $\psi = 54.7^\circ$ taken 10 $\mu m$ below the Au position. (b) Diffraction spectra at $\psi = 54.7^\circ$ taken at the gold position. Each spectrum is labeled with the hydrostatic pressure values of diamond and gold estimated from the observed lattice parameters at $\psi = 54.7^\circ$ using Occelli’s equation of state. (c) XRD patterns of diamond at $\psi = 0^\circ$, $54.7^\circ$, and $90^\circ$ for loading step 8. The hydrostatic pressure values of diamond are calculated from the observed cell volume by using Occelli’s equation of state (EOS) (Ref. 18). Diamond cell volume is obtained with XRD lines of (111), (200), (220), and (311). We used Shim’s EOS (Ref. 19) for the gold hydrostatic pressure calculation.
diamond grains at initial compression. The thin gold foil fills only a small volume in the sample cell and apparently does not completely fill the gaps between the diamond grains. Gold deforms plastically at low stress levels and will flow toward the lowest stress regions in the grain pockets. Thus, the gold grains become highly concentrated in the pore space among diamond grains at low stress levels. The stress due to the axial load would then be mainly supported by the diamond grains alone. The observed Au pressure change may be mostly due to compaction of the void space between diamond grains under load as the diamonds grains themselves are elastically compressed, i.e., the diamond anvils squeeze the diamond powder, and sample thickness supported by the diamond grains is forced to shrink. The Au distributed in the void space is then compressed by the compaction of the surrounding diamond grains. In this way, the relative volume change for diamond and Au should be roughly about the same. Considering that the bulk modulus of diamond is about three times of that for Au, our experimental data likely supports the above explanation. The pressure achieved in diamond and gold will not be the same unless the initial quantity of gold is sufficiently large to preclude the formation of isolated void pockets or plastic deformation of diamond occurs resulting in closing of pore space. The diamond grains themselves, however, form an interconnected network and are compressed against each other in a near isostress condition and the same is true for the polycrystalline gold, but the boundary between diamond and gold grains is under a near isostrain condition. When gold is used as a pressure standard in the DAC, the above situation may occur especially if it is used together with strong materials. So special attention should be paid when the soft pressure markers are used for the strong materials in the DAC high-pressure experiments. The soft pressure makers may yield the wrong pressure value, especially when the strong materials have not yielded under nonhydrostatic compression. To obtain accurate pressure calibration, it will be necessary to choose pressure maker that has appropriate elastic properties and yield strength with the sample material for DAC high-pressure experiments under nonhydrostatic environment.

The macroscopic differential stress, \( t \), and microscopic deviatoric stress, \( \nu \), of diamond were obtained by analyzing x-ray diffraction peak shifts together with lattice strain theory, and peak broadening. In this analysis, the single-crystal elastic moduli, \( C_{ij} \), of diamond and their pressure derivatives were obtained from ultrasonic measurements at 25 °C up to 0.14 GPa. The \( C_{ij} \) at higher pressure were calculated using third-order Eulerian finite-strain equations and the aggregate shear modulus (Reuss bound) and Young’s modulus were derived form the \( C_{ij} \) at high pressure. Comparing \( t \) and \( \nu \) as a function of pressure (Fig. 4), we found that the microscopic deviatoric stress of diamond becomes much larger than its macroscopic differential stress as the pressure increased. This may be due to the deformation of diamond anvil culet (cupping effect) at high pressure. Normally, the microscopic deviatoric stress and macroscopic differential stress will increase similarly with pressure under nonhydrostatic compression. Once the sample yields, both
will attain their maximum value (yield strength).\(^6\) In our experiment, the volumetrically dominant sample in the cell was diamond powder which is much harder than the surrounding Be gasket. As a result, the gap between the diamond anvil culets should be larger at the sample area and smaller at the Be gasket area under higher pressure as a result of elastic deformation of the anvil. The diamond anvil culets are thus likely cupped upon compression and this will lead to the stress in the radial direction, \(\sigma_1\), enhanced and the stress in the axial direction, \(\sigma_3\), restrained. Thus the cupping effect of diamond anvil prevent the macroscopic differential stress from a further increase. But this does not affect the microscopic deviatoric stress development. The maximum microscopic deviatoric stress approached 160(18) GPa at the highest load and there is no obvious evidence indicating the yielding of diamond grains. Therefore, it seems that the yield strength of diamond is larger than 160(18) GPa at a mean pressure of 360(40) GPa. The calculations from first-principles methods report that the ideal strength of diamond is 180–200 GPa at ambient conditions.\(^{25,26}\) Eremets et al. observed the strong photoluminescence spectra at the diamond anvil culet (compressed to 190–200 GPa) which indicated the plastic deformation of the diamond culet. From this, they estimated a yield strength of diamond of 130–140 GPa according: \(Y = 2\tau_{\text{max}}\), \(\tau_{\text{max}} = (1-2\sigma)P_0/2.45\) (\(Y\) is the yield strength, \(\tau_{\text{max}}\) is the maximum shear stress, \(\sigma\) is the Poisson ratio for diamond, and \(P_0\) is the starting pressure of plastic deformation).\(^8\) Recently, dynamic ramp-wave compression experiment of diamond gave the initial yield strength of diamond 69–90 GPa at stress 74–104 GPa and the diamond appeared to retain strength up to 800 GPa.\(^{30}\) Akahama and Kawamura (2007) investigated the shear stress of a DAC with loading axes along the [111] and [110] crystal direction.\(^{5,31}\) They claimed that the [111] diamond anvil can endure a maximum shear stress \(\tau\) of 40 GPa (corresponding to differential stress, \(t=80\) GPa) at the maximum pressure of 220 GPa and the stress \(\sigma_1\) (radial direction) was enhanced above 100 GPa. The enhancement of \(\sigma_1\) above 100 GPa may be indicative of the [111] anvil culet cupping. For the [110] anvil the shear stress \(\tau\) increased with pressure and reached to 50 at 250 GPa. Those results are shown together in Fig. 4. The difference between our macroscopic differentials stress \(t\) value with Akahama’s may depend on the details of the DAC: diamond type, anvil crystallographic orientation, and culet design.\(^32\) Comparing the yield strength of other studied superhard materials under nonhydrostatic compression (to ~65 GPa) such as B\(_2\)O (26–30 GPa),\(^8\) c-Si\(_3\)N\(_4\) (15–18 GPa),\(^{33}\) and c-BC\(_2\)N (38 GPa),\(^{34}\) diamond remains much stronger under extreme stress condition.

### V. SUMMARY

In summary, we found the boundary between the diamond and gold grains was close to an isostrain condition under a nonhydrostatic compression up to above 300 GPa (as obtained from the mean stress of diamond). For pressure calibration in static DAC compression experiments, the stress discontinuity caused by the strength difference between the studied sample and pressure standard should be taken into account, especially using soft pressure markers together with hard samples. Polycrystalline diamond was observed to support a microscopic deviatoric stress of 160(18) GPa at a mean pressure of 360(40) GPa without yielding. Due potentially to the cupping effect of the anvil tip, the microscopic deviatoric stress developed in the polycrystalline diamond was larger than the macroscopic differential stress.

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