HIGH-PRESSURE, HIGH-TEMPERATURE PLASTIC DEFORMATION OF SINTERED DIAMONDS

Julien Gasc^{1@}, Yanbin Wang¹, Tony Yu¹, Ion C. Banea², Benjamin R. Rosczyk², Toru Shinmei³ and Tetsuo Irifune^{3,4}

¹Center for Advanced Radiation Sources, the University of Chicago, Argonne National Lab, 9700 S. Cass Avenue, Argonne, IL 60439, USA

²Engis Corporation, 105 W. Hintz Rd., Wheeling, IL 60090, USA

³Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan

⁴Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo 152-8550, Japan

@Corresponding author: gasc@cars.uchicago.edu

Abstract

The strength of polycrystalline diamond (PCD) was investigated through a high pressure (P) and temperature (T) deformation experiment. Prior to the deformation experiment, two bulk samples were sintered back to back under identical conditions with two different precursors, which shared identical initial grain size distribution. Precursor of one sample (2E) had lower concentration of crystalline defects than that of the other sample (1S). In crushing strength tests, precursor of 2E exhibited an enhanced crushing strength compared to that of 1S. During the high P-T deformation experiment, the two samples were stacked back to back and deformed together. Their mechanical properties were investigated in situ using synchrotron X-ray diffraction and imaging in the deformation DIA apparatus. The strain data based on imaging showed that the two samples were deformed at identical strain rates (ca. $1.5 \times 10^{-5} \text{ s}^{-1}$) and analysis based on lattice plane distortions in the diffraction patterns showed that sample 2E exhibits marginally higher strength than that of sample 1S. The X-ray data indicate that, upon deformation, larger elastic lattice strain builds up within the grains in sample 2E, indicating greater strength at grain-to-grain level in this sample. In addition, lower micro-stress levels are evidenced upon hydrostatic loading of sample 2E, strongly indicating a better sintering state than that in sample 1S. We interpret these differences as due to a lower defect concentration, particularly on the grain surfaces of the precursor powder, that results in stronger diamond-diamond bonding. Altogether, these data suggest that the use of diamond grains with reduced defect concentration and cleaner surfaces as precursors will likely improve the wear resistance of the resulting PCD via stronger individual grains and better sintering.

Keywords

Sintered diamond, deformation-DIA, strength, high pressure and temperature, synchrotron, X-ray diffraction

1. Introduction

Diamond is the stiffest and hardest material known. Years of technical development for synthesizing large sintered Polycrystalline Diamond (PCD) parts has made diamond a material of choice for various types of machining tools and engineering processes. One example of such applications is oil and gas drilling, for which it is known that PCD bits encounter the greatest wear. Comparative studies

available on PCD's mechanical properties[1, 2]show that PCD surpasses by far all other materials typically used for similar applications, such as WC.

The performance of PCD bits is essentially determined by their ability to resist fracture under loading. During a down-hole impact event, the PCD bit absorbs impact energy, by deforming under the applied load. PCD bits with higher strain energy capacity will be able to absorb more impact energy during drilling without exceeding the diamond yield strength or fracture toughness limit [3-7]. Therefore, the strength and the fracture toughness of the PCD are the main properties that control its wear resistance and durability. The failure mode of the PCD bits (intra-granular vs. inter-granular fracture) is not well understood, although it is known that it depends on the concentration of crystal defects in diamond powder precursors as well as on the quality of the sintering, i.e., the strength of the diamond-diamond bonds.

The elastic properties of single crystal diamonds and PCD's have been studied extensively in the literature[8-11]. The strength of PCD's, however, remains poorly documented, essentially due to the difficulty to deform diamond plastically at ambient conditions[12, 13]. A way to access plastic deformation of diamond is to subject it to high temperature, where ductility is enhanced[12]. However, this requires high pressures in order for the diamond to remain thermodynamically stable and not convert to graphite. In this context, we have performed a high pressure (P) and temperature (T) deformation experiment in which the mechanical properties of PCD samples were investigated in situ using synchrotron diffraction and imaging techniques. During this experiment, two samples were deformed together, under identical P-T conditions. The samples, extracted from PCD cutter bits for oil and gas drilling, were sintered from two different monocrystalline diamond powder precursors sharing identical particle shape and size distribution. However, for one sample, 1S, a standard diamond powder (unprocessed for the reduction of crystallographic defects) was used, whereas for the other one, 2E, the precursor powder was processed through mechanical, thermal and chemical steps to reduce the concentration of crystallographic defects in the grains (as described in the US patent #8,734,753 [14]). This results in a greater mechanical strength of the individual grains as evidenced by the crushing strength test results (see section 2.1 for details), which in turn may be responsible for enhanced wear resistance of the PCD. In the present study, we report characterization of the two precursors and investigate how the difference in the precursors impacts the quality of the sintering and bulk strength of the PCD.

2. Experimental protocol

2.1 Starting materials

Two different diamond powder precursors were used to sinter the PCD cutters 1S and 2E. Both diamond powders share similar particle shape and size distribution. A relatively new technique, dynamic image analysis[15], was used to characterize the two diamond powders with respect to particle shape and size distribution (Table 1).

Particle Shape	1S	2E
Total Particle Count	~ 5000	~ 5000
Average Aspect Ratio	0.717 ± 0.005	0.712 ± 0.0009
Particle Size (Equivalent Spherical Diameter)		
5%	23.3 ± 0.5	22.48 ± 0.02
50%	27.6 ± 0.5	26.9 ± 0.1
95%	32.7 ± 0.5	31.9 ± 0.1

99.9%	38.4 ± 0.9	36.9 ± 0.3
Maximum size	46.2 ± 2.9	39.7 ± 1.7

Table 1 : Results of dynamic image analysis. Particle sizes are in microns.

The majority of the particles exhibit 3-D blocky shapes, ranging in size from 22 to 36 μm , as shown by Scanning Electron Microscopy (SEM) characterization (Figure 1).

Figure 1: Panels a and b show SEM secondary electron images of the starting diamond powders used to sinter PCD bits 1S and 2E respectively.

Figure 2 shows Fourier-Transform Infrared (FTIR) [16, 17] spectra of the precursors for 1S and 2E. The spectra are consistent with type Ib diamonds (typical of synthetic diamond), where N defects are primarily present in the form of single substitutional atoms [18], rather than aggregated clusters [19]. These defects result in the sharp absorption band at 1130 cm^{-1} and the broader one at 1340 cm^{-1} [20, 21]. The absorptions at 1488 cm^{-1} for 2E and at 1458 cm^{-1} for 1S might be indicative of H related defects [22]. For this latter sample, the absorption band at 1372 cm^{-1} indicates additional H defects although, for both samples, the absence of the characteristic H absorption band at 3017 cm^{-1} precludes the presence of a significant amount of H defects [23].

A full characterization of the nature of the defects (including dislocations and twins) and their concentration in these powders would require a detailed study using transmission electron microscopy (TEM). Nevertheless, we note that the lower baseline transmittance observed in the starting powder used for 2E suggests a lower concentration of crystallographic defects [16, 24]. FTIR transmittance is related to elastic light scattering due to crystallographic defects such as dislocations, stacking faults, twins and grain boundaries – the higher the concentration of these intrinsic defects, the lower the baseline transmittance (see [25, 26] and references therein). This is consistent with the thermal treatment consisting in a high temperature ($\geq 700^\circ\text{C}$) water vapor etching [14] – applied to powder 2E. In most materials, indeed, annealing is expected to reduce the concentration of intrinsic defects, resulting in an improved infra-red transmittance [27]. Variations in baseline transmittance may also be caused by changes in the surface conditions. However, due to the etching treatment of 2E, the surface roughness of this latter sample is expected to be larger (due to the presence of additional etch pits [14]), which, if significant, would result in a lower transmittance. Since the baseline transmittance difference observed is the opposite (i.e., larger for sample 2E), we infer that it is the consequence of a lower intrinsic crystal defect concentration [28].

However, FTIR data cannot be used to infer surface defect concentrations, which may be different for different in the two samples, as suggested in figure 1 by additional charge accumulation at the grain surfaces of 2E. Time-of-Flight Secondary Ion Mass Spectroscopy (ToF SIMS) analyses are summarized in Figure 3. Spectra were collected for 5 min over a $100\text{ }\mu\text{m}^2$ area with a sampling depth up to 0.5 nm. These results thus reveal impurities mostly on the surface of the diamond grains. As shown in

figure 3a, all the data collected in negative mode seem to indicate that 1S contains higher concentration of O and H impurities. The ToFSIMS is operated under high vacuum conditions, at pressures <1 kPa, which ensures that little to no background atoms contribute to the measurement. However, since both samples contain very little H defects (as shown by the FTIR data), the corresponding low detector counts obtained here may be influenced by the minute amounts of residual hydrogen gas present in the chamber during the analysis, which may explain the disagreement between data in positive and negative mode regarding H. The present data can therefore not be interpreted in terms of relative H defect concentration. In positive mode (figure 3b), aside from the H peak, only data corresponding to an atomic mass number of 28 (i.e., N_2) show higher concentration in 2E than in 1S. The fact that all other peaks are higher in 1S than in 2E indicates that sample 1S contained more surface impurities than 2E. The integrated number of counts over all channels in positive mode is much larger for sample 1S, indicating larger impurities (including N defects) concentrations. These observations, together with the FTIR data presented in figure 2, thus convincingly demonstrate that precursor for 2E contained lower defect concentrations with cleaner surfaces than precursor for 1S.

Figure 2: FTIR spectra collected on diamond powders used for PCDs 1S and 2E. Absorption bands are labeled for the precursor used for 1S. Note that compared to 2E, this latter powder presents a lower baseline transmittance as well as an additional absorption band at 1372 cm^{-1} . Consistent with the presence of additional H related defects (see text for details).

Figure 3: Time of Flight (ToF) SIMS analysis of diamond powders used for PCDs 1S and 2E. Charts a and b are in negative and positive ion mode, respectively.

The mechanical strength of these powders was determined through crushing tests (see US Patent 7,275,446 for a description of the apparatus and technique used). The Crushing Strength Index (CSI) – the percentage of “on size” particles (particles between 50% and 95% of the number distribution) in the crushed and uncrushed diamond powder – was used to evaluate the mechanical strength. **Three trials were run on each of the powders used in 1S and 2E, the average values and corresponding standard deviations, σ , are 37 ± 0.3 and $44 \pm 4.1\%$, respectively (see Table 2). The lower standard deviation in 1S shows a better reproducibility. It is believed that the processing of powder 2E results in the presence of some grains with drastically increased fracture toughness. The proportion of such grains may vary from test to test causing the larger standard deviation observed here in powder 2E. In any case, since all three tests indicate larger CSI value, it is clear that the process utilized to reduce the defect concentration within and**

at the surface of the grains somehow results in an enhanced average toughness of the diamond grains in 2E.

Sample	Trial 1	Trial 2	Trial 3	Average	σ
1S	37.34	36.99	36.71	37.0	0.3
2E	47.5	45.04	39.46	44.0	4.1

Table 2 : CSI tests results. All values are in percentage units.

The PCD cutters, designated as 1S and 2E, were sintered simultaneously, back to back, under the same P-T conditions (above 6 GPa and 1,400°C). In this process, the diamond precursor powder is placed on a sintered Co and WC substrate, from which W and Co diffuse into the diamond layer, forming diamond-diamond bonds[3]. Cylindrical PCD samples, having 0.8 mm in diameter and 0.4 mm in length were then laser cut perpendicular to the diamond table of the PCD cutters.

2.2 Experimental details

We present here the results of one deformation experiment, where these cylindrical samples, from PCD cutters 1S and 2E, were stacked and deformed together (Figure 4). The experiment was carried out using the deformation-DIA (D-DIA) apparatus installed at beamline 13BM-D of the Advanced Photon Source (APS, located at Argonne National Lab., Illinois, USA). This experimental setup has been extensively used for rheology studies at high P-T [29-31]; experimental details can be found in the literature, e.g., [32, 33]. The D-DIA is a cubic type multi-anvil apparatus capable of generating pressures in excess of 10 gigapascals (GPa), with the top and bottom anvils advanced or retracted independently to generate tri-axial stress and strain fields with the unique principle stress/strain component along the vertical axis (i.e., parallel to the sample stacking direction).

The two samples were loaded in a boron nitride (BN) capsule, which was surrounded by a graphite sleeve for resistive heating purpose. This assembly was in turn loaded into a cubic pressure medium cell, made of mullite (Fig. 4). Because of the unusually high strength of the samples, a nano-polycrystalline diamond (NPD, aka Hime-DIA), the strongest material available to date [11, 34], was used to deform the PCD samples. The NPD rods, with large diameters of 1.6 mm, were used to sandwich the two PCD samples and acted as deformation pistons during the experiments (Figure 4).

The samples were first pressurized at room temperature and then heated before the deformation began. The temperature was estimated to be 1273 ± 50 K based on previous temperature-power calibrations established with the use of W/WRe (type C) thermocouple. Diffraction patterns taken from the gold strain markers located at the ends of the samples indicated that the pressure at the beginning of the deformation cycle was ~ 6 GPa.

Figure 4: Schematic drawing of the high pressure cell assembly used for the deformation experiments. All dimensions are in mm. Sample 2E was placed on top of 1S in the experiment.

Bulk strains of the samples were calculated by measuring the sample length on X-ray radiographs that were taken throughout the deformation cycle (e.g., see [30, 32, 35]), based on the relation $\epsilon = (l - l_0)/l_0$, where l is the sample length at a given time and l_0 is a reference sample length. Although the differential rams, which control the inward motion of the top and bottom anvils, were driven at the same motor speed, the resulting strain rates can vary from one sample to the other, as well as with time. In the present case, the strain rate increased with time before reaching a rather steady deformation rate of typically $\sim 10^{-5} \text{ s}^{-1}$. Finite bulk strains of $\epsilon \sim 15\%$ were achieved over a few hours.

2.3 Data reduction and analysis

Throughout the high P-T deformation cycle, X-Ray Diffraction (XRD) patterns were taken alternatively on the two samples using a monochromatic beam with a photon energy of 62 keV in conjunction with an area detector (MAR-165 CCD). This angle-dispersive XRD technique allows collecting full Debye diffraction rings [36]. The circular 2D diffraction patterns (Figure 5a) were binned azimuthally (at 10° intervals). Each binned segment was then integrated to yield a 2θ -versus-intensity pattern. The diffraction angle 2θ was finally plotted as a function of the detector azimuthal angle, χ , in so-called cake plots (Figure 5b), using the software package Mulifit/Polydefix© developed by S. Merkel. The 2θ values corresponding to the diffraction peak maxima were then converted to d-spacings using Bragg's law.

Figure 5: XRD pattern taken on sample 2E at ambient conditions. a and b show the raw 2D pattern collected and the corresponding cake plot of the same data after azimuthal binning, respectively. The position and the miller indices of the diffraction lines of various phases are indicated by the arrows on top. Diamond (DIA), $\text{CoC}_{0.01}$ and WC are phases that compose the PCD samples. Diffraction lines of hexagonal BN (hBN), used as part of the high P-T cell assembly, are also visible. The spotty diffraction lines correspond to the diffraction of the Co and W phases formed during the sintering process (see 3.1 and figure 7 for details).

Under hydrostatic conditions, diffraction rings are perfect circles. In a cake-plot, the diffraction rings observed for a given material are therefore visualized as straight lines under hydrostatic conditions. Diffraction rings become ellipses when the material is subject to a macroscopic differential stress; so in the cake plots (e.g., Fig. 6a) diffraction peaks appear as wavy lines[37]. In this case, the d-spacing of a given (hkl) plane, on which the 2θ diffraction angle depends, is related to the true azimuth angle, ϕ , as follows:

$$d(hkl) = d_p [1 + (1 - 3\cos^2\phi)Q(hkl)], \quad (1)$$

where d_p is the d-spacing under pressure with no differential stress and $Q(hkl)$ the elastic lattice strain for the given plane. Note that the true azimuthal angle is related to the detector angle as follows: $\cos\phi = \cos\theta \cos\chi$. The presence of deviatoric stress can be seen on the cake plot presented in Figure 6a for the (111) and (220) reflections of diamond. In order to retrieve stress information, each cake plot was integrated in 36 intensity-versus- 2θ diffraction patterns, each corresponding to a 10 degree azimuthal slice. The corresponding d-spacing of the diamond (111) and (220) reflections was first retrieved for each of these patterns (Figure 6b). Lattice distortion values, i.e., $Q(hkl)$, were then extracted by fitting the d-spacing as a function of ϕ according to Equation 1. Finally, the obtained $Q(hkl)$ were converted to differential stress values, $t(hkl)$, using:

$$t(hkl) = 6 \times Q(hkl)G(hkl), \quad (2)$$

where G is the elastic modulus for the considered (hkl) plane[37]. In this case, $G(111)$ and $G(220)$ for diamond were calculated using the elastic constants and first order P-T derivatives found in [38].

Figure 6: XRD data collected on sample 2E during deformation at high P-T. a shows a cake plot of the data. Since the sample is subject to deviatoric stress, the wavy nature of the diffraction lines of diamond can be observed. For reference, the Bragg reflections of $\text{CoC}_{0.01}$ are also indexed; note that, compared to diamond, the $\text{CoC}_{0.01}$ reflections display straight lines, due to the softer nature of this material. b shows a portion of the azimuthal bin for $\phi = 270^\circ$. Results of the fitting of the CoC_x (111) and the diamond (111) peaks are shown. Note that the two peaks are overlapping and were therefore fitted together, as shown by the yellow curves. The dashed line indicates the position of the diamond (111) peak and the grey arrows show the FWHM (see text for details).

The evolution of the confining pressure throughout the deformation cycle was retrieved by measuring the d-spacing of the diamond (111) plane for $d(hkl) = d_p$, which, according to equation [39], corresponds to the “magic” azimuthal angle of $\phi = \cos^{-1}(1/\sqrt{3}) \sim 54.7^\circ$ [40], where $\phi = 0$ in the maximum compression direction (i.e., parallel to the uniaxial deformation direction). In the present case however, contrary to Singh et al. [37], $\phi = 0$ is found parallel to the minimum stress direction, i.e., offset by 90° . Therefore, the magic angle becomes 35.3° . Pressure was calculated using the equation of state for diamond [9].

Breadths of the diamond (111) plane diffraction rings were also analyzed, since the evolution of the Full Width at Half Maximum (FWHM) can be used as a proxy for the micro-stress induced at the contact between diamond grains (Figure 6b). Indeed, as the deformation of the samples takes place, it can be shown that the FWHM of a given peak increases, due to stress heterogeneities across the grains [41].

3. Results and interpretation

3.1 Ambient conditions

As revealed by Rietveld refinement on the XRD patterns taken at ambient conditions, the samples are mainly composed of diamond and CoC_x (where x is approximately 0.01), a face-centered cubic (fcc) phase [42]. No pure Co phase was observed. Minor amounts of $\text{Co}_y\text{W}_z\text{C}_a$ are also evidenced here, with $y \approx 2$ and $z \approx 4$ (Figure 5b). The presence of Co and W is a result of infiltration from the Co-cemented WC substrate used during the high P-T sintering of the PCD's. Co is used as a binding agent during sintering; its gradient across the diamond/WC interface is controlled by a vertical temperature gradient in the high

P-T capsule during the sintering process. The spotty nature of the XRD lines of the Co-rich phases (Figure 5b) indicates a rather inhomogeneous orientation distribution. SEM images of the samples, on the other hand, show a heterogeneous interstitial distribution of the Co-rich phases (brighter phases in Figure 7). The smoother diamond diffraction lines indicate relatively fine grain size; in agreement with the starting powder used.

Figure 7: Panels a and b show back-scattered electrons SEM images of the 1S and 2E PCD bits, respectively. The brighter areas correspond to Co and W phases; they highlight boundaries of the diamond grains, whose dominant size ranges between 22 and 36 μm . Rietveld refinements (i.e. quantitative analysis) of the samples performed on XRD patterns show that CoC_x amounts to ~ 6 wt.% and $\text{Co}_y\text{W}_z\text{C}$ represents less than 1 wt.% of the bulk samples.

3.2 Strain rates

During the high P-T deformation experiment, X-ray radiographs were taken alternatively on the two samples (which were both subjected to deformation since they were stacked on top of each other). After ~ 3 hours of high P-T deformation, the two samples exhibited strains of 15.8 and $14.1 \pm 1\%$, for 2E and 1S respectively, which are virtually identical within the experimental error (Figure 8a). Therefore, for both samples the strain rate is $\sim 1.5 \times 10^{-5} \text{ s}^{-1}$.

Figure 8: Panels a and b show the bulk standard strain (i.e. length shortening) and confining pressure as a function of time for samples 1S and 2E (squares and triangles, respectively). Bulk strain of the samples is simply inferred from length measurements on X-ray images. Pressure is estimated using the position of the diamond (111) plane diffraction (see 2.3 for details).

The pressure-time curves (Figure 8b) show a somewhat different behavior for the two samples towards the end of the deformation cycle. Both pressure values are in good agreement up to 5500 s ($\sim 6\%$ strain) before the pressure measured on sample 2E progressively decreases. In the meantime, the values for 1S remain steady until ~ 9000 s ($\sim 10\%$ strain) and then start decreasing. The decrease in pressure may be caused by the gradual opening of the gaps between the four horizontal anvils, due to the inward motion of the top and bottom anvils[33].

3.3 Stress-strain curves

Following the approach described in Section 2.3, stress information was retrieved from the diffraction rings for the diamond (111) and (220) planes. However, in the conditions of our experiments, only the diamond (111) diffraction ring could be consistently resolved throughout the entire deformation cycle. Lattice distortion information from the (220) plane could only be obtained for the first half of the experiments.

Figure 9: Stress-strain curves for samples 1S and 2E (squares and triangles, respectively). Filled and empty symbols are values for $\tau(111)$ and $\tau(220)$, respectively. The uncertainty corresponds to one standard deviation, σ , resulting from the fitting procedure described in section 2.3. The $\tau(111)$ data from [13], collected on loose diamond powder at 1273 K and 3.5 GPa, are also shown for comparison (star symbols). No errors were reported in this latter dataset.

The stress values returned from the lattice plane distortion analysis are as high as 15.6 GPa for 2E (Figure 9). The high values (ca 8 GPa) obtained at the beginning of the deformation cycle are due to stress buildup upon compression before the controlled deformation began. At this point, the values obtained on both samples for $\tau(111)$ and $\tau(220)$ are in good agreement, respectively lying around 8 and 6 GPa. The stresses measured on these two lattice planes are significantly different and depart even further as the deformation proceeds: for both samples, $\tau(220)$ values remain virtually constant, indicating a flow stress of ~6 GPa, whereas, the $\tau(111)$ values show a hardening at least up to 10% of strain.

For sample 1S, the $\tau(111)$ curve appears to reach a plateau, where a flow strength of 12 GPa is attained. This is not the case for 2E, for which shows further hardening. However, error bars reported in figure 9 only reflect one standard deviation from the fitting to equation [39]. Other sources of error may contribute to the actual uncertainty. One of these is the systemic error due to the fitting of the diffraction peak for each d-spacing at various azimuth angles, as illustrated in figure 6b. P-T gradients may also contribute to additional uncertainties. Consequently, actual uncertainties are expected to be much greater than displayed in Fig. 9. Notably, the confining pressure difference measured between the two samples towards larger bulk strains (figure 8b) may cause an apparent difference in strength. In fact, only the last $\tau(111)$ data point corresponding to >13% of strain indicates a significantly larger strength for 2E. Hence, bulk strength of sample 2E may be considered only marginally greater than that of sample 1S.

Yu et al. [13] analyzed the $\epsilon(111)$ of diamond in their deformation experiments performed at 1273 K and 3.5 GPa using the D-DIA. In their experiments the strain rate was estimated to be $\sim 10^{-5} \text{ s}^{-1}$, very similar to the present study. They reported a flow strength of $\sim 7.9 \text{ GPa}$ to 15% strain (Figure 9). Their lower flow strength is clearly due to the nature of the samples, since their experiments were performed on loose powders, as opposed to sintered samples in the present study. This shows that the stress values measured with the present technique are not only related to the strength of individual grains but also to the bulk strength of the sample, which, in turn, directly depends on the quality of the sintering. In fact, in the case of Yu et al. (2012), at 3.5 GPa and 1273 K (outside the P-T stability field of diamond), it is unlikely the diamond powders will be sintered without any binding agent. The difference observed here between the sintered and non-sintered cases demonstrates the importance of the quality of the sintering on the measured PCD strength.

Under the present experimental P-T conditions, dislocation creep is expected to be the preferred deformation mechanisms[43]. Other mechanisms such as deformational twinning [44] and formation of stacking faults [45] may be at play, especially at lower strains. However no evidence for these mechanisms, such as preferred orientation or hexagonal diamond, was found in the XRD patterns. On the other hand, Devries[46] has shown that high pressure conditions favor plasticity of diamond and that dislocation creep was the dominant deformation mechanism at 6 GPa and at temperatures above 1173 K. This was further confirmed by more recent high pressure studies [12, 13], which identified large concentrations of dislocations in the $\{111\}$ planes with burgers vectors in the $\langle 110 \rangle$ directions, which are typical of fcc materials like diamond. The fact that the $\epsilon(220)$ values are weaker than the $\epsilon(111)$ and remain constant with strain suggests that dislocation glide takes place preferentially along the $\{111\}$ lattice planes, thereby limiting the strength perpendicular to the $\{220\}$ planes.

Figure 10: Comparison of FWHM values at ambient conditions (darker shaded box), at $\sim 6 \text{ GPa}$ and room temperature (lighter shaded box) and their evolution as a function of strain at high P and T. Squares and triangles are for samples 1S and 2E, respectively. Each data point corresponds to the average FWHM of the diamond (111) reflection measured from 6 azimuthal slices centered on 90 and

270°, as shown in figure 6b. These azimuths correspond to the maximum stress direction (see 2.3 for details). Error bars correspond to one standard deviation, σ .

Figure 10 shows the FWHM values of the diamond (111) reflection at ambient conditions, at about 6 GPa and room temperature after hydrostatic loading, as well as their evolution at high P-T, throughout the deformation cycle. From ambient conditions to high P-T, the two samples show a very different behavior, which is interpreted as resulting from distinct mechanical response upon pressurization. Indeed, for an ideally sintered material loaded hydrostatically, the macroscopic load is homogeneously distributed within the sample at the microscopic level with minimum stress gradient across the grains. Hence, better sintering leaves less residual stress at the contact between diamond grains, which explains the lower FWHM value for sample 2E at ambient conditions. This is better evidenced by the larger difference in FWHM observed between the two samples upon cold compression, which shows that much larger micro-stress levels build up in 1S. For both samples, FWHM values drop dramatically upon heating due to the release of micro-stress concentrations at the grains contacts. Note that for 1S, this stress relaxation mechanism causes the FWHM to drop even below that of the initial ambient value, indicating a release of the initial stress concentrations (i.e., heterogeneities) present in the sample, whereas for 2E, the FWHM simply return to the initial ambient conditions value.

At high P-T, it can be seen that stress heterogeneities build up again in both samples with increasing strain. The larger values of 2E for bulk strains greater than ~5% may reflect the ability to support larger stress levels at the contact among the grains. This is very consistent with the stronger nature of the diamond grains, as pointed out by the crushing tests, and could also be due to a better bonding strength across the grains (i.e., sintering), thanks to the cleaner surfaces evidenced by FTIR and ToF-SIMS data.

Some studies reported that the presence of planar defects, like platelets in the case of type Ia diamonds [47], can increase the strength of diamond by hindering the displacement of dislocations. This appears unlikely for two reasons. Firstly type Ib diamond generally do not have large N clusters such as platelets, unlike type Ia. Secondly, planar defects tend to significantly weaken the grains, especially for diamonds, whose normal crystal lattice consists of strong sp^3 bonding. In fact, there is experimental evidence that larger amounts of N impurities present in the PCD can weaken the strength of individual grains by creating local strain concentrations in the lattice [48]. Here, it is the sample with most defects, 1S, that shows the evolution of FWHM towards the lowest values. In addition, the lower dislocation concentration will also favor a greater strength for sample 2E.

4. Concluding remarks

In the present study, two PCD samples were deformed jointly at 1273 K and pressures above 6 GPa. The initial samples shared the same grain size distribution and binding material. However, the diamond powder used for 2E contained lower crystal defect concentration and cleaner grain surfaces. Sample 2E thus exhibits greater CSI, which may improve the wear resistance of the PCD bits.

Our high P-T deformation experiment was likely in the dislocation creep regime for diamond. Our results indicate that, at least up to 12% of strain, sample 2E exhibits marginally higher macroscopic (i.e., bulk) strength than that of 1S. Sample 2E also appears to be able to support greater stress gradients at grain-to-grain level. Our observations show that 2E is a better sintered material than 1S. Altogether, these data suggest that the use of the enhanced crushing strength diamond powder as a precursor for PCD sintering may improve the wear resistance of the PCD, thanks to the stronger nature of individual grains; and also results in a stronger and better sintered PCD, possibly due to the cleaner surfaces of the grains.

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