Electronic supplementary information

Automated high pressure cell for pressure jump X-ray diffraction


High pressure cell

Notes on cell design

There are design techniques that can be used to increase yield pressures above those possible with a simple single walled cylindrical design. To achieve this, the material at the bore needs to be submitted to compressive tangential stresses to counteract the high tensile stress due to the internal pressure. This can be done using different techniques or constructions such as multilayer cylinders with interference fits between the layers, autofrettage, wrapping or variable external restraints.

When designing and constructing Bridgman seal packing rings, some materials will perform better than others for specific pressure ranges and often several packing rings with different mechanical properties are used for a single seal. This arrangement allows the seal to operate over a wider pressure range with the softer materials sealing at lower pressures and the harder materials sealing at higher pressures. For the operational pressure range of this cell (0 – 500MPa) one packing ring is sufficient.

Windows

It is worth noting that synthetic type IIa CVD diamond is often referred to as type IIIa to distinguish it from natural type IIa; however they are chemically identical.

<table>
<thead>
<tr>
<th>Material Properties</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>3.52</td>
</tr>
<tr>
<td>Mass absorption coefficient (cm$^2$/g)</td>
<td>0.663</td>
</tr>
<tr>
<td>$\lambda = 0.73$ Å (17 keV)</td>
<td>4.6</td>
</tr>
<tr>
<td>$\lambda = 1.54$ Å (Cu K$_\alpha$, 8keV)</td>
<td>1400</td>
</tr>
<tr>
<td>Tensile Strength, $\sigma_{\text{max}}$ (MPa)</td>
<td>1000</td>
</tr>
<tr>
<td>Elastic Modulus, $E$ (GPa)</td>
<td>0.07</td>
</tr>
<tr>
<td>Poisson's Ratio, $\nu$</td>
<td></td>
</tr>
</tbody>
</table>

Table S1. Physical and mechanical properties of diamond. X-ray absorption extrapolated from the International Tables for X-ray crystallography$^1$, mechanical properties were taken from Applied Diamond Inc’s website$^2$. 
Figure S1. Geometry of the X-ray window model, t is the window thickness, a is the unsupported aperture radius and wc is the maximum window deflection at applied pressure p.

Validating threads

For a threaded assembly where both parts are made from the same material, the internal thread is stronger than the external thread; as such, validating the external thread against failure is sufficient to validate the assembly. The plug thread will fail if the shear stress ($\tau$) exceeds the shear strength of the material, $\tau_{\text{max}}$ (for a ductile material this is generally assumed to be 0.58 times its tensile strength, $\sigma_{\text{max}}$). The shear stress on the thread is equal to the axial load ($F$) divided by the shear area ($A_s$), which for the external plug thread is given by:

$$A_s = \pi n L_e K_n \max \left( \frac{1}{2n} + 0.57735 (E_s \min - K_n \max) \right)$$

(S1)

where $n$ is the number of threads per unit length (1/pitch), $L_e$ is the engagement length of the thread, $K_n \max$ is the maximum minor diameter of the internal thread and $E_s \min$ is the minimum pitch diameter of the external thread. From this, it can be seen that to ensure the plug thread does not fail the following condition must be satisfied:

$$\frac{F}{A_s} \leq 0.58 \sigma_{\text{max}}$$

(Bridgman seals)

An important aspect of this seal is that the low pressure side of the seal has a smaller surface area than the mobile high pressure surface (window and window support). As the force on the window and support has to equal that on the packing ring, the pressure on the packing ring ($P_{\text{seal}}$) is higher than the internal water pressure ($P_{\text{water}}$) by a factor of $d_1^2/(d_1^2-d_2^2)$, see Figure 2 (main manuscript). For the window seals as well as for the sample closure packing ring $d_1=14\text{mm}$ and $d_2=8\text{mm}$, which intensifies the pressure in the seals by 148%.
The surfaces of the packing ring and window support that meet have both been machined at 45° to the inner surface of the cell body to improve sealing at low pressure. The geometry of the packing ring in the sample closure seal (part L, Figure 1b (main manuscript)) is more complex as the seal needs to be easily removed when changing the sample. The fitting between the seal and the body of the cell is much looser than that for the window packing rings and has been designed with a central groove that gives the seal a little flexibility allowing it to spring back slightly on its support when the pressure is released, reducing the amount of friction between the packing ring and the body of the cell when the seal needs to be removed. A small o-ring is placed in the groove enabling the seal to perform well at low pressures despite the initial loose fit of the packing ring.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
<th>Max Temp (long term) °C</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torlon 4301</td>
<td>164</td>
<td>7</td>
<td>230</td>
<td>Not suitable</td>
</tr>
<tr>
<td>PEEK (bearing grade)</td>
<td>118</td>
<td>3</td>
<td>260</td>
<td>Not suitable</td>
</tr>
<tr>
<td>PEEK 450G</td>
<td>92</td>
<td>5</td>
<td>260</td>
<td>Good</td>
</tr>
<tr>
<td>Delrin (acetal homopolymer)</td>
<td>70</td>
<td>40</td>
<td>100</td>
<td>Good (&lt; 100°C)</td>
</tr>
<tr>
<td>PTFE</td>
<td>25</td>
<td>50</td>
<td>260</td>
<td>Limited</td>
</tr>
</tbody>
</table>

**Table S2.** Mechanical properties of materials used for the packing rings of the window seals and sample closure seal.

**Figure S2.** (1) Extrusion of PTFE window seal with window nut in place. (2) Extrusion of PTFE window seal with window nut removed. (3) Extrusion of the PTFE window seal on the window support. (4) Extruded PTFE window seals.
**Increasing accessible diffraction angle**

The accessible diffraction angle could be increased by tilting the high pressure cell relative to the X-ray beam as shown in Figure S3. The cell can be tilted 15° without clipping the incident beam and up to 21° before the beam is totally blocked, this would allow the accessible diffraction angle to be increased to 36° and 42° respectively. While the accessible diffraction angle is increased, tilting the cell also increases the X-ray path length through the windows and sample so increasing X-ray absorption, however this increase is relatively small, the path length is increased by 3.5% at 15° and around 7% at 21° tilt.

![Figure S3. (a) High pressure cell with X-ray beam normal to the windows (b) Cell tilted at 15° relative to incident beam.](image)

**Pressure cell assembly and disassembly**

**Assembly**

To reduce stress concentrations in the cell caused by geometric discontinuities such as changes in bore diameters, the core of the cell has been designed to be as simple as possible. The cell’s central bore is continuous with the exception of the intersection of the sample loading slot and the two small holes used to connect the cell to the pressure network and to purge the cell of any trapped air. Having one unique diameter for the central bore of the cell removes any shoulders that could be used for the positioning of the window holders but makes window removal easier by enabling them to be pushed through and out of the cell. To position the windows in the cell a mobile window spacer (part B, Figure 1a. (main manuscript)) and a positioning tool (see Figure S4) are used.

The window spacer serves two purposes. The first is to accurately fix the gap between the two diamond windows. That gap is equal to the thickness of the spacer and can be changed by changing the spacer. The second is to provide a guide for positioning the sample carriers precisely in the X-ray path. The
positioning tool is effectively a solid sample carrier but is much longer in length enabling it to be held out of the cell when it is placed in the sample loading slot. Inserting the positioning tool in the sample loading slot allows the window spacer to be correctly orientated in the cell. Keeping the positioning tool in place, to maintain the position of the window spacer, the window units (parts C, D, E & F, Figure 1a (main manuscript)) are inserted either side of the window spacer followed by the window nuts (part G, Figure 1a (main manuscript)). Tightening of the window nuts is done gradually and in turn so that the positioning tool remains free to slide in and out of the cell. This procedure allows the centering of the window spacer relatively to the sample loading slot. When correctly adjusted the window supports press against the window spacer and do not touch the positioning tool or sample carriers which are marginally thinner than the window spacer. The window nuts must be tightened sufficiently to pre-compress the packing rings of the window seals so that an initial low pressures seal is formed (in practice this is up to about 20 MPa), as discussed above, as the pressure is increased the dynamic Bridgeman window seals improve.

The window supports have been machined with a square section recess at their back (visible in Figure 1 a and c (main manuscript)) that enables them to be rotated around the X-ray beam axis which can help minimize parasitic scatter from the diamonds. Rotation of the windows requires the window plugs to be loosened a little and the positioning tool to be in place to prevent the window spacer from rotating with the window supports.

Figure S4. Positioning of windows in the cell. This task requires the use of a positioning tool shown on the picture on the left. The picture on the right shows how the tool fits in the window spacer.
Disassembly

Removal of the seals can be challenging as the packing rings flow a little under pressure and this causes the originally machined slide fit between the packing ring and the cell’s body to become a “tight” fit. As mentioned previously, this slight plastic deformation is desirable and improves the seal however, removal of the window supports requires a special extraction tool that is fitted in place of one of the window plugs (part G, Figure 1a (main manuscript)) and uses a screw-driven piston to gently push the window supports out of the cell body. Removal of the sample closure seal is easier as the seal support is connected to the sample plug (part H, Figure 1a (main manuscript)) enabling the seal to be pulled away from the cell body by unscrewing the sample plug itself.

Finite element analysis

Simulated Body of cell submitted to 500 MPa

Figure S5. Finite Element Analysis (FEA) of the body of the pressure cell at 500 MPa. The stress is concentrated at the edges of the sample loading slot but it is possible that the stress here is overestimated due to imposing a finite mesh on the sharp corners in the model. All calculated stresses are below the yield strength of the material.
Figure S6. Finite Element Analysis of the closure parts of the pressures cell submitted to 700 MPa.
High pressure network

Pressure motor
It should be noted that while the motor is rated to 115 volts, the power supply is limited to 88 volts to prolong the life of the motor.

A tachometer fitted to the drive motor generates a 0 – 40 volt signal which is connected to the motor control unit as a speed feedback signal.

Quick exhaust valve
The QEV contains a small mobile diaphragm which allows different gas routes for filling and emptying of the pneumatic actuator; when gas flows through the solenoid valve (Figure 5, 1 (main manuscript)), the QEV allows this gas to fill the diaphragm which closes the high pressure valve. When the solenoid valve is switched, the gas pressure is released from the inlet of the QEV, the QEV diaphragm then moves and the pneumatic valve actuator is allowed to empty extremely rapidly via an alternative route through the QEV which is directly open to the surroundings (Figure 5, 2 (main manuscript)).

Note that the control circuit is designed so that the motor will not operate if the limit switches are disconnected from the control unit or if there is a failure in the power supply that is used to monitor the limit switches.

Valves
Note that the slow remotely operated valves are normally closed so that in the event of gas or electrical failure, any pressure in the network becomes isolated rather than causing an uncontrolled pressure release.

Network volume
The volumes of the pressure network on either side of the jump valves can be estimated from the design specifications of the system as follows:

Cell and associated tubing and fittings to cell side of jump valves: 6.8 cm³
Tubing and fittings on reservoir side of jump valves (with reservoir valve closed): 4.1 cm³
Tubing, fittings and reservoir on reservoir side of jump valves (with reservoir valve open): 56.0 cm³
Control system

Main control panel

The main user interface window is shown in Figure 8 (main manuscript). This window has two functions; firstly, it displays the status of the pressure cell and network and secondly, it can be used to initiate changes to the system. The system pressure is indicated by a digital display, pressure dial and ‘pipe color’, the latter giving a quick visual indication of pressure differences within the system. The pressure generator’s piston position is indicated by a digital display and a visual indication is given by the displayed position of the pump piston. The remotely operated valve states are indicated, with green showing open and red closed and the cell temperature is shown as a digital display above the pressure cell. Finally, calibration and diagnostics systems have been built in and an alternative text based user interface has been developed which supports scripting.

It should be noted that the current status of the system is always displayed and requested changes are only reflected after they have happened. For example: if valve 1 is closed, it will be displayed in red; double clicking on valve 1 runs a routine which queues a digital out command to open valve 1 and once this signal has been written to the digital out DAQ module, the user interface will detect this and update the window to display valve 1 as open.

Interaction with data acquisition hardware

![Figure S7. Simplified schematic showing key components of the pressure system control software.](image-url)
The software has been designed in a series of layers as shown in Figure S7. At the core of the software are 4 server modules which run continuously and form the bridge between the software and the DAQ hardware. There is one server for each of: analogue input, analogue output, digital input and digital output. Both input servers continuously read data from the input DAQ modules, process the raw data and feed this processed data into a series of shared variables from where other software elements can access it. The output servers each read data from an output queue, process this data and write the data to the output DAQ modules. Output commands can be placed in the queues by other software elements. The output servers are mediated by a ‘safety server’ program which monitors the pressure readings and valve states to prevent excess pressure generation or uncontrolled pressure release.

There is a further server program, the ‘motor acceleration server’, which ensures the pressure pump motor accelerates and decelerates smoothly. This server writes speed signals to the analogue out queue based on a speed setpoint shared variable.

In addition to the input / output servers, routines have been developed that can use the high speed digital input / output DAQ module to exchange TTL trigger signals with the beamline. Specifically, trigger signals can be sent to initiate image acquisition by the beamline and the DAQ hardware can be configured to accept a hardware trigger to open the pressure jump valves as discussed in the control hardware section. It should be noted that before the DAQ system is configured for hardware triggering, the digital out server has to be suspended so software data is not accidentally written to the jump valve output during a pressure jump experiment. After the pressure jump has been performed, the digital out server is restarted.

**Data acquisition unit – pressure system signals**

The hardware DAQ signals are summarized in Figure 7 (main manuscript) but are further explained below.

**Pressure motor control unit**

The motor control unit accepts 3 remote control signals: speed (0 – 10 volts), motor on/off (24 volt digital), motor direction (24 volt digital). The speed signal is provided by the 0 – 10 volt analogue output module of the DAQ system while the on / off and direction signals are provided by the 24 volt digital output module.
Valve control
Allowing 6 bar of gas into the valve actuator switches it from its resting state, so for the normally closed slow valves, the valve is opened and for the normally open fast valves, they are closed by allowing gas to flow into the diaphragm actuator.

When a solenoid valve is energized, gas is allowed to flow into the high pressure valve actuator then when the solenoid valve is de-energized, gas is allowed to vent out of the actuator.

The 24 volt supply to the solenoid valves is provided directly by the 24 V digital output DAQ module.

Pressure measurement
They require a 10 volt excitation signal and output 0 – 10 mV which is proportional to the pressure; both the excitation and detection are provided by the bridge input DAQ module.

Temperature
The DAQ module both provides a 1 mA excitation current and measures the resistance of the sensor.

Pressure pump piston position
This transducer is excited with 5 volts provided by the 0 – 10 volts analogue output DAQ module and this produces a 0 – 5 volt output signal proportional to position which is read by the 0 – 10 volt analogue input DAQ module.

Hardware clocked digital output
When the pressure system is armed ready for a pressure jump, a small buffer of data is loaded onto the Compact DAQ chassis to be written to the 24 V digital out module, a TTL signal produced by the beamline detector electronics is then routed via the high speed digital I/O module to produce a clock signal to write the buffer data. In this way, energizing the pressure jump valves can be synchronized very precisely (timing is accurate to 100 nanoseconds), with the start of a specific image acquisition. While this process may appear rather complex, the user interface software configures the hardware automatically when a pressure jump is set up.
Pressure calculations

To a first approximation, effectively applying the perfect gas equation, the resulting pressure can be calculated from the following equation:

\[ P_f = \frac{P_r V_r + P_c V_c}{V_r + V_c} \]  \hspace{1cm} (S3)

Where \( P_f, P_r \) and \( P_c \) are the final, reservoir and cell pressure respectively and \( V_r \) and \( V_c \) are the reservoir and cell volumes respectively. This can be further simplified by considering the ratio of cell and reservoir volumes rather than their absolute valves to give:

\[ P_f = \frac{P_r R + P_c}{1 + R} \]  \hspace{1cm} (S4)

Where \( R \) is the ratio \( V_r / V_c \).

Despite the obvious shortcomings in this model, it can be surprisingly successful. After fitting experimental data to equation S4 to find the ratio of the two volumes, the average deviation between experimental and calculated post jump pressures is around 12 MPa.

A significantly more appropriate model is that of water as a compressible fluid with a defined bulk modulus. The bulk modulus \( K \) gives the pressure required to cause a relative reduction in volume of a material i.e.:

\[ P = K \left( 1 - \frac{V_p}{V_0} \right) \]  \hspace{1cm} (S5)

Where \( V_0 \) is the volume at zero relative pressure (0.1 MPa absolute pressure) and \( V_p \) is the volume at pressure \( P \). Rearranging equation S5 gives:

\[ V_0 = \frac{V_p}{1 - \frac{P}{K}} \]  \hspace{1cm} (S6)

When considering a pressure jump, it is useful to calculate \( V_0 \) for each section of the pressure system as this only depends on the molar quantity of water in that section and not on pressure. Combining equation S6 for cell and reservoir volume and equating this sum to the post jump combined volume gives:

\[ \left( V_c + V_r \right) \frac{1 - \frac{P_f}{K}}{1 - \frac{P_r}{K} + \frac{P_c}{K}} \]  \hspace{1cm} (S7)

Again the ratio of the reservoir and cell volume can be considered rather than absolute volumes to give:
Equation S8 can be used to fit the volume ratio $R$ using experimental data (using a constant value of $K$ which is 2.2 GPa for water at atmospheric pressure and 25 °C). Despite this model being significantly more physically appropriate than the perfect gas model, the bulk modulus approach gives an average absolute deviation of nearly 20 MPa between calculated and experimental final pressure values.

Key to improving this mode is that the bulk modulus of water increases with pressure, i.e.: water becomes harder to compress with increasing pressure. The pressure dependence of the bulk modulus of water can be modeled by a second order polynomial:

$$K = K_0 + A_1 P + A_2 P^2$$  \hspace{1cm}  (S9)

Where $K_0$, $A_1$, and $A_2$ are temperature dependent constants and specifically $K_0$ is the bulk modulus at atmospheric pressure. Using equations S5 and S9 the following relationship can be found:

$$\frac{1}{1 - \frac{P_f}{K_f}} = \frac{1}{1 + R} \left( \frac{1}{1 - \frac{P_r}{K_f}} \right) + \frac{R}{1 + R} \left( \frac{1}{1 - \frac{P_r}{K_f}} \right)$$  \hspace{1cm}  (S10)

Here, $K_c$, $K_r$, and $K_f$ are the bulk modulus values at pressure $P_c$, $P_r$, and $P_f$ (final pressure after jump) respectively and $R$ is the ratio of reservoir to cell volume. As $K_f$ is a quadratic function of $P_r$, this equation is best solved iteratively using 2.2 GPa as an initial guess for $K_f$, calculating $P_f$ and using this to calculate a refined value for $K_f$.

References