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Modified design and use of a high-pressure environmental stage for laboratory X-ray powder diffractometers

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The popularity of supercritical CO₂ for materials processing makes the *in situ* study of pressures up to 10 MPa in the laboratory particularly interesting. This paper describes a modified design for a 12.4 MPa (1800 psi) variable-temperature pressure vessel based on an existing cell reported by Koster van Groos, Guggenheim & Cornell [*Rev. Sci. Instrum.* (2003), **74**, 273–275]. The modifications satisfied the demands of the American Society of Mechanical Engineers design code 31.3, leading to legal design registration, construction and subsequent hydrostatic test. The thinner windows that the finite element analysis indicated as sufficient allow for rapid data collection, even using a laboratory-based Mo source. This type of application is demonstrated with a time-resolved data set showing the crystallization of a polylactic acid–clay nanocomposite under 6.8 MPa CO₂.

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1. Introduction

High-pressure (GPa range) high-temperature diffraction work has usually been regarded as a tool of geologists and mineralogists to better understand processes within the Earth's crust. These workers usually use diamond anvil cells (DACs) to obtain the extremely high pressures required, and synchrotrons (Nelmes & McMahon, 1994; Hemley *et al.*, 2005) or time-of-flight neutron sources (Besson *et al.*, 1992; Jørgensen *et al.*, 2004) to acquire data of sufficient quality. The limited sample volumes in DACs make rapid data collection on laboratory diffractometers without two-dimensional detectors problematic because of weak reflections and poor powder averaging.

More modest pressures (MPa) and temperatures are now of interest to those studying gas hydrates and materials processing. The system of interest in this case is supercritical and subcritical CO₂ processing of bio-based polymers (Liao *et al.*, 2006). For the envisaged work a maximum pressure of 12.4 MPa (1800 psi) is required in order to exceed the supercritical point for CO₂ (7.4 MPa) comfortably. A conventional pressure vessel is perfectly practical for these moderate pressures. Laboratory systems with a line-focus X-ray tube and para-focusing optics are best suited to reflection geometry, and the addition of a gas reservoir and transducer to balance and monitor the gas pressure make the gas cell a more attractive proposition. The highest pressure available in a commercial stage is 6 MPa (Edmund Bühler GmbH, HDK

HD60), so it was necessary to design and build a custom stage for a Bruker D8 diffractometer.

A design was found in the literature that could form the basis of this stage (Koster van Groos *et al.*, 2003); the existing design was successfully used up to 5 MPa for the *in situ* study of novel gas hydrate phases (Guggenheim & Koster van Groos, 2003). The estimated maximum pressure for the stage was 10 MPa. The stage was designed such that the volume of gas was reduced to a minimum, so reducing the deleterious effects of any component failure. In addition, the capability of varying sample temperature using a circulating fluid was present. The design had most of the features required but had to be approved and certified for higher pressures before it could be built. Since the starting point in the design of the current stage was the published cell of Koster van Groos *et al.* (2003), its general appearance closely resembles its 'relative'. However, the design was re-examined from scratch using finite element analysis, and there are some differences in terms of design, materials and construction that stem from our particular requirements and the regulatory environment. The functionality is essentially equivalent except for the higher attainable pressures and ability to collect data more rapidly owing to the use of thinner windows. Coupled with an Mo tube source and modern detector technology, kinetic studies that would previously have required synchrotron beam time may come within the reach of laboratory instruments. An example of the possibilities using a laboratory source is given. Time-resolved data were obtained using a position-sensitive

detector (PSD) in snapshot mode from a crystallizing polylactic acid (PLA)–clay nanocomposite under 6.8 MPa CO₂.

2. Experimental

It was determined that any design would be a category ‘H’ fitting under the Canadian Standard Association (CSA) B51-03 pressure vessel code (Canadian Standards Association, 2003), and had to be designed, built and tested to the ASME B31.3 (process piping) design code (American Society of Mechanical Engineers, 2004).

A standard exploded CAD-view of the modified stage design can be seen in Fig. 1. Some changes were made to the earlier design of Koster van Groos *et al.* (2003) in order to simplify and strengthen certain parts of the construction for the higher design pressure. The pressure boundary between the gas and cooling/heating fluid circuit was changed to three standard 69 MPa ASME-rated hex socket fittings (part 12 in Fig. 1). Together with a cross-drilled hole this assembly is an easier analytical problem for finite element analysis. The vent-release used by Koster van Groos *et al.* (2003) was removed in favor of a commercial Swagelok bleed valve that is also ASME-rated to 69 MPa. From the point of the pressure boundary this requires only a straight drilled hole rather than a more complicated construction. Again this simplifies the analysis of the design. The window assembly is probably the most obvious change. Swagelok compression fittings are a standard design, familiar to pressure engineers, so their use once again simplifies the design from the perspective of certification. The design incorporates Viton compression o-rings for both the window and the cover assemblies (parts 7, 8 and 18 in Fig. 1). The o-rings should be replaced regularly if CO₂ is the working gas, as even Viton is not totally impervious to CO₂ at high pressure. A special tool was made to install and remove the window retainers without damaging the windows themselves. Standard pin-wrenches are used to assist in tightening the retaining collar (item 5 in Fig. 1) to obtain a gas-tight seal. The degassing of the Viton on release of CO₂

Table 1

Key to the part numbers in Fig. 1.

Item	Description	Material
1	Goniometer mounting plate	Aluminium
2	Stage alignment plate	Aluminium
3	Thermal insulating plate	Delrin
4	Sample holder	SA182-F304 S
5	Retaining collar	Nitronic 60 (SA192-B85)
6	Window cover	SA182-F304 S
7	Be window	SR-200 Be
8	Window retainer	Nitronic 60 (SA192-B85)
9	Window retainer tool	SS303
10	Gas and water connectors (1.5625 mm NPT)	Swagelok S-100-1-1
11	Thermocouple compression fitting	Omega SSLK-116-116
12	Plugs (1.5625 mm NPT)	SA182-F316
13	Sample slide	Glass
14	Sample support	SS303
15	K-type thermocouple	–
16	Beam path	–
17	Dowel pins	–
18,19	Viton O-rings	–
20,21	Screws	–
22,23	Hex set screws	–

pressure can be quite spectacular, with a significant increase in volume. Consequently, after using CO₂ at high pressures, it is recommended that the gasket is left to shrink back to size before attempting to access the sample.

An additional port was added to monitor the internal gas pressure; a Gem Sensors 3101 pressure transducer (0–2000 psi, 0–13.8 MPa range) being used for this purpose, with a compensated temperature range from 233 to 398 K. In common with the parent design (Koster van Groos *et al.*, 2003) the temperature of the sample is monitored using a K-type thermocouple probe (Omega HGKMQSS-062G-2.5”) which is held by a Swagelok compression fitting. The angled connector on this thermocouple helps to avoid fouling the mounting plate. The 3101 pressure transducer also outputs a temperature signal and can be monitored in addition to the thermocouple. Both the gas pressure and the thermocouple sample temperature are monitored and logged by computer using RS232 connections to the two Eurotherm 32h8i meters.

Except for the beryllium windows, all of the materials comprising the pressure boundary were ASME-approved materials. The parts comprising the pressure boundary are made from SA182-F304 stainless steel (as per code), and the retaining collars for the beryllium windows and window cover from SA193-B85 stainless steel (Nitronic 60) for improved thread wear. SA182-F304 stainless steel of the main body does not have the antigalling properties of Nitronic 60, therefore the use of a molybdenum-based antiseize compound is highly recommended to avoid problems during service.

The plates used to mount the stage to the diffractometer (Figs. 1 and 2) are almost identical to those described by Koster van Groos *et al.* (2003), as the Siemens D5000 and Bruker D8 use a common mounting. The mounting plate was made from aluminium, and contains setscrews to allow for vertical adjustment of the stage height, as the sample height is critical for measurements at low angles. A spacer made from Delrin plastic is situated between the aluminium mounting

Figure 1

A standard exploded CAD-drawing of the bare pressure stage as per the hydrostatic test. The key to the part numbers is in Table 1, and differences from the stage as described by Koster van Groos *et al.* (2003) are described in the text.

Figure 2

Photograph of the assembled stage mounted on the diffractometer. None of the external fittings/pipework is connected.

plate and the stainless-steel pressure chamber. As described by Koster van Groos *et al.* (2003), this provides thermal insulation between the stage and the diffractometer for variable-temperature measurements. The maximum design leak rate of the pressure chamber was $5 \times 10^{-5} \text{ ml s}^{-1} \text{ He}$ at 1.24 MPa (180 psi).

The windows used for the stage are 3.175 mm (1/8") thick, 19.05 mm (3/4") diameter, SR-200 beryllium, with a BR-127 anticorrosion coating on both sides, supplied by Brush-Wellman. This structural grade of beryllium is not normally supplied for X-ray windows and has a slightly lower purity (98.0% Be) than the 99.0% Be grade (PF-60) that would normally have been chosen. The lower purity impacts the transmission of the windows, but to satisfy the regulatory authorities, the material had to have certified physical/mechanical properties over the range of operating temperatures.

A certified pressure engineer examined the modified design, and a full finite element analysis was carried out, with an allowable temperature range of 233 to 473 K. The window design allows data to be collected between 1 and $60^\circ 2\theta$. Using a molybdenum X-ray tube, this corresponds to a d -spacing range of 40.6–0.71 Å. The use of Mo $K\alpha$ (0.7093 Å) radiation means that data collection at lower angles is necessary, but the attenuation of Cu $K\alpha$ (1.5418 Å) would be too great to achieve the time resolution required.

After construction, the finished vessel was tested hydrostatically at 20 MPa (2903 psi). This had to be performed with the windows *in situ*, as beryllium is not a certified material for use in pressure vessels. The certification covers use of the stage with air, carbon dioxide or nitrogen. Additional regulatory requirements would have to be satisfied for use with flammable/explosive gases such as methane or hydrogen.

It is notable that the windows used in this stage are 3.175 mm thick as opposed to the 6.35 mm thickness used by Koster van Groos *et al.* (2003), despite the requirement for a higher pressure. Thinner windows are desirable to achieve

reduced X-ray attenuation. The transmission of Mo radiation is 92.7% *versus* 86.0% for 6.35 and 12.70 mm of beryllium, respectively. Consequently, the requirement for finite element analysis before certification had a beneficial side effect, as it was found that the thicker windows were not necessary to achieve the required pressures.

In this design implementation, 1.5625 mm (1/16") national pipe thread (NPT) ports were used as opposed to 3.125 mm (1/8") NPT, which removed less metal from the structure of the stage, but requires the use of adapters to attach the various fittings. In operation, 316SS 1.5625 mm (1/16") male NPT to 3.125 mm (1/8") Swagelok fittings are used to connect the gas and water lines. 1.5625 mm (1/16") NPT is too small for commercially available transducer and bleed valve fittings, so 316SS 1.5625 mm (1/16") male NPT to 3.125 mm (1/8") female NPT adapters from Swagelok are used to mount these fittings to the stage.

When mounted on the diffractometer, the stage is coupled with a molybdenum anode long-fine-focus X-ray tube, a variable divergence slit, and a Vantec-1 PSD. The data shown in this paper were taken using the X-ray tube at 50 kV and 45 mA, with a 0.2° divergence slit and a 9° detector window. The diffractometer is set up in Bragg–Brentano parafofocusing mode with a 500 mm circle, and the detector is used in ‘snap-shot’ mode. This allows data across $10^\circ 2\theta$ to be collected in real time. Usually when using a PSD at relatively low angles, radial Soller slits are used to reduce the background. However, these cannot be used with ‘snap-shot’ mode. Low-angle scattering is expected to be a particular issue when using this stage (increased scattering from the windows and the denser, pressurized gas *etc.*), so a knife-edge was constructed from 0.125 mm tungsten sheet. Lead may have been a more obvious choice, but the increased stiffness of tungsten together with its high absorption with Mo $K\alpha$ ($\sim 1800 \text{ cm}^{-1}$) makes it a good choice for a knife-edge.

Samples can be used in either thin rectangular sections or thicker round discs depending on the application. The sample is tensioned using a setscrew from below. A small spring is inserted between the screw and the sample to accommodate volume changes that will occur on gas absorption in polymer samples.

Tools were also designed and constructed to help with the alignment and height adjustment of the stage on the diffractometer. The first is a small metal disc containing a fluorescent screen for adjustments to the centre of the goniometer circle. The second is a metal tool containing a narrow slit to check and adjust the zero degree ω and 2θ reference points of the diffractometer to account for rotation of the stage. A couple of sample holders for powdered samples were also produced.

The characteristics of the stage were demonstrated using a sample of crystalline polypropylene under CO_2 between 0 and 6.9 MPa (1000 psi) at room temperature. Polypropylene does not crystallize but does absorb some CO_2 . CO_2 should be liquid under 6.9 MPa pressure at room temperature (Fig. 3), but the equilibrium temperature inside the cabinet was 302 K owing to the extra heat generated by the X-ray tube. Conse-

Figure 3
Pressure-temperature phase diagram of CO₂.

Figure 4
Plot showing the diffraction patterns from crystalline polypropylene between 0 and 6.9 MPa (1000 psi) in 0.69 MPa (100 psi) steps. The low-angle background increases with increasing pressure whilst the peak intensity drops.

Figure 5
Variation of CO₂ density with pressure at three different temperatures around the critical temperature. Data from the NIST Chemistry WebBook (<http://webbook.nist.gov/>).

quently, all of the data sets are in the gaseous state. Severe attenuation of the reflection intensities would be expected with the higher densities in either liquid or supercritical CO₂. Data from the crystallization of a PLA-clay nanocomposite under 6.8 MPa CO₂ were also taken to demonstrate the real kinetic capabilities of the stage. After evacuation of the sample under vacuum (10^{-2} torr, 1.333 Pa) for 2 h, the CO₂ gas was introduced. 30 s snapshots were taken every minute for 1 h. The crystallinity was determined using a Pawley fit to a literature unit cell for α -PLA (Hoogsteen *et al.*, 1990), fitted using *TOPAS* (Bruker, 2005) with a linear background. A two-phase fit with a phase for the amorphous and one for the crystalline phase was used. The crystallinity was calculated using the integrated areas under the crystalline and amorphous phase.

3. Preliminary results

The diffraction data from polypropylene from 0 MPa up to 6.9 MPa CO₂ are shown in Fig. 4. Variation of the background and peak intensities was expected because of the increasing density of the gas within the stage with increasing pressure. The fact that the intensities for the final data set (6.9 MPa) in Fig. 4 were not very significantly lower than those for the previous data set demonstrates that the gas had not liquefied when the data set was taken, confirming the effect of increased ambient temperature. The variation in density expected under typical operating conditions is shown in Fig. 5. The longer beam path length through the gas means that the absorption of the gas becomes the major cause of attenuation at higher pressures. Fig. 6 shows the theoretical beam attenuation using the stage at 30° 2 θ , including the gas and beryllium windows, with pressure at the same three temperatures as in Fig. 5. It is evident that better data will be obtained in the supercritical regime than in the denser liquid phase, but all of the

Figure 6
Theoretical transmission of the sample stage under different CO₂ temperature/pressure conditions for 30° 2 θ with Mo K α . Attenuation due to both the pressurized gas and the beryllium windows has been taken into account.

Figure 7
1 s snapshot data from crystalline polypropylene at room pressure both with and without the window cover assembly.

Figure 8
Theoretical transmission of the sample stage where helium or nitrogen gas is used instead of CO₂. Although the actual stage constructed is not certified for them, the theoretical characteristics of the stage design with hydrogen and methane are also shown given their potential interest to many researchers. Density data from the NIST Chemistry WebBook (<http://webbook.nist.gov/>).

Figure 9
Plot showing the crystallization (intensity versus 2θ) of a polylactic acid–clay nanocomposite under 6.8 MPa CO₂ over a period of 60 min with a 1 min time resolution.

temperatures converge to approximately 10% transmission at the maximum achievable pressure of 12.4 MPa.

In order to obtain real-time data during crystallization of a polymer, rapid data collection with a suitable time resolution must be possible. Under many conditions, the crystallization occurs in a matter of minutes. Fig. 7 shows the data obtained from the crystalline polypropylene at room pressure in a 1 s snapshot. Data are shown for when the cover is both present and absent. It demonstrates that usable data may be obtained in a matter of seconds, and that the attenuation caused by the windows and cover assembly is acceptable. The significantly greater beam attenuation at higher CO₂ pressures shown in Fig. 6 will obviously affect the achievable time resolution given that the theoretical transmission drops from 90 to 10%. Should an experiment be concerned solely with gas pressure rather than the nature of the gas, it may be preferable to reduce attenuation using helium gas which has a much lower absorption. Nitrogen may also be used but has a significantly higher attenuation than helium. The theoretical transmission characteristics of the stage with different gases, including hydrogen and methane at 298 K, are shown in Fig. 8.

The data showing the behavior of a polylactic acid (PLA)–clay composite under 6.8 MPa CO₂ are shown in Fig. 9. In this instance the crystallization was quite slow, so a short time resolution was not necessary. 30 s data sets taken every minute were perfectly adequate, and the improved signal–noise helped with the Pawley fitting used to determine the crystallinity of the polymer *in situ*. The initial crystallization was quite rapid, reaching a plateau around 17% after 10 min (Fig. 10). The *in situ* X-ray diffraction yields information not readily available using other techniques. High-pressure differential scanning calorimetry could give quantitative results for crystallinity with time but is not capable of distinguishing between the α - and β -phase of PLA. A study of the crystallization behavior of PLA and PLA–clay nanocomposites in the sub-critical regime has been successfully carried out and will be the subject of a further paper.

Figure 10
Calculated crystallinity of the PLA–clay composite over a period of 60 min.

4. Conclusions

A high-pressure gas cell has been built for a laboratory Bruker D8 diffractometer. The existing literature design by Koster van Groos *et al.* (2003) was examined and modified where necessary to meet current legal requirements and for a higher maximum working pressure of 12.4 MPa (1800 psi). In common with the parent design, the stage is easy to mount and align on the diffractometer. Mounting of samples is quick, and very little time is required to depressurize the stage before disassembly.

The stage has been demonstrated up to 6.9 MPa (1000 psi) with CO₂. CO₂ is a particularly challenging gas given the presence of a gas/liquid boundary and a supercritical region and given the gas absorption by many gasket materials. The data quality obtained using Mo K α together with a modern PSD is excellent, with 1 s snapshots being perfectly possible in the low-pressure gaseous regime. This rapid data collection leads to the possibility of carrying out kinetic studies of relatively rapid processes, although the time resolution will suffer at higher CO₂ pressures owing to rapidly increasing gas density and the resulting beam attenuation. Although it only required a 1 min time resolution, *in situ* data from the crystallization of a polylactic acid–clay nanocomposite at 6.8 MPa does show the type of experiments that can be attempted.

Should the aim be to study materials under pressurized inert gas, the use of nitrogen, or more ideally helium, may be desirable to improve the transmission of the beam at higher pressures. The design should also produce excellent results with other gases, such as high-pressure hydrogen and methane, as long as the gases are compatible with the beryllium, stainless steel and gasket material. It should be noted that non-inert gases could not legally be used in a duplicate chamber without recertification.

The design and construction of the stage followed the certification requirements of the Canadian Standards Association. Mounting of the stage to other diffractometers should

not require changes to the pressure-bearing portion of the stage, so should not cause regulatory problems. Regulations in the USA and elsewhere are similar, so certification of the design in other jurisdictions should be possible with minimal alterations.

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