Modular *in-situ* reaction chamber design for time resolved diffraction

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Abstract. In an effort to mitigate the expense and uncertain performance of customised environment chambers, researchers at the University of Melbourne and the Australian Nuclear Science and Technology Organisation (ANSTO) have designed and are currently constructing a modular reaction chamber, capable of separating the necessities of diffraction methodologies from those of the desired sample environment. The *In-Situ Reaction Chamber* (ISRC) abstracts many of the details intrinsic to the diffractometer, allowing users to design inexpensive environmental inserts that may be readily customised to their individual needs. Overall, the modularised design aims to reduce the development costs of performing *in-situ* diffraction experiments, while minimising the experimental setup time and overall uncertainty of ancillary performance.

Introduction

Progress in many technological fields including energy production, aerospace and biomedicine is increasingly dependent upon novel materials with exceptional mechanical, thermal and chemical properties. Often these materials are produced via complex processing techniques, the traditional optimisation and validation of which have contributed to making them costly both economically and environmentally. However, there is increasing experimental evidence to suggest modern time-resolved diffraction techniques, given sufficient time-resolution, can substantially reduce the time involved in process optimisation. This can be achieved through an examination of the fundamental mechanisms by which a material is synthesised, on a time scale commensurate with the rate limiting kinetic mechanisms [1].

Time resolved *in-situ* diffraction is a particularly powerful technique in materials research, capable of observing the time evolution of phases as they change in quantity and composition, and correlating these changes with processing parameters such as temperature, pressure and time [2]. This provides a vital insight into the kinetics of materials synthesis and processing; information essential to process optimisation [3]. There are however, several challenges inherent in time resolved diffraction techniques, which generally might be categorised into the flux and resolution of modern diffractometers (both of which need to remain high), the development of analysis software capable of handling very large data sets (>10,000 diffraction patterns) and the ability to construct sample environments that mirror the processing or operational environments of the materials under investigation.

The time resolution of an *in-situ* diffraction experiment is determined by the flux of radiation at the sample position and limited by the speed and dynamic range with which detectors might acquire the data. The development of position sensitive detector (PSD) technology for very high flux powder diffractometers (such as D20, GEM and WOMBAT for neutrons and various synchrotrons for X-rays) has enabled diffraction pattern acquisition and data readout times to be reduced to less than a second. This has allowed diffraction studies of rapid material reactions and transformations with the same or better time resolutions as conventional methodologies [4]. A result of these high speed detectors is the accumulation of extremely large data sets, of the order of >10,000 diffraction patterns per reaction sequence. To then quantitatively process this data for information such as phase analysis, reaction kinetics and thermal expansion, has traditionally been a laborious and time consuming task, if it can be performed at all. Software with the ability to either sequentially refine patterns or simultaneously fit 2-dimensional data sets (i.e. Rietveld surface fits) have begun to address this issue and make the quantitative analysis of data sets of this size feasible.

Overall, the development of reliable sample environment instrumentation remains a limiting factor in time resolved *in-situ* studies. If the results of a time resolved in-situ experiment are to be applied to the interpretation of a real process, it is critical that the sample environment be representative of the system under consideration. Often the environment chambers available at major research facilities are optimised for particular instruments and are restricted in their capabilities, or alternately are developed at great expense by user communities for a single, specialised experiment. These approaches often result in the development of chambers customised to the needs of a specific instrument or user and hence restrict the wider application of these techniques. Unfortunately, the difficulty and expense of producing a customised chamber has frequently resulted in poorly performing experiments or has deterred further experimental development.

These issues can be addressed by identifying and separating the experimental aspects associated with a particular instrument or technique, from those associated with sample environment or process simulation. The result is a modular system in which the relatively expensive, instrument specific technology can be developed once by a research institution, while the highly customised environment chambers are developed as needed by individual users. This method significantly reduces the cost of customised chambers and allows users to focus on creating an environment that accurately simulates their system of interest. Furthermore, the user may then have the opportunity to completely characterise the insert off-line, prior to performing their experiment *in-situ*, thereby minimising the uncertainty of the experiment and hence improving the quality of the data obtained. This directly addresses the increasing over-subscription of proposals to high-flux diffractometers around the world by significantly reducing the time and complexity of experimental setup.

Design of the *in-situ* reaction chamber

Researchers at the University of Melbourne have designed and are currently constructing in collaboration with ANSTO, a modular reaction chamber capable of achieving this separation of technologies. The ISRC (figure 1) has been designed specifically for use on the high intensity powder diffractometer WOMBAT, located at the OPAL Research Reactor (Lucas Heights, Sydney, Australia), and is representative of the instrument specific chamber required by the modular technique.

The ISRC has been designed to address the following issues associated with high-flux neutron powder diffraction:

- **Air scatter** has been identified as a major contributor to instrumental background and loss of incident neutron flux and as such, the body of the ISRC is to be evacuated to high vacuum (sample atmospheres provided within the environmental insert). While a temporary flight tube from monochromator housing to the sample environment is not envisaged for standard operation, the beam inlet window will allow for the fitting of a continuously evacuated neutron guide. In general, the present design aims to maximise chamber diameter and hence provide the largest sample volume, while removing as much air-scatter as is feasible given the limiting inner dimensions of the curved position sensitive detector.
- **Flux attenuation** is critical for ultra fast acquisitions, where time resolution is defined by the ultimate flux at the sample position. Aluminium has been used for incident and diffracted beam windows to reduce flux attenuation, the thicknesses of which have been reduced to a minimum. These windows constitute the only component of the ISRC positioned within the incident and diffracted beams.

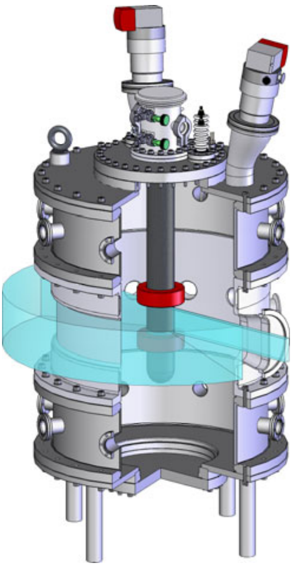

Figure 1. Section view of the assembled ISRC and high temperature insert, showing passage of incident and diffracted beams.

- **Maximum angular resolution**, while ultimately defined by the angular acceptance of the PSD, the ISRC can limit the angular range if the beamstop and flight tubes are not correctly integrated. Care has been taken in the design of the ISRC to minimise the impact of these features (figure 2a).
- **Diffraction window uniformity** has also been determined to be a significant contributor of anomalous background features. High manufacturing tolerances have been established for the window thickness, producing a +/– 0.01mm variance over the full 160° range (figure 2b).
- **Sample alignment** is achieved on the ISRC by the use of standard, self-locating vacuum flanges, which are set at a specific height from the centre of the incident beam (figure 2c).
- **Incident beam definition** can minimise divergence from the monochromator, hence improving the full-width half-maximum peak definition. Masking of the incident beam is performed at the flight tube vacuum port, allowing for the use of materials normally sensitive to high temperatures to be applied at an external position (figure 2d).
- **Concurrent experimentation** can be used to gather more information or verify data while the diffraction measurement is being taken. The ISRC features vacuum ports set at various angles and heights to facilitate these experiments (figure 2e).
- **Chamber activation** has been addressed in the ISRC by selecting materials that exhibit little if any activation, minimising the down time between experiments/users.
- **Thermal loadings** have been addressed by incorporating active water cooling within the double wall of the main chamber, permitting the use of very high temperature sample environments (figure 2f).

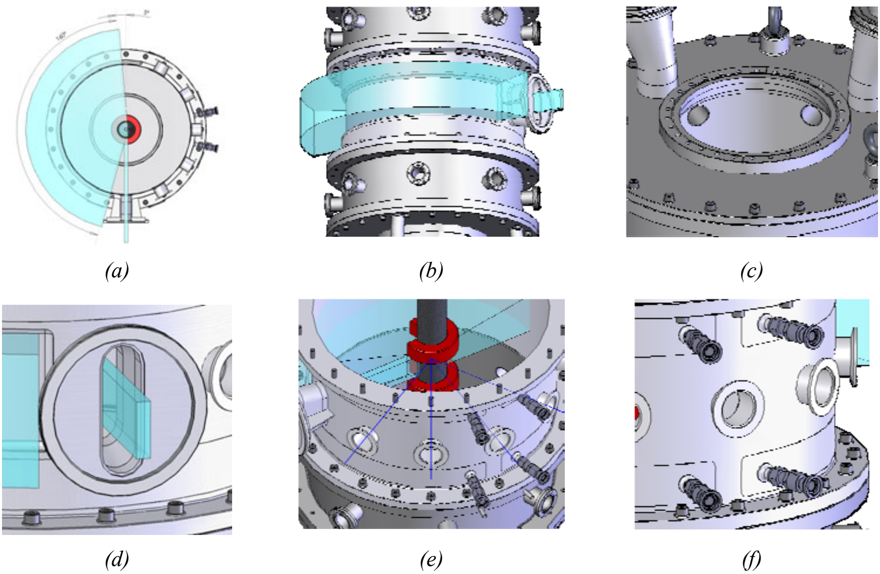

Figure 2. Features of the In-situ Reaction Chamber (ISRC).

With the equipment specific to neutron powder diffraction incorporated into the ISRC, customised environmental inserts can be developed with minimal restrictions on design and geometry, provided it conforms to standard dimensions (height, interface flange and volume of chamber). Production costs can be minimised as only the equipment necessary for a specific experiment is required, although the possibilities for multiple applications of the insert may justify substantial development. Careful design may even allow this development to occur in stages, spreading the cost over several experiments.
An example of a customised insert is the high temperature chamber (figure 3) being developed concurrently with the ISRC, which has the following attributes:

- **Radiative band heaters** mounted external to the sample environment (in the vacuum of the ISRC), above and below the beam height. These heaters allow very high temperatures to be reached accurately and repeatedly without contaminating (or being contaminated by) the sample environment or affecting the diffraction pattern.
- **Capacity for independent control** of heaters enables users to accurately control thermal gradients in the axial direction.
- **High thermal mass** of the environment tube assists in thermal stability. This is the only material other than the sample (and sample vessel) to be placed in beam.
- **Gas atmospheres** are possible with ports for gas flow in and out of chamber. Controlled circulation is achieved via a second internal tube located out of the beam path. Vacuum ports also allow a vacuum to be maintained within the sample environment if required.
- **Active cooling** of the sample port allows for the use of standard vacuum fittings, facilitating accurate sample alignment.

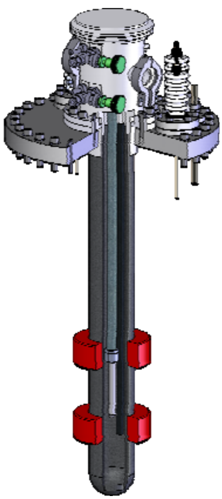

Figure 3. One specific insert device is the high temperature furnace shown here in section view. It has been designed for high temperature assessment of oxide ceramic materials (>1600°C) under partial oxidising or reducing atmospheres and is intended for use in the investigation of catalytic reactions, crystallographic phase transitions and structural integrity of oxide ceramics as a function of time.

- **Multiple feedthrough ports** to allow multiple instrument connections. For example, stationary control thermocouples can be positioned within environment chamber to aid in reproducibility, while sample thermocouples are mounted to the stalk.
- **Remote loading** of the sample is a possible future extension of the insert.

Discussion

Traditional methods of performing in-situ diffraction have been limited by the availability of customised reaction chambers. Cost has been a significant factor in limiting this development due to the unique design constraints of each reaction vessel. The present modular design of the ISRC deliberately separates the unique experimental aspects from the generic diffraction requirements; more specifically, customised inserts have been developed to meet the requirements of each reaction, which can then be placed into a diffraction specific chamber. Designed carefully, a single insert may be used on a variety of instruments.

An additional benefit of the modular technique is the ability to easily characterise each insert prior to use, minimising setup time and maximising the likelihood of a successful experiment. For time resolved studies in particular it is essential to minimise the effect of the environment chamber on the passage of the diffracting radiation. Customised inserts allow users to do this via methods most appropriate for their circumstances. Since process optimisation typically involves experimentation using multiple techniques, the ability to use a single, well characterised environment chamber can significantly reduce errors.

Concluding remarks

High time resolution in-situ diffraction is capable of providing a vital insight into the kinetics of materials processing. The information gathered by this technique can be applied to the optimisation of materials synthesis and the enhancement of operational performance.

Successful material development is dependent upon the quality of the sample environment, which must accurately simulate the conditions of the system under consideration. The feasibility of developing high quality sample environments is increased by separating the technology associated with particular diffraction techniques from the technology necessary for environment simulation.

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