Development of customised environmental chambers for time-resolved \textit{in situ} diffraction studies

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Abstract. In an effort to mitigate the expense and broaden the applicability of customised environment chambers, researchers at the University of Melbourne and the Australian Nuclear Science and Technology Organisation (ANSTO) have designed and are currently commissioning a modular reaction chamber, capable of separating the necessities of diffraction methodologies from those of the desired sample environment. The \textit{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. The first insert to be developed for use with the ISRC is a high temperature furnace capable of providing an oxidising sample environment up to 1600\textdegree C.

1. Introduction
Progress in many technological fields including energy production, aerospace and bio-medicine is increasingly dependent upon novel materials with exceptional properties. Often these materials are produced via complex and energy intensive processes, 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 and cost involved in process optimisation and validation by providing vital insight into process kinetics [1]. 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 [2].

Time-resolved \textit{in situ} diffraction is a particularly powerful technique in materials research, capable of observing the evolution of phases as they change in quantity and composition, and correlating these changes with processing parameters such as temperature, pressure and time [3]. The time resolution of an \textit{in situ} diffraction experiment is determined by the flux of radiation at the sample position and the speed at which detectors acquire the data. Modern position sensitive detector (PSD) technology has enabled diffraction pattern acquisition and readout times to be reduced on several high flux instruments (e.g. D20, GEM and WOMBAT), enabling diffraction studies of rapid material reactions and transformations with the same or better time resolutions as conventional methodologies [4]. Consequently time-resolved experiments can now generate extremely large data sets, with 10,000 diffraction patterns or more becoming common place. While quantitative analysis of data sets of this size (for information such as phase composition and reaction kinetics) has traditionally been laborious and time consuming,
new software packages with the ability to either sequentially refine patterns or simultaneously fit 2-dimensional data sets (i.e. Rietveld surface fits) have begun to make quantitative analysis of these data sets 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 the 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 to accurately simulate their system of interest and improve the quality of data obtained.

2. The In Situ Reaction Chamber

Researchers at the University of Melbourne in collaboration with ANSTO have designed, constructed and are currently commissioning 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 main chamber of the ISRC can be either evacuated or filled with helium. Additionally, the beam inlet window will allow for the fitting of a neutron guide. In general, the present design aims to maximise chamber diameter, as limited by the collimator and PSD, providing the largest sample volume, while minimising air-scatter.
- 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, which have been reduced to a constant minimum thickness over the full 160° range.
- 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.
- Concurrent experimentation can be used to gather complimentary 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.
- 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.
3. Customised environmental insert: The high temperature furnace

The first custom insert device to be developed for the ISRC is a high temperature furnace for the assessment of oxide ceramic materials (Figure 2). It has been designed to operate at temperatures up to 1600°C with partial oxidising or reducing atmospheres and is intended for use in the investigation of catalytic reactions, ceramic processing (sintering) and structural integrity of oxide ceramics as a function of time.

- 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.
- 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.

4. 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. This allows customised inserts can be developed to meet the requirements of each reaction, and then placed into a diffraction specific chamber via a standard interface. 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...
Figure 2. Section view of the high temperature furnace insert. It has been designed for an operating temperature of 1600°C under partial oxidising or reducing atmospheres. Note the sample cannister located between radiative band heaters.

Figure 3. Section view of the assembled ISRC and high temperature insert, illustrating passage of incident and diffracted beams.

diffracting radiation. Customised inserts allow users to do this via methods most appropriate for their circumstances, using only the equipment necessary for their experiment. Since process optimisation typically involves experimentation using multiple techniques, the ability to use a single, well characterised environment chamber multiple times can significantly reduce errors.

5. 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 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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