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A flow-through hydrothermal cell for in situ neutron diffraction studies of phase transformations

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Abstract

A flow-through hydrothermal cell for the in situ neutron diffraction study of crystallisation and phase transitions has been developed. It can be used for kinetic studies on materials that exhibit structural transformations under hydrothermal conditions. It is specifically designed for use on the medium-resolution powder diffractometer (MRPD) at ANSTO, Lucas Heights, Sydney. But it is planned to adapt the design for the Polaris beamline at ISIS and the new high-intensity powder diffractometer (Wombat) at the new Australian reactor Opal. The cell will operate in a flow-through mode over the temperature range from 25–300 °C and up to pressures of 100 bar. The first results of a successful transformation of pentlandite $(Fe,Ni)_9S_8$ to violarite $(Fe,Ni)_3S_4$ under mild conditions (pH~4) at 120 °C and 3 bar using in situ neutron diffraction measurements are presented.

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Keywords: Flow-through hydrothermal cell; X-ray and neutron diffraction; Phase transformations; Pentlandite; Violarite

1. Introduction

Diffusion processes at low to moderate temperatures (25–250 °C) are important in controlling the chemical, structural and physical properties of minerals and are also important in mineral processing. The kinetics and transformation mechanisms in inorganic compounds, such as metal sulphides and zeolites, are poorly understood. Therefore, new techniques for preparing these materials, understanding their properties and transformations are essential. The use of hydrothermal reaction methods in the laboratory that mimic the conditions of nature is an important approach to studying these reactions. We have developed a flow-though hydrothermal system for in situ neutron diffraction on the MRPD at ANSTO, Lucas Heights, Sydney. With minimal adaptations the cell will be can be used on the new high-intensity powder diffractometer, Wombat, on the new Opal reactor. The cell is based on the closed hydrothermal cell developed at Oxford and ISIS [1].

The design and fabrication of a low-temperature flow-through cell was a major part of a study on Fe–Ni sulphide mineralogy and more specifically the transformation of pentlandite, $(Fe,Ni)_9S_8$, to violarite, $FeNi_2S_4$. Pentlandite is the most important ore of nickel found in massive Ni–Fe sulphide ore bodies and violarite is commonly formed by the oxidation of pentlandite in the upper parts of the deposits due to the movement of hydrothermal fluids [2,3]. Understanding the thermodynamics and kinetics of the formation of violarite is important for unravelling the complex alteration process that occurs in ore bodies and could also improve ore processing. Since pentlandite and

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violarite both share a cubic close-packed S lattice, the mineral transformation can take place topotactically, but a dissolution–reprecipitation mechanism seems more likely [4]. The successful transformation of pentlandite to violarite under mild hydrothermal conditions is used to demonstrate the cell's performance. Results of the initial tests on the MRPD neutron beamline at ANSTO permit the assessment of the capabilities and limitations of the current cell design.

2. Instrument description

The experimental assembly is illustrated in Fig. 1. The cell is designed to operate in a flow-through configuration, so that the hydrothermal fluid can be recycled continuously through the cell using a micropump to drive the flow. This allows an increase in the volume of the fluid (mild acids) and at the same time greatly reduces the effects of any compositional changes to the fluid during the course of the reaction. However, due to the Teflon bearings in the micropump, the initial sets of experiments were undertaken at temperatures below 150 °C (pressure < 10 atm). A pressure relief system, consisting of a series of valves and an expansion tank, has been incorporated into the design for safety. Since the hydrothermal fluids are usually both mildly oxidising and acidic, the whole cell apparatus has been machined from thin, highly resistant stainless steel.

The cylindrical reaction vessel has an internal diameter of 19.4 mm and is 70 mm high with a 0.3 mm wall thickness (see the inset in Fig. 1). Neutrons can easily penetrate the thin-walled stainless steel vessel and its diffraction pattern can readily be accommodated in the Rietveld refinement procedures. However, in spite of the cell's low cost and adequate physical properties, it is planned to replace the actual sample vessel with one made from a null scattering Zr/Ti alloy as used at ISIS [1]. Two $\frac{1''}{4}$ diameter copper cartridge heaters are positioned in each of the two blocks at the ends of the reaction vessel. The fluid temperature is

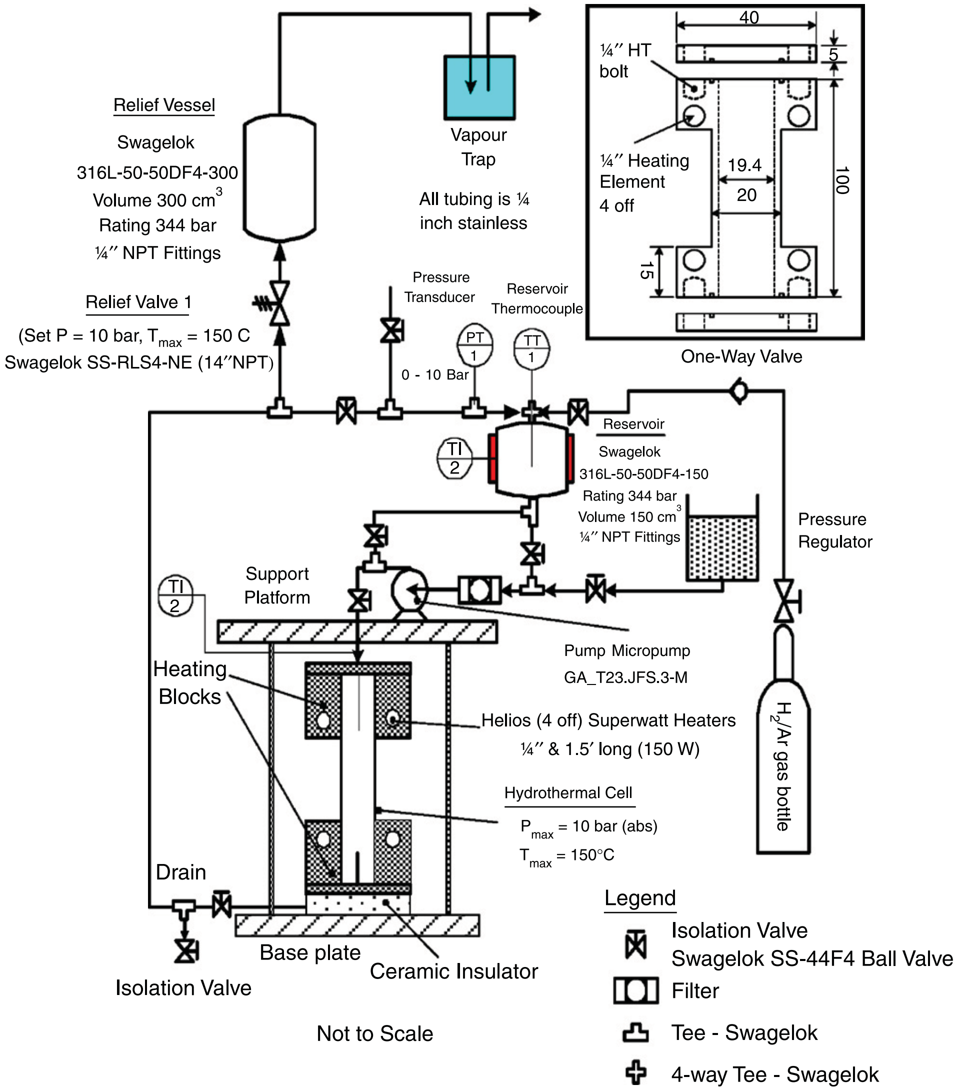

Fig. 1. Schematic description of the hydrothermal cell with the reaction vessel in inset (all dimensions in mm unless shown).

measured using a K-type thermocouple immersed in the reaction vessel. The removable upper and lower blocks are sealed onto the vessel by Viton O rings. A ceramic insulator, under the lower block and on the base plate, is used as a support for the cell. A 250 mm diameter 1 mm thick aluminium cylinder acts as a containment vessel for leaks.

The pumping circuit and reservoir unit are designed as a pressurised system. The pumping and reservoir circuit (see Fig. 1) is connected to the cell by two 1 m long hoses (in and out of the vessel). The circuit includes a 250 mL reservoir surrounded by a Helios heating jacket, a 5 μm stainless steel filter, a micropump (flow of 150 mL/min), a relief reservoir fitted with a relief valve set to open at a maximum pressure of 10 bar and a vapour trap filled with water. A small tank placed before the pump is used to fill in the whole system with the solution. All tubing is made from $\frac{1''}{4}$ stainless steel and connected with standard Swagelok fittings. The fluid temperature is controlled by a thermocouple inside the reservoir tank that drives the heating jacket surrounding it. A pressure transducer with a digital display is attached to the circuit. Drainage of the apparatus is achieved via a valve positioned at the base plate level. The hydrothermal cell also has an inlet allowing experimental work under specific gas atmosphere.

3. Experimental results

To test the hydrothermal cell efficiency and stability for in–situ neutron diffraction measurements on MRPD, successive tests were made using a number of reference samples including silicon to verify peak positions, shapes and intensities. The neutron diffraction pattern of stainless steel (type 316) consists of five main peaks at $d_{\text{spacings}}\sim1.04$, 1.08, 1.27, 1.80 and 2.08 Å and can be subtracted to give just the sample pattern. Due to the incoherent scattering of hydrogen, heavy water was used to make up the aqueous solutions. The deuterated water increases absorption and the background and thus lowers the overall quality of the diffraction patterns during in–situ operation.

Preliminary in–situ tests of the hydrothermal cell were performed at operating temperatures up to 120 °C with 4 h runs (2–138° 2θ, 0.1°/step, $\lambda = 1.6605$ Å) on natural violarite at four successive temperatures (25, 60, 90 and 120 °C). While increasing temperatures slightly reduce the overall peak intensities in the diffraction patterns, the thermal variation of the cell parameters could readily be followed showing that the stainless steel from the cell and sample holder could be used as an internal phase standard and proving the accuracy and thermal stability (±1 °C) of the cell.

The hydrothermal cell was successfully used in the transformation of natural and synthetic pentlandite into violarite. Preliminary X-ray diffraction measurements show that pentlandite progressively transforms to violarite at 120 °C in acid solution (pH~4) before seemingly stabilising after 2 or 3 days with pyrrhotite then transforming into pyrite. Around 4.6 g (~3.5 cm^3) of a synthetic pentlandite/pyrrhotite (27/73wt%) (grain size < 2 mm) that had been pre-exsolved from an $Fe_{0.8}Ni_{0.2}S$ mss [5] and annealed for a month at 350 °C was used to follow the transformation in situ. Dilute acetic acid solution (350 mL) with 98% D_2O (pH = 3.9) was introduced into the hydrothermal cell before heating up to 120 °C. Neutron diffraction patterns were then recorded every hour (using the same measurement conditions as above). Due to a relatively low peak intensity to background ratio and the slow reaction, normalised diffraction patterns were summed by sets of 10 runs before subtracting the vessel + holder contribution. Fig. 2 shows that the amount of

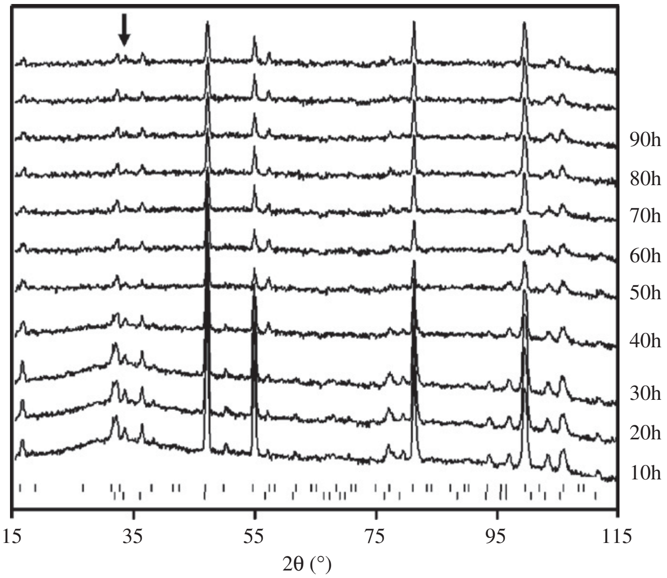

Fig. 2. In situ variation (bottom to top) of a pentlandite/pyrrhotite assemblage at 120 °C and 3 bar (see text for details). Bragg reflections are marked by vertical lines (pentlandite on top). The arrow indicates the violarite main reflection.

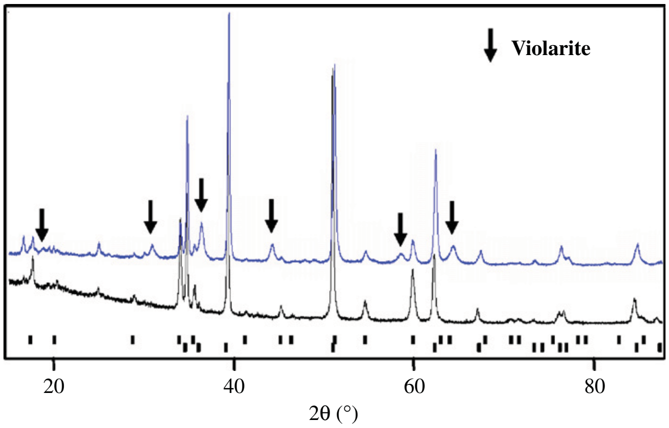

Fig. 3. Room temperature X-ray diffraction patterns of starting (bottom) and final (top) materials used in the in situ pentlandite to violarite transformation study. Bragg reflections are marked by vertical lines (first line is pentlandite).

pentlandite is greatly reduced over the first 2 days of the experiment. The overall proportion of pyrrhotite slightly decreases and a small peak at $2\theta{\sim}33.5^{\circ}$ ($d{\sim}2.86\,\text{Å}$) corresponding to the main reflection of violarite can be identified. X-ray diffraction measurements of both the starting and final materials were recorded using a Guinier camera ($\lambda_{\mathrm{CoK}\alpha 1} = 1.78892\,\text{Å}$) and confirm the success of the transformation (Fig. 3). Rietveld refinement performed on the X-ray data using Rietica software showed that only 12 wt% of the pentlandite remained after 4 days of the in situ experiment together with 67 wt% pyrrhotite and 21 wt% violarite had formed.

Thus, the pentlandite to violarite transformation has successfully demonstrated that the flow-through cell provides a means to study such reactions in situ. However, refinements to the apparatus design and specifically the reaction cell and sample holder configuration are needed to improve the peak to background ratios for better performance.

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