THE DESIGN AND APPLICATION OF A NEW BASSETT-TYPE DIAMOND ANVIL CELL FOR SPECTROSCOPIC ANALYSIS OF SUPERCRITICAL AQUEOUS SOLUTIONS

A.J. Anderson[1], P.R. Meredith[1], W.A. Bassett[2], R.A. Mayanovic[3] and C. Benmore[4]
[1] St. Francis Xavier University, Nova Scotia, B2G 2W5, Canada
[2] Cornell University, Ithaca, New York, 14853, USA
[3]Missouri State University, Springfield, Missouri, 65897, USA
[4]Argonne National Laboratory, Argonne, Illinois, 60439, USA

Abstract

The Bassett-type hydrothermal diamond anvil cell has been modified to facilitate direct x-ray and Raman spectroscopic analysis of aqueous solutions and/or coexisting solid samples at temperatures and pressures above the critical point of water. The new cell provides more sample-detector geometry options for x-ray micro beam analysis and the reduced size of the cell affords a smaller working distance (≥ 14 mm) required for better Raman spectroscopic analysis and microscopic inspection. A shallow recess (300 × 300 × 26.5 μm) milled into one of the diamond anvils is used instead of a metal gasket to contain the aqueous solution. These modifications significantly improve our ability to directly monitor the composition and structure of supercritical fluids and have eliminated the problem of contamination due to the reaction of a metal gasket with supercritical water. The use of the modified hydrothermal diamond anvil cell to characterize the MoO_3–H_2O system up to 500 ºC will be discussed.

1. Introduction

A quantitative understanding of the kinetics, thermodynamics and chemistry of aqueous systems at extreme radiation and temperature conditions is requisite for the successful deployment and long-term viability of supercritical water-cooled reactors. At present there is insufficient experimental data on high temperature (>350 ºC) aqueous systems to accurately predict and control water chemistry to minimize radionuclide transport and to reduce corrosion effects. Over the past decade, important advances in our ability to obtain high quality *in situ* x-ray spectroscopic data on aqueous systems at extreme conditions in hydrothermal diamond anvil cells has provided new insights into the physics and chemistry of hydrothermal solutions. A major advantage of the hydrothermal diamond anvil cell (HDAC) is the capacity to view a fluid and/or solid sample at high pressures and temperatures while collecting spectroscopic or x-ray diffraction data [1]. Although this capability has been utilised in previous studies [2,3], the current design of the Bassett-type HDAC is not optimised for simultaneous viewing and collection of x-ray fluorescence, x-ray absorption or x-ray scattering data. In this communication we describe a new HDAC designed to reduce the distance between the sample and the HDAC surface so that higher power objectives with smaller working distances can be used for Raman spectroscopic analysis, and to increase the angular range at which x-rays can enter and exit the fluid sample between the diamond anvils. The redesigned Bassett-type HDAC facilitates new experimental

configurations and eliminates gasket-related problems, such as spectral interferences and contamination caused by the reaction between the fluid and the gasket [4].

2. The Bassett-type diamond anvil cell

A detailed description of the HDAC is given in previous publications [5,6] and so only a brief explanation will be provided here. Bassett-type hydrothermal diamond anvil cells consist of two circular stainless steel platens with diamond anvils fitted into tungsten carbide seats at the centre of each platen. There are three guide posts in the lower platen that are positioned at 120º to one another. The posts are inserted into holes in the upper platen and a drive screw, adjacent to each guide post, is used to draw the diamond anvils together. A fluid and/or solid sample is enclosed within the hole of a thin (50 to 200 micrometer) metal gasket by compressing the gasket between two diamond anvil faces using the three drive screws.

The sample between the diamond anvils is normally viewed along the axis of compression using a microscope with a long working distance objective lens. X-rays may enter the sample chamber from a direction that is either parallel or normal to the axis of compression. However, for the latter, the beam-sample-detector geometry options are severely restricted by the placement of the three posts and three screws that surround the sample chamber. The metal gasket also obstructs x-rays conceals the sample from x-rays.

3. The redesigned hydrothermal diamond anvil cell

Three major modifications have been made to the HDAC to make the sample more accessible for *in situ* measurements during visual inspection. These are: 1) the reduction of the number of guide posts and screws from three to two, 2) the reduction of the overall size of the cell, and 3) the use of a milled recess in one of the diamond anvils to contain the sample, instead of a metal gasket. Figure 1 is a schematic diagram of the new diamond anvil cell. The new HDAC is 9.5 cm in length, 3.2 cm wide and 2.5 cm in height.

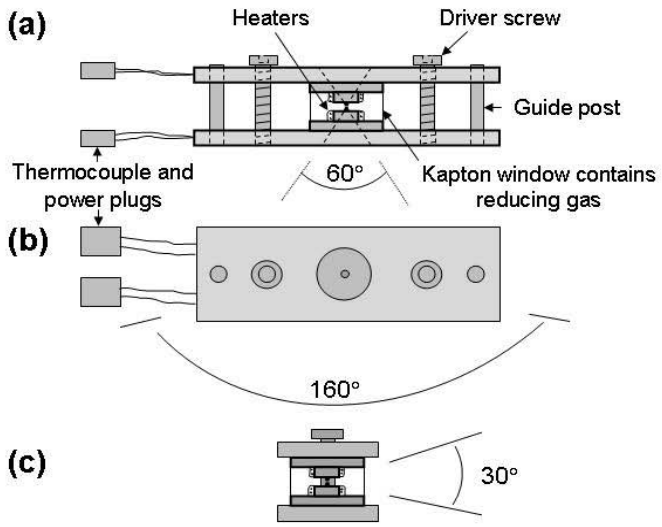

Figure 1 Schematic diagrams of the redesigned Hydrothermal Diamond Anvil Cell as viewed from the side (a), plan (b) and the end (c).

The diamond anvils are surrounded by a Kapton cylinder (2.54 cm in diameter) that is filled with a reducing gas which is introduced through a hole in the lower platen. The sample chamber is a small (<100 μm deep) recess in the lower diamond anvil. The recess is produced by using either a laser or a focussed ion beam (FIB) (Figure 2). The distance between the sample chamber and the surface of the upper platen is 14 mm, making it possible to safely use a 50 X objective lens (working distance 20.5 mm) while the cell is operating at high temperatures.

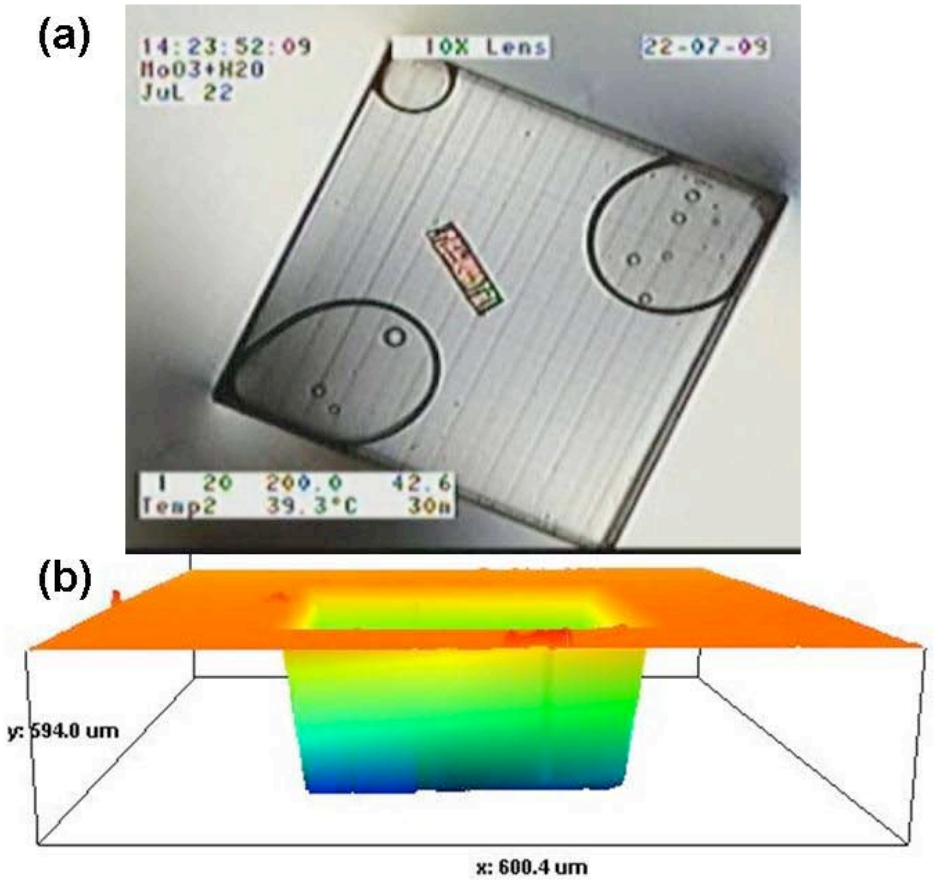

Figure 2 (a) Photograph of a FIB milled sample chamber (300 × 300 × 27 μm) containing a MoO_3 crystal (80 μm in length) and H_2O liquid and vapour bubbles at 40 ºC. (b) Map of sample chamber produced from surface profilometer measurements.

The minimum distance between the sample chamber and the edge of the platen is 1.6 cm, compared to 3.2 cm in the old HDAC. This reduced distance increases the vertical exit angle (i.e., parallel to the axis of compression) to 30 degrees which is sufficient for x-ray scattering measurements. Having two posts instead of three affords a 160º opening in the horizontal plane on both sides of the guide posts.

4. Applications

Most spectroscopic analyses benefit from the large solid angles afforded by the new design of HDAC. Signal strength of emitted radiation is enhanced; the range of angles that can be utilized in x-ray

diffraction is significantly increased. These permit better statistical treatment of data. Access to the sample from several different directions offers greater versatility for techniques in which geometry plays an important role. These advantages allow faster and more accurate data collection when applied to techniques like those described in this paper.

4.1 Synchrotron x-ray fluorescence analysis

In order to reduce the scattering background, which is always present in fluorescence spectra, the detector should be placed at 90º to the incident x-ray beam [7]. This sample-detector-geometry can be easily achieved when the incident beam is either parallel to or normal to the axis of compression. Figure 3 shows a XRF spectrum obtained from a standard solution (500 µg/mL Mo) using an incident x-ray energy of 22 keV. The minimum detection limit (mdl) for Mo is 1 ppm.

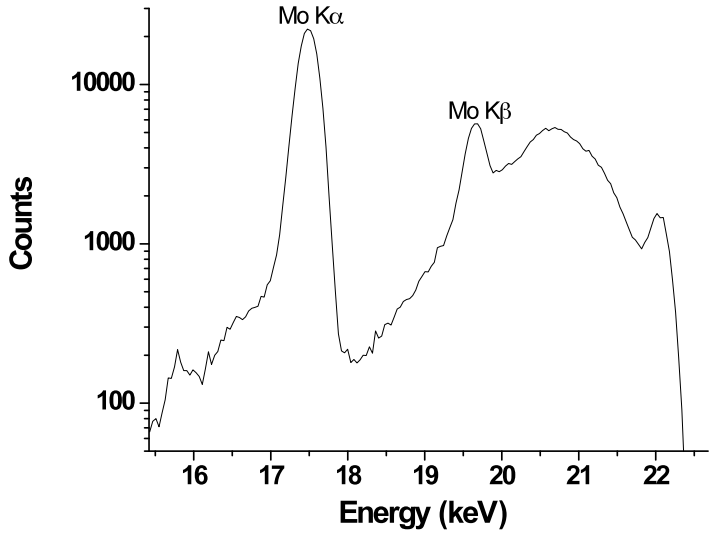

Figure 3 X-ray fluorescence spectrum of a standard aqueous solution (500 µg/mL Mo) in the sample chamber of the new HDAC

4.2 X-ray absorption spectroscopy (XAS)

The HDAC may be used for *in situ* XAS measurements of samples in either fluorescence or transmission mode [6]. The reduced dimensions typically cause fewer restrictions in the positioning of the redesigned cell relative to the x-ray beam, the x-ray optics and instrumentation of a beam line. Transmission-mode XAS measurements, where the x-rays enter the sample chamber along a normal to the axis of compression, are more accessible using the redesigned HDAC due to fewer posts and screws and a lack of gasket. The reduced platen size, hidden wiring, fewer posts and screws and a lack of gasket significantly reduce background noise from stray radiation in the measurement of fluorescence XAS from samples in the redesigned HDAC. This is particularly advantageous for optimization of signal-to-noise statistics during measurement of fluorescence XAS from very dilute samples (i.e., a few ppm of target element). The use of an imaging microscope and fluorescent diamonds that reveal the path of the x-ray beam greatly facilitates positioning and orienting of the new

cell for optimum data collection. This is especially valuable when the x-ray beam is incident along a direction normal to the axis of compression where omission of the gasket provides greater visibility. Figure 4 shows the XANES portion of Mo *K*-edge XAS spectra measured from Mo oxide particles, varying in size from nanometers to a few micrometers in their maximum dimension, in H_2O at temperatures ranging from 300 to 500 °C.

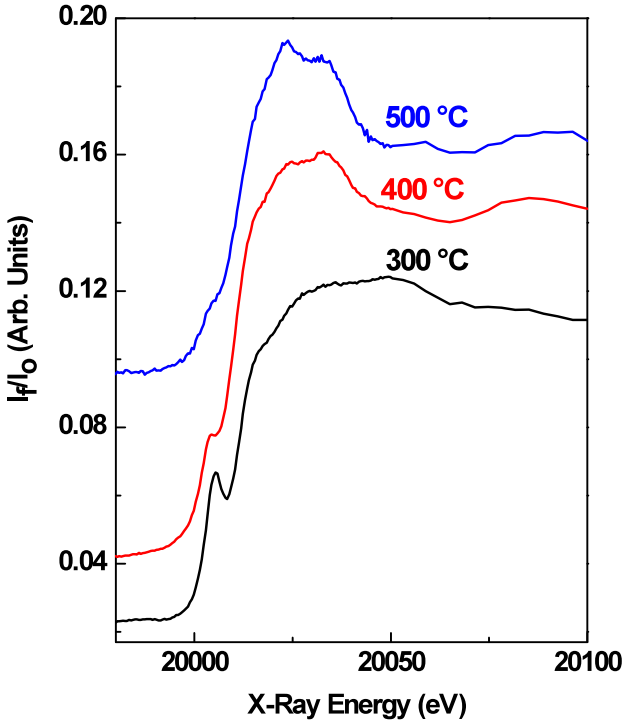

Figure 4 The XANES portion of the Mo K-edge XAS spectra of Mo oxide particles in H_2O at 300, 400 and 500 ºC.

4.3 High energy x-ray diffraction

High-energy diffraction can be used to directly probe the local atomic and nanometer range structure of aqueous solutions within the HDAC. Figure 5 shows a plot of x-ray intensity versus momentum transfer, Q, obtained from NaCl powder within the sample chamber of a milled diamond anvil. The measurements were performed in transmission mode using an incident energy of 115 keV, thereby minimizing geometrical, attenuation, and multiple scattering effects. The large solid angle (30 degrees) on the side of the new cell (Figure 1c) is more than sufficient to acquire the intensity over a wide Q-range (0.5 to 30$Å^{-1}$), a prerequisite for performing an accurate Pair Distribution Function (PDF) analysis [8]. This feature, combined with the use of a large area amorphous-silicon flat detector, will be important in time resolved studies involving phase changes. In this geometry the main contribution to the background signal is from the Compton scattering from the diamond and individual single crystal Bragg peaks (typically from the 004 and 220 family) can be removed in the data reduction software. The resulting PDF describes the average structure of the fluid and will contain information on bond distances and local coordination numbers, providing a rigorous test of any theoretical structural model.

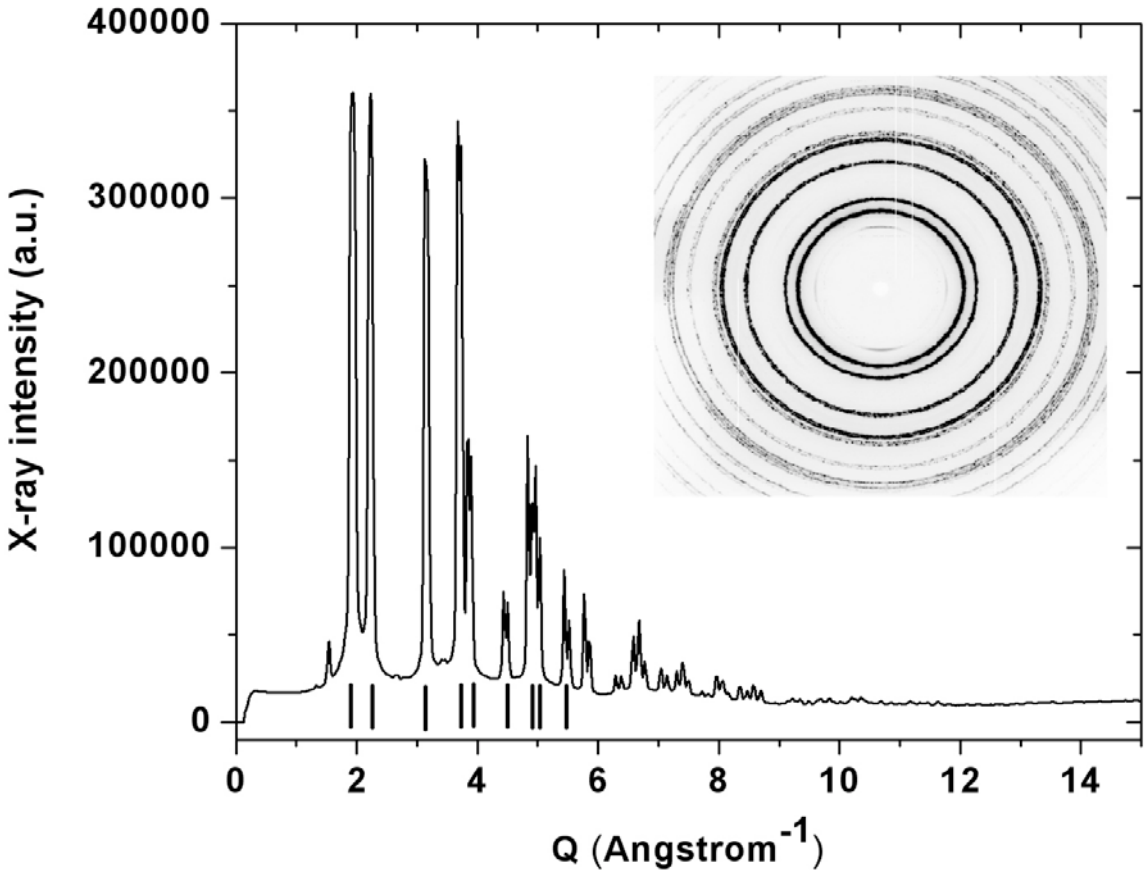

Figure 5 A two dimensional contour plot from the image-plate detector (inset figure) and the x-ray signal versus momentum transfer, Q. The data are from NaCl powder within the recess of a diamond anvil. The NaCl crystal structure peaks are marked as lines.

5. Additional advantages

The binding of the guide posts to the upper platen is a common problem encountered when operating the original HDAC at high temperatures. In the new HDAC, a Kapton cylinder helps insulate the posts from the heat generated from the resistive heating wires wound around the tungsten carbide seats. This modification ensures that the temperature of posts does not exceed 90 ºC when the sample is heated to 800 ºC.

6. Conclusions

The new HDAC described in this communication improves our ability to visually monitor a sample while collecting high quality spectroscopic or x-ray diffraction data at extreme conditions. The recognition of phase changes, which may occur in response to changing temperature and pressure conditions or from exposure to synchrotron radiation, is useful for interpreting the spectral and diffraction data obtained.

7. Acknowledgments

A.J.A. and P.R.M. were supported from an NSERC Discovery Grant and an NSERC CRD grant. W.A.B. and R.A.M. were supported as part of the EFree, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001057. The PNC/XOR facilities at the Advanced Photon Source, and research at these facilities, are supported by the US Department of Energy - Basic Energy Sciences, a Major Resources Support grant from NSERC, the University of Washington, Simon Fraser University and the Advanced Photon Source. Use of the Advanced Photon Source is also supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357.

8. References

[1] W.A. Bassett, "Diamond anvil cell, 50th birthday", *High Pressure Research*, Vol. 29, No. 2, 2009, pp.163-186.

[2] A.J. Anderson, S. Jayanetti, R.A. Mayanovic, W.A. Bassett, and I-M. Chou, "X-ray spectroscopic investigations of fluids in the hydrothermal diamond anvil cell: the hydration structure of aqueous La^{3+} up to 300 ºC and 1600 bars", *American Mineralogist*, Vol. 87, 2002, pp. 262-268.

[3] R.A. Mayanovic, A.J. Anderson, W.A. Bassett, and I-M. Chou, "On the formation and structure of rare-earth element complexes in aqueous solutions under hydrothermal conditions with new data on gadolinium aqua and chloro complexes", *Chemical Geology*, Vol. 239, 2007, pp. 266-283.

[4] I-M. Chou and A.J. Anderson, "Diamond dissolution and the production of methane and other carbon-bearing species in hydrothermal diamond-anvil cells", *Geochimica et Cosmochimica Acta*, Vol. 73, 2009, pp. 6360-6366.

[5] W.A. Bassett, A.H. Shen, M. Bucknum, and I-M. Chou, "A new diamond anvil cell for hydrothermal studies to 2.5 GPa, and -190 to 1200 ºC", *Review of Scientific Instruments*, Vol. 64, 1993, pp. 2340-2345.

[6] W.A. Bassett, A.J. Anderson, R.A. Mayanovic, and I-M. Chou, "Modified hydrothermal diamond anvil cells for XAFS analyses of elements with low energy absorption edges in aqueous solutions at sub- and supercritical conditions", *Zeitschrift für* Kristallographie, Vol. 215, 2000, pp. 711-717.

[7] M. Haller, and A. Knöchel, "X-ray fluorescence analysis using synchrotron radiation (SYXRF)", *Journal of Trace and Microprobe Techniques*, Vol. 14(3), 1996, pp. 461-488.

[8] H.F. Poulsen, J. Neuefeind, H.-B. Neumann, J.R. Schneider, and M.D. Zeidler, "Amorphous silica studied by high energy X-ray diffraction", *Journal of Non-Crystalline Solids*, Vol. 188, 1995, pp. 63-74.