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Pressure Composition Temperature Curves of Hydride Moderators

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Background

Microreactors are compact and mobile reactors which operate at low power and high temperatures. These reactors generate heat which is then converted to electricity for use in a variety of special purpose applications. Microreactors are of interest due to their light weight, compact size and the ability to meet the needs for high energy in difficult or remote areas. Metal hydrides have been studied for nuclear and aviation applications [1,14]. The emergence of microreactors the interest in metal hydrides is significant due to their ability to moderate neutrons in a light weight and solid form [2,3]. In case of an off normal event, more accurate data is needed for the absorption/desorption rates of the hydrides due to the high uncertainties on hydrogen redistribution in the moderator. The literature shows considerable discrepancies in the PCT curves for yttrium and zirconium. The uncertainty is much more notable at higher stoichiometries of the hydride phase at high temperature. To understand the in-pile performance, a detailed understating of the impurities and microstructure is needed.

Yttrium has been determined to be an excellent high temperature moderator for advanced thermal neutron reactors due to its high hydrogen retention at high temperatures [4]. Yttrium is also considered for such applications due to low neutron absorption cross section and high neutron scattering cross section [5,6]. Metal hydrides are considered for use in thermal reactors, because the core weight and volume must be carefully considered and minimized for operation. In such reactors, metal hydrides can serve multiple purposes, as moderators or shielding materials; however, the focus of this work will be on moderator applications. ZrH_{2-x} and YH_{2-x}, are considered to be the most promising moderating materials due to their high hydrogen density [3].

Since retention of hydrogen in these compounds is imperative for proper operation of the reactor, the thermodynamic properties, such as the absorption/desorption and diffusion kinetics, as well as equilibrium properties, such as the Pressure Composition Temperature (PCT) curves at elevated temperature are needed [7]. One of the best approaches to study the thermodynamic properties and to reach a conclusion on the partial phase diagram is to perform accurate measurements of the PCT curves [8,9]. The PCT curve is significantly influenced by even small impurities in the hydride being tested which strongly affects the results[7,10]. Impurities are found in both the gas (e.g. nitrogen and oxygen) and the feedstock metal [10]. This leads to large uncertainties encountered in literature for the thermodynamic properties and the phase equilibrium [10,11,12] because the purities tested in these studies is often not fully described.

Hydrogen can dissipate energy from neutrons due to its high scattering cross section. To use this effectively in reactor, a lower partial pressure of hydrogen is desirable in a moderator for slowing down neutrons. The purity of the sample is expected to influence how much hydrogen can be absorbed into the sample. Similarly, alloys are expected to influence properties such as absorption/desorption kinetics and thermal stability.

For this reason, this study investigates alloys of yttrium and the effect of impurities on the thermodynamic and phase equilibrium data of Y-H systems by using PCT measurements. The samples of interest are of high purity as well as samples with trace impurities of Zr and Ta and a Y5Wt%Cr. The addition of trace impurities will allow us to observe the effects on the thermodynamic and PCI measurements and provide insight into the behavior of these materials. The measurements are carried out in a Sieverts apparatus with 99.99% pure hydrogen and a Pd membrane filter.

Instrument description

The Sieverts shown in Figure 1a uses a conflat-to-VCR fitting to seal the testing material in a high vacuum. Samples in the form of disks, 10mm diameter and 2.5mm in thickness, are used in the experiment. The instrument is made of SS tube consisting of three pressure sensors ranging from 0.01 to 100 torr. The system also uses an expansion volume of 55 cc to provide a wider range of pressure and volume for the system. The sample sits on a boat made from molybdenum foil 0.005” thick with a layer of tungsten mesh to prevent reactions and ensure the sample in the boat is exposed to adequate hydrogen flow. This is contained in an Inconel vessel. Inconel is initially used in lower temperature experiments due to its superior mechanical performance and resistance to hydrogen diffusion below 750 °C. The sample tubes were then switched from Inconel to quartz, at 800 °C and beyond, as quartz has a much lower hydrogen leakage at higher temperatures (Figure 2a,2b).

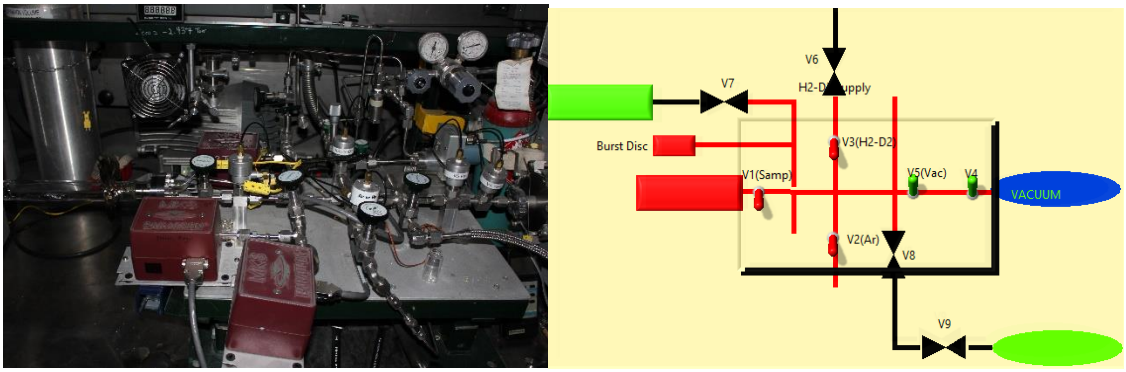

Figure (1a) Sieverts apparatus (1b) schematic of Sieverts in LabView

The system is controlled and automated with LabVIEW, which provides a range of choices in data acquisition and unattended experimentation. Figure 1b shows the setup of the Sieverts in the LabVIEW system, consisting of three pneumatic valves that power on/off to operate the Sieverts. The script controls the valves that allows us to cycle through in a manner to introduce hydrogen and monitor the pressure and temperature. The Sieverts is divided into two sections: Left and Right sides. The left and the right sides are identical and were created to perform two measurements simultaneously. Currently only the left side is being used due to the limited number of pressure sensors for the desired pressure range; however, there is a continuing effort to bring the right side online for future experiments.

Experimental method

The sample is cleaned with ScotchBrite to minimize the amount of any existing surface oxide immediately before the test, wiped with ethanol, and then placed in an Inconel or a quartz tube approximately 1" diameter and 10" in length. Thermocouples are attached to the inside of the vessel to measure temperature at two different locations. The vessel containing the sample is then attached to the Sieverts, and evacuation of the vessel is initiated. The vessel is left under vacuum for two to three hours to reach a desired pressure (typically 10^{-8} Torr). Once the vessel reaches this pressure, a furnace is used to heat it overnight, which allows moisture in the vessel to be removed. Once the moisture removal step is complete, data recording can begin, and the LabView script is initiated. The initiation of the script causes the pneumatic valves to open and close in an order to deliver pressurized hydrogen to the sample and wait for the system to reach equilibrium. To ensure equilibrium has been achieved, and to move from one cycle to the next, the change in slope of the pressure drop is observed. When the slope reaches the specified constant rate of change, the system waits 10 minutes before initiating the next cycle. The slope is the pressure drop caused by gas expansion into large volume (sample can) and the absorption of hydrogen by the heated sample, as the aliquot of hydrogen is introduced to the sample. The rate of change of pressure drop is observed to determine when equilibrium has been reached.

The samples tested consisted of pure yttrium and yttrium 5wt% chrome. Chrome was added to yttrium by arc melting to study the impact of impurities on the PCT curves. A detailed chemical analysis of these materials is in progress to determine the exact chrome ratio, so 5 wt% should be considered an estimate.

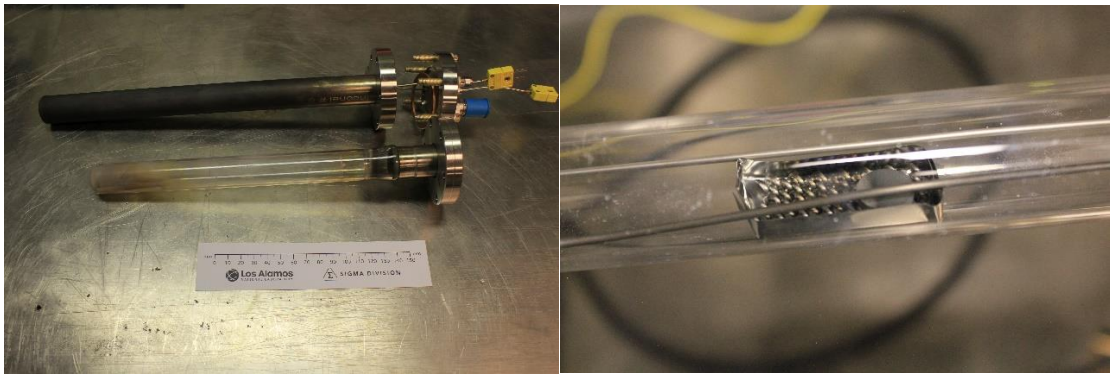

Figure 2: The picture on the left(2a) shows the images of the Inconel and the quartz vessels used for sample when being dosed with hydrogen gas at temperature. The right figure (2b) shows the sample in the Mo boat with W foil for support inside the quartz tube after the experiment.

To determine the optimal size for the sample, a 1D diffusion model was used [10, Eq. 5.22]. For example, during the shake-down tests of the experiment, 10x10mm cylinders were used. Figures 3 and 4 show the estimated amount of time required for hydrogen to reach the center of the sample at high stoichiometry. Due to the large amount of time required for diffusion in thick samples, the samples were reduced to 2.5mm to decrease the time to achieve equilibrium.

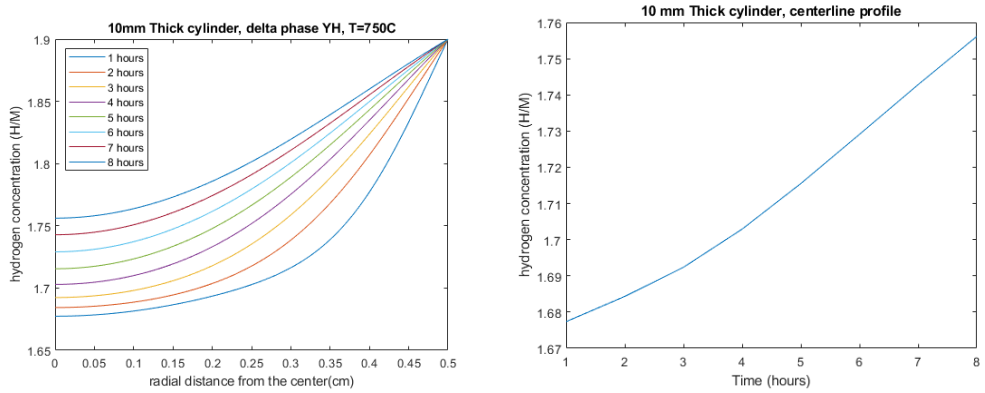

Figure 3: Centerline hydrogen concentration vs radial position (left) and time (right) for 10 mm high cylinders.

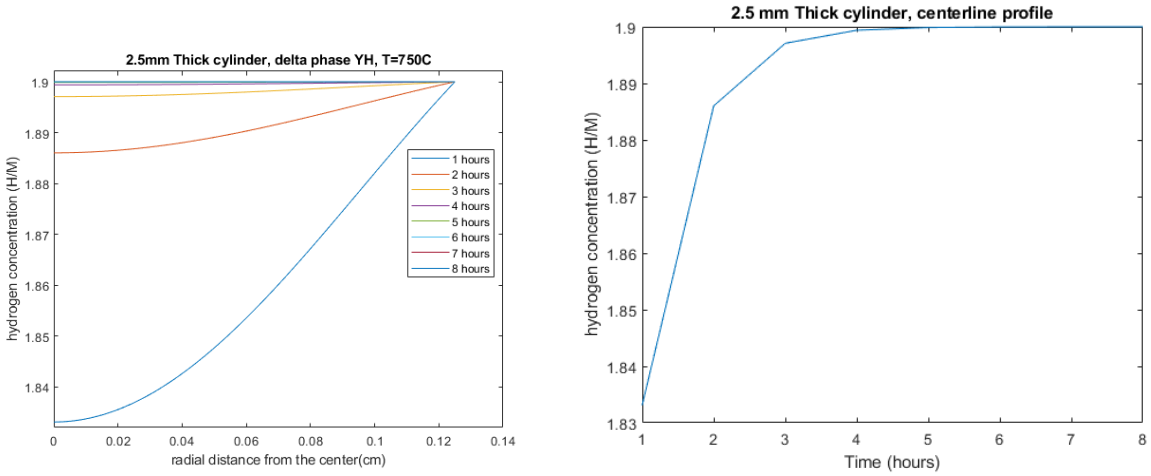

Figure 4: Centerline hydrogen concentration vs radial position (right) and vs time (right) for 2.5 mm high cylinders.

Leak checks were performed on the current setup with Inconel at 750 °C, 800 °C, and 850 °C, and for empty quartz tubes at 850 °C. To perform the leak check, the tube was heated to the desired temperature and then left under vacuum until the pressure inside reached 10^{-8} torr. A 45 Torr aliquot of hydrogen was then introduced to the heated tube and left until the slope constant, the derivative of the slope (0.63 Torr/ms), was reached. Hydrogen leakage was undetectable at room temperature in the Inconel vessel. At 750 °C the leak is determined to be 1 Torr per cycle (0.26Torr/hour), and at 800 °C, 10 Torr of pressure (0.35 Torr/hour) is lost at the end of each cycle. The leakage will be of significance at 800 °C if the cycle time is longer than two hours. but in this case the leakage can be disregarded due to the hydrogen absorption speed of the samples. At 850 °C the difference is much more noticeable and may be of concern when performing experiments, as shown by longer cycle times and a drop in pressure over time. The quartz tube performed extremely well with little to no release of hydrogen from the vessel; therefore, no PCT measurements were performed in Inconel above 800 °C.

Results and discussion

The following plots represent the PCT curves for yttrium and a nominal yttrium 5wt% chromium (Y5wt%Cr). Comparison of literature and experimental data for yttrium shows good agreement. As seen in Figure 5, the experimental partial pressure of hydrogen is lower at the plateau than what is seen in literature, with a difference of approximately 2 Pa at 750 °C and approximately 14 Pa at 800 °C and 850 °C [7]. Measurements were conducted multiple times until two successful runs were established at the same temperatures to determine the repeatability of the plots.

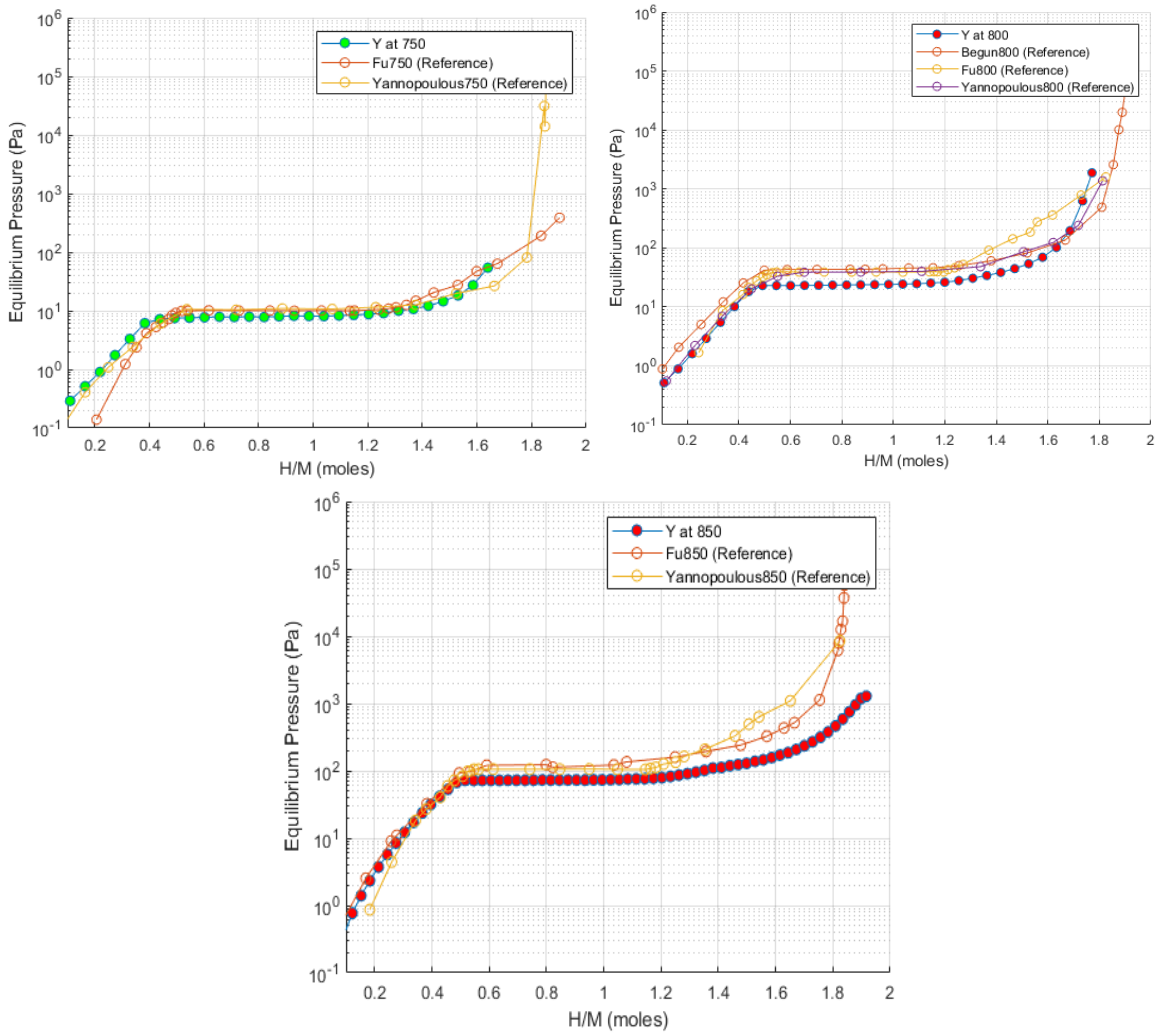

Figure 5: Yttrium PCT measurements at 750 °, 800 °, and 850 °C compared with values from Fu et al [7] ,Begun et al [10], and Yannopoulos [11].

Due to the lack of literature on the YCr alloy, the data is compared with yttrium experimental data produced in this work to observe the difference (Figure 6). A total of four

temperatures have been tested (750, 800, 850, and 900 °C). As seen in the plot, at 840 °C one of the experiments reaches a plateau and never increases. Though the data is curious, it should be considered anomalous while possible causes for this are investigated. The data is only included here for reference. New testing is underway to determine the repeatability of data at 840 °C. Comparing the data for YCr at 850 °C and the Y 840 °C data, the plateau pressure for YCr is seen to be slightly higher.

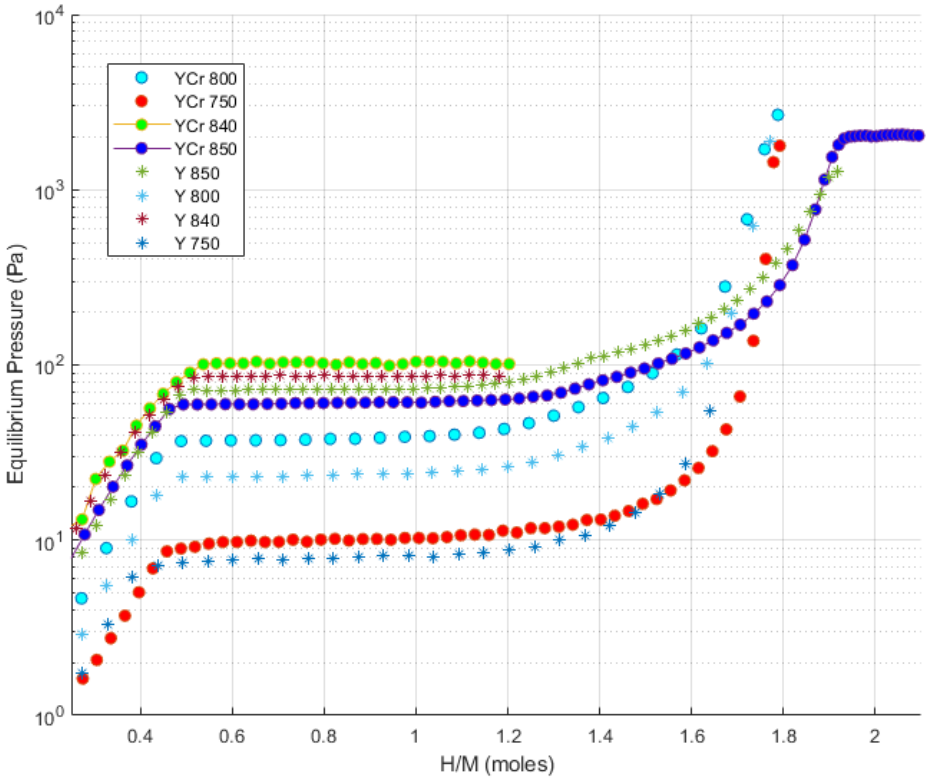

Figure 6: YCr at 750, 800, and 850 °C for Y and Y 5wt% Cr.

Hydrogen analysis

LECO hydrogen analysis was performed on two hydride samples to determine the hydrogen, nitrogen, and oxygen contents of the samples, (Table 1). The measurement shows hydrogen content of approximately 1.8wt% and 2.05wt% for two of the Y 5wt% Cr samples with a low standerd deviation. The hydrogen content also was measured by directly measuring the sample before and after hydriding, m_f and m_h respectivey. By dividing the final weight by the initial weight, we are then able to deterine the weight gain due to hydrogen absorption. The differences between LECO and direct weight measuring methods were negligable. In the future, more samples will be analyzed using LECO, as it also provides oxygen and nitrogen content in the samples. Although the nitrogen content was small, the oxygen content was high. Initial studies suggest oxidation and nitridation are possible when samples are left in an open environment after the PCT measurement.

To determine if oxygen and nitrogen pickup is possible in hydrided samples, samples placed in a vacuum environment after removing from the Sieverts will be compared with air exposed samples.

Table 1: LECO testing for YCr samples

Type	O	N	H
813(1)	0.35±0.011%	0.05±0.01%	1.80±0.004%
813(2)	0.33±0.011%	0.04±0.01%	1.81±0.004%
814(1)	0.04±0.012%	0.28±0.03%	2.05±0.04%
814(2)	0.35±0.012%	0.03±0.03%	2.04±0.04%

Kinetics

Figure 7 shows the time taken to absorb the hydrogen to reach the H/M. Each point on the plot represents the equilibrium hydrogen absorption for a cycle and the time required to reach that H/M. The measurements were conducted at 750, 800, and 850 °C for Y and YCr. When comparing the absorption for different yttrium alloys, it can be observed that the shape of the curve is similar for each temperature. The average absorption time for each cycle was 32 minutes, but some cycles required a longer time to be absorbed. This large discrepancy in absorption is observed mainly at higher stoichiometries. This is expected because the hydrogen surface reaction rate and hydrogen diffusion rate decrease as the alloy becomes hydrogen saturated. Desorption efforts have begun and are expected to produce a full desorption plot soon. Additional analysis of this data is in progress and expected to provide additional information.

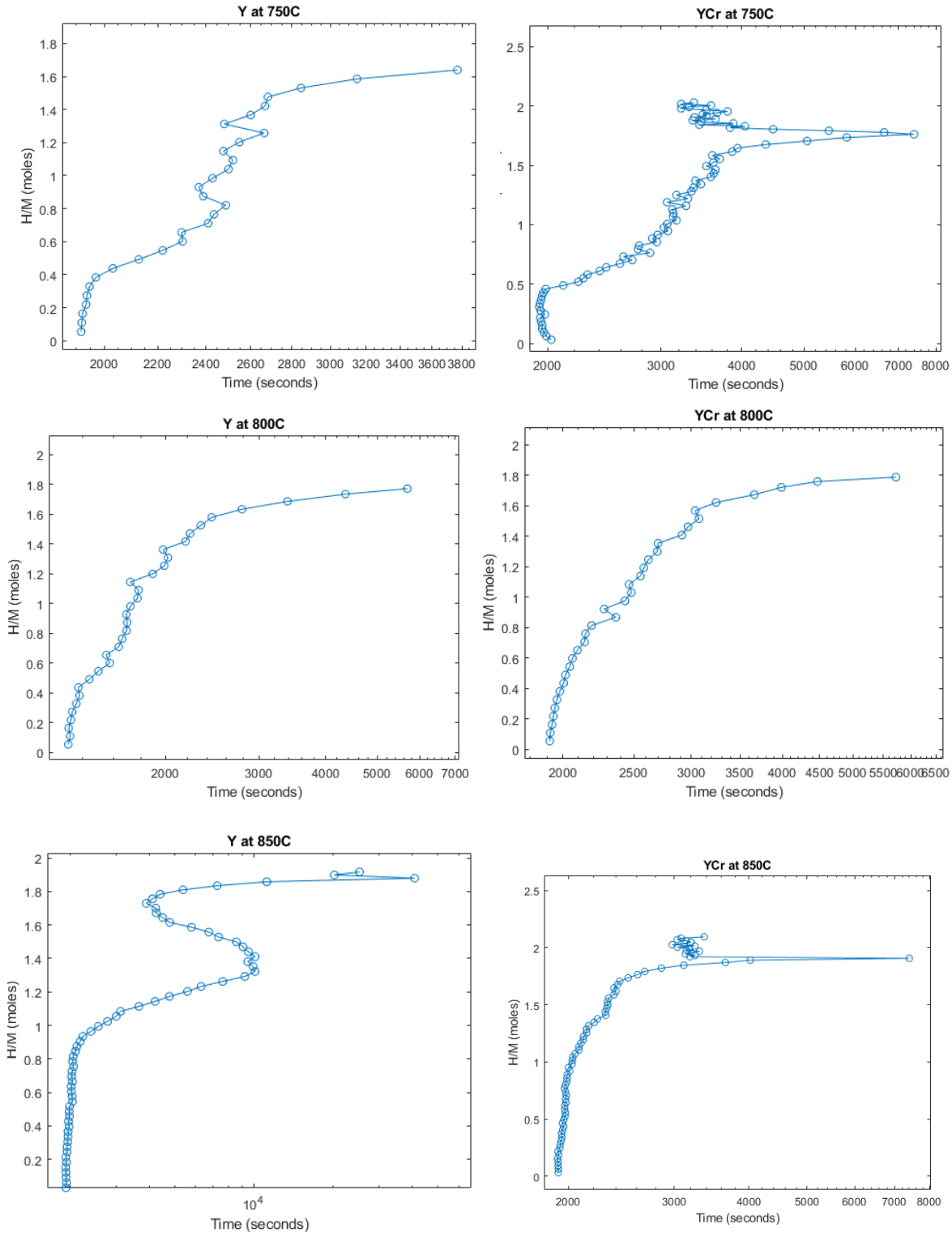

Figure 7: Absorption of hydrogen in Y and YCr at 750, 800, and 850 °C.

Conclusions/future work

Multiple measurements for the absorption and the PCT have been performed on Y and YCr samples. The measurements were performed at 750 and 800 °C using an Inconel vessel and switched to a quartz vessel at 850 °C. This data will be expanded to include measurements at 900 °C. The results show that relatively small alloying additions of chromium can affect the hydrogen absorption behavior, leading to differences in the equilibrium pressures at the same temperature. If the sample has high purity, then it is expected to absorb more hydrogen compared to a sample with impurities.

To use moderators effectively in a reactor, a lower equilibrium pressure, as encountered in pure yttrium, is desirable for moderating neutrons. In the case of YCr, a higher equilibrium pressure is obtained, when compared to yttrium. More information is needed to study the diffusion behavior of hydrogen in these samples, as retaining hydrogen at higher temperatures is the key to higher efficiency. Alloys and samples with different impurities should be tested to develop a moderator with higher hydrogen absorption capability than pure yttrium for better neutron moderation.

The next steps in this work are to continue producing PCT curves at higher temperatures with additional alloys and to expand the results of the kinetics experiments. Reaction rate data was generated during these experiments, which will be analyzed and presented. Efforts are under way to produce additional samples to observe the effects of size and volume on the behavior of kinetics. The chemical results of the samples to observe the trace elements present in the samples are expected in April. Y/Ta and Y/Zr ingots are being processed to fabricate samples for PCT measurements. PCT measurements on such samples are expected to begin in April.

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