Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

Disclaimer:

THE ABSORPTION OF HYDROGEN ON LOW PRESSURE HYDRIDE MATERIALS

Gregg A. Morgan, Jr. and Paul S. Korinko
Savannah River National Laboratory
Aiken, SC 29808

ABSTRACT

For this study, hydrogen getter materials (Zircaloy-4 and pure zirconium) that have a high affinity for hydrogen (and low overpressure) have been investigated to determine the hydrogen equilibrium pressure on Zircaloy-4 and pure zirconium. These materials, as with most getter materials, offered significant challenges to overcome given the low hydrogen equilibrium pressure for the temperature range of interest. Hydrogen-zirconium data exists for pure zirconium at 500°C and the corresponding hydrogen overpressure is roughly 0.01 torr. This manuscript presents the results of the equilibrium pressures for the absorption and desorption of hydrogen on zirconium materials at temperatures ranging from 400°C to 600°C. The equilibrium pressures in this temperature region range from 150 mtorr at 600°C to less than 0.1 mtorr at 400°C. It has been shown that the Zircaloy-4 and zirconium samples are extremely prone to surface oxidation prior to and during heating. This oxidation precludes the hydrogen uptake, and therefore samples must be heated under a minimum vacuum of 5×10^{-6} torr. In addition, the Zircaloy-4 samples should be heated at a sufficiently low rate to maintain the system pressure below 0.5 mtorr since an increase in pressure above 0.5 mtorr could possibly hinder the H_2 absorption kinetics due to surface contamination. The results of this study and the details of the testing protocol will be discussed.

INTRODUCTION

The capture, storage, and release of hydrogen and hydrogen isotopes are important features for safe implementation of the hydrogen economy. Sample preparation methods, testing methods, and data on the behavior of hydrogen getter materials (metals and intermetallic compounds) are of particular interest for additional research and development. Zirconium and its alloys are important materials for technological applications in the field of energy production, in particular as hydrogen storage materials[1], as well as in the nuclear industry as hydrogen getter materials[2]. Given that the equilibrium pressure of zirconium is < 0.1 mtorr at 400°C, zirconium and its alloys are well suited for getter materials instead of reversible hydrogen storage materials. Zirconium can be loaded to a Q/M (where Q is the moles of H, D, or T and M is the moles of metal atoms) to 2.0, which corresponds to a weight percent of roughly 2.2%. The reaction of hydrogen with Zr at its surface, e.g. chemisorption or transport of hydrogen atoms from the surface to the bulk determines the H_2 absorption, which is of importance in H_2 storage applications. The zirconium-hydrogen system has been extensively studied by a variety of techniques over the years[1-10]. However, very little information is currently available regarding the equilibrium pressures of the H_2 isotopes adsorbed on zirconium or its alloys at low temperatures (i.e. 300°C – 500°C).

Hydrogen gettering materials (Zircaloy-4 and pure zirconium) with exceptionally high affinity for hydrogen (and low overpressure) have recently been investigated to determine the hydrogen equilibrium pressure on Zircaloy-4 and pure zirconium. The primary objective of this work was to determine the equilibrium pressure-composition-temperature data for the absorption and desorption of protium and deuterium on Zircaloy-4 and pure zirconium. Protium-zirconium hydride data exist for temperatures in excess of 500°C, and at a temperature of 500°C correspond to a pressure of roughly 10 mtorr[11]. The equilibrium pressure for the absorption and desorption of protium on Zircaloy-4 at temperatures ranging from 400°C to 600°C have been determined. The absorption equilibrium pressures in this temperature region range from 150 mtorr at 600°C to less than 0.1 mtorr at 400°C. As a result of this study, it has been determined that the Zircaloy-4 and zirconium samples are extremely prone to surface oxidation, which inhibits the hydrogen uptake, and therefore must be heated under a minimum vacuum of 5×10^{-6} torr. In addition, the Zircaloy-4 samples should be heated at a rate of 5°C per minute in order to maintain the system pressure below 0.5 mtorr. An increase in pressure above 0.5 mtorr will hinder the H_2 absorption kinetics due to surface contamination.

EXPERIMENTAL

Two different gas handling manifolds were used to complete the experiments reported here, Manifold I and Manifold II. The two manifolds are shown in Figure 1 and Figure 2, respectively. Both manifolds consist of a series of valves, stainless steel tubing, calibrated volumes, and pressure transducers. Both gas handling manifolds are evacuated and maintained at the high vacuum range (1×10^{-7} torr). Manifold I is equipped with an Alcatel Drytel 31 vacuum pump and Manifold II is equipped with a Pfeiffer turbomolecular pump back by a Varian tri-scroll vacuum pump.

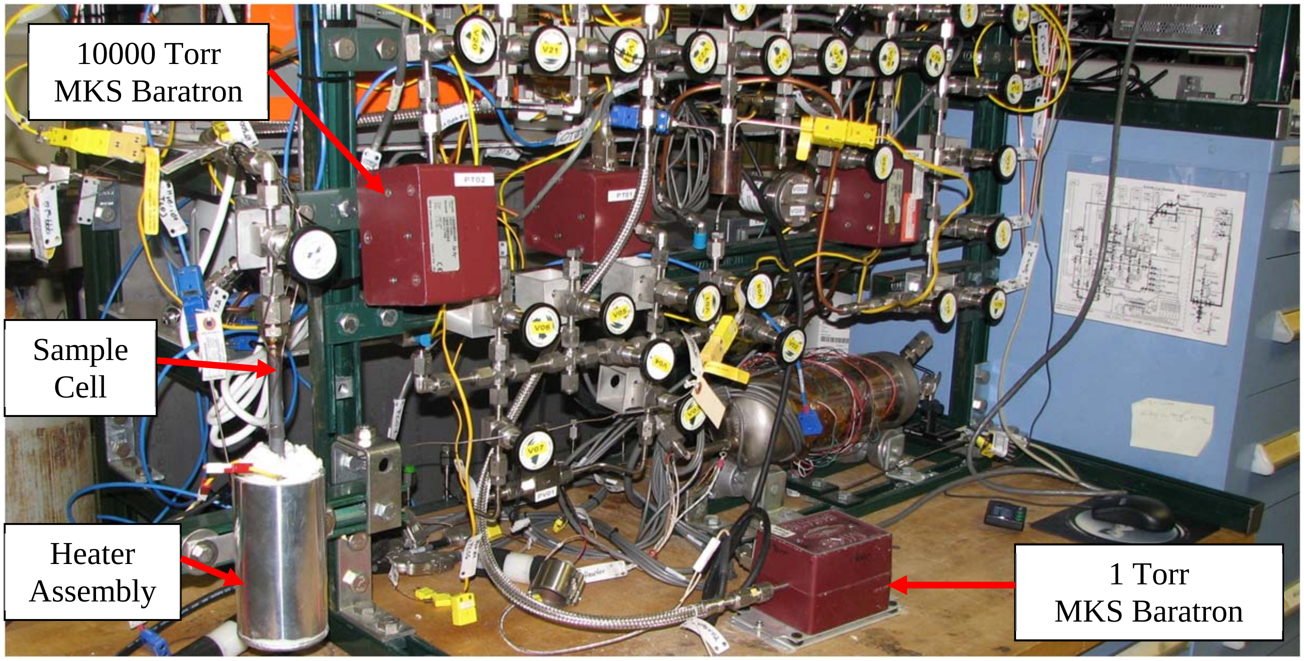

Figure 1. (Color Online) Photograph of Manifold I, showing the sample cell, the heater assembly, the 10K torr MKS Baratron, the 1 torr MKS Baratron.

Manifold I is equipped with a 0 – 1 Torr MKS Baratron and a 0 – 10K Torr MKS Baratron, which were both calibrated along with the associated displays. Manifold II is equipped with a 0 – 100 mtorr MKS Baratron for low pressure measurements. The internal volume of both manifolds was approximately 130 mL, excluding the volume of the sample vessels, which was roughly 15mL. Manifold I was primarily constructed of gasketed fittings, whereas Manifold II was constructed primarily of specially cleaned, welded fittings with gaskets only at the valves and sample ports. The minimization of gasketed fittings would ideally result in a system that was able to achieve a lower ultimate pressure. The initial results were obtained on Manifold I with a 0-1 Torr MKS Baratron, which was only accurate down to 0.1 mtorr. Manifold II was subsequently designed to include a 100 mtorr Baratron, which would be accurate down to 0.01 mtorr.

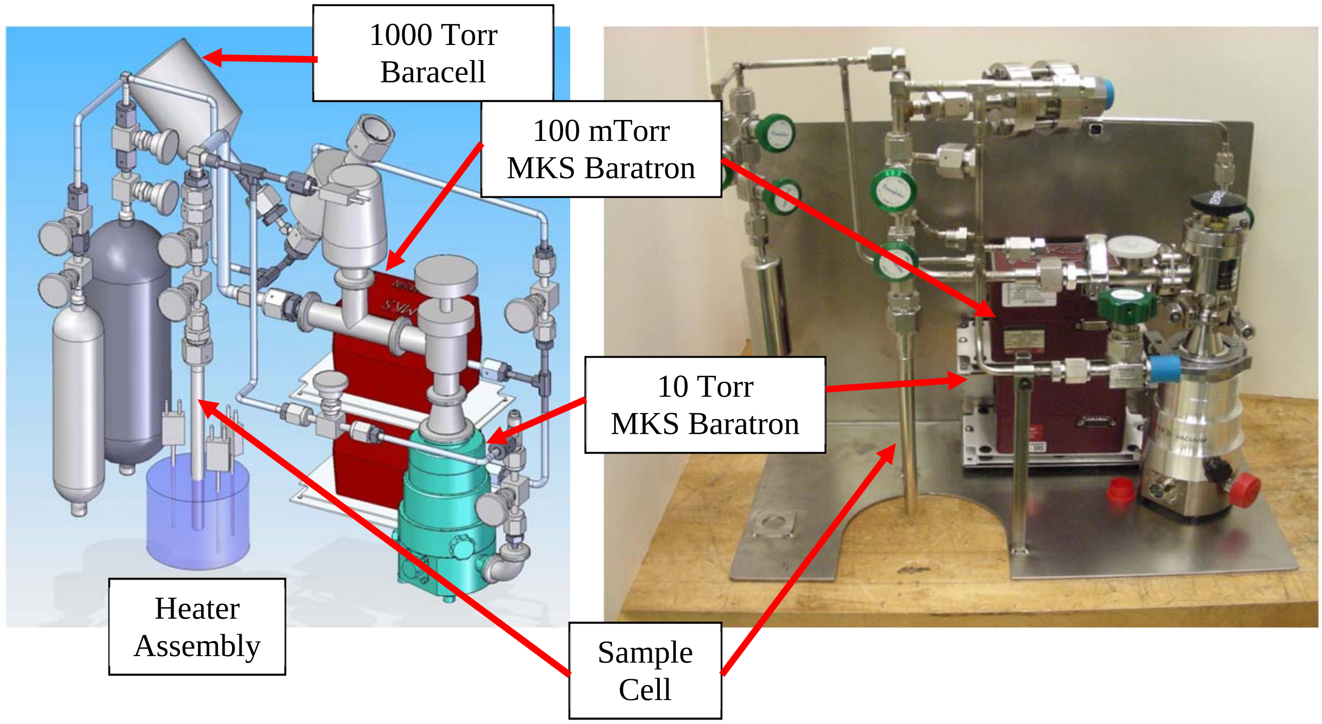

Figure 2. (Color Online) Solid Edge model of Manifold II (left) and photograph of the as constructed Manifold II (right).

The sample vessels were constructed of Type 316 stainless steel (SS) 0.5” x 0.049” tube with a Type 316 SS endcap welded to the tube and a ½” Type 316 L VCR fitting welded to the other end of the vessel. After construction, the sample vessels were thoroughly degassed in a large vacuum furnace. The vessels were loaded into the furnace and then evacuated ($<1 \times 10^{-5}$ torr at room temperature). The furnace was heated at 15°C/minute to 1050°C and held for four hours while continually being pumped. The furnace was then cooled under vacuum, and the sample vessels removed, capped, and placed in a bag that was purged with N_2 until they were ready for use. This procedure removed (or minimized) any potential impurities present in the stainless steel sample vessel that would desorb when the vessel was initially heated for testing. Due to the low hydrogen equilibrium pressure of zirconium at the target temperatures[11], it was expected that any impurities would adversely affect the overall performance of the zirconium getter. In addition, any off-gassing from the sample vessels would adversely influence the background pressure in the test manifold.

The sample vessels could be reused for new samples if the necessary measures were taken to clean the vessels of adsorbed hydrogen. The empty vessel was heated to 600°C for at least 12 hours under high vacuum conditions to desorb any hydrogen that may have diffused into the stainless steel. The heater assembly consisted of a temperature controller, an over temperature controller, and a split cylindrical Watlow ceramic heater. The two halves of the heater were placed around the sample vessel. The sample vessel was placed completely inside the heater assembly in order to heat the entire vessel. The sample vessel was cooled under vacuum then backfilled with 1 atm of argon prior to opening the sample vessel to load a sample.

Samples consisted of one inch long Zircaloy-4 tubes and pure zirconium strips that had been weighed to achieve nominal 1 gram samples. The samples were mechanically abraded with P1200 grit grinding paper on all surfaces to remove any surface oxide that may have been present since preliminary testing had demonstrated that a surface oxide layer would inhibit the hydriding ability of the Zircaloy-4. The H_2 absorption was considerably slower on samples that were not cleaned, either mechanically or chemically, due to the presence of the oxide film. The samples were rinsed in acetone and in 200 proof ethanol, wiped with lint free wipes and cotton swabs and allowed to air dry before being weighed on an analytical balance. The offgassed, nitrogen or argon filled sample vessel was opened and the new sample loaded such that the sample vessel was open to the atmosphere for a minimum amount of time, typically less than 20 seconds.

The sample vessel was attached to the manifold with a 0.5 micron filter gasket and the system was evacuated overnight. Prior to heating the sample, the system with an internal volume of ~150 mL passed a rate of rise of less than 0.05 mtorr in 10 minutes. The bottom two inches of the sample vessel were heated incrementally (in 100°C steps) to the desired temperature (typically 550°C) while being evacuated. Following each increase in temperature of the sample vessel, the system was evacuated until $P < 0.10$ mtorr. The maximum temperature (550°C) was held for several hours (3-4 hours) such that the rate of rise was less than 0.05 mtorr in 10 minutes. The middle of the sample vessel was roughly 180°C and the top of the sample vessel was roughly 80°C when the sample was at 600°C.

High purity hydrogen (Air Liquide, Research grade, 99.9995 %) and high purity deuterium (Spectra gases, Research Grade, 99.999 %) were used. Two different methods of testing were utilized to measure the equilibrium pressure of the H_2 on the zirconium and Zircaloy-4. In the first method, Method A, the samples were evacuated overnight, tested for rate of rise at room temperature, step heated to the loading temperature (550°C), tested for rate of rise, evacuated, loaded with protium or deuterium to the target Q/Zr (hydrogen atom/zirconium atom), then absorption tested by cooling in roughly 30°C increments to temperatures as low as 300°C. For Method B, the samples were evacuated overnight, tested for rate of rise at room temperature, step heated to the desired loading temperature, rate of rise tested, loaded with H_2 to the desired Q/Zr, then cooled to room temperature, and the over pressure evacuated. Desorption tested proceeded by heating the sample to 300°C initially followed by roughly 50°C increments to 550°C. The sample was allowed to reach equilibrium and data was taken at each step. Absorption testing followed after the sample temperature reached 550°C by cooling in 30°C increments to as low as 300°C; data was collected in the same manner. The Method B technique was developed because of concerns of He ingrowth associated with proposed subsequent tritum testing and its effect on measured pressures.[12]

RESULTS AND DISCUSSION

Manifold I: Zircaloy-4

Zr-4 alloy samples were loaded with either protium or deuterium to Q/Zr of 0.5 on nominally 1 gram pieces. Method A testing for absorption was used to collect the equilibrium pressure data. The results of the testing are listed in Table I and displayed graphically in Figure 3. Note that the data is not linear below about 450°C. The loss of linearity is attributed to a combination of off-gassing, in-leakage, and gas impurities. One can see from these data that the lower temperature data are clearly not on the same slope as the higher temperature data. There is also some off-set between the literature data[11] and the experimental data, since no repeat data were generated; it is unknown where this difference arises. There is also a pressure difference between the protium and deuterium, with deuterium having a higher measured presure. The original plot of the referenced literature data is shown in Figure 4, while the interpolated and extrapolated data is listed in Table II.

Table I: Equilibrium Absorption Pressures of Protium and Deuterium over Zr-4 using Manifold I, Method A

Equilibrium Pressures for Protium		**Equilibrium Pressures for Deuterium**	
Temperature	**Pressure**	**Temperature**	**Pressure**
(°C)	**(mtorr)**	**(°C)**	**(mtorr)**
599.10	87.78	598.80	137.03
548.90	14.64	548.84	20.85
498.50	2.28	498.48	3.01
448.50	0.35	448.71	0.41
398.50	0.10	397.64	0.08
348.30	0.08	347.65	0.08

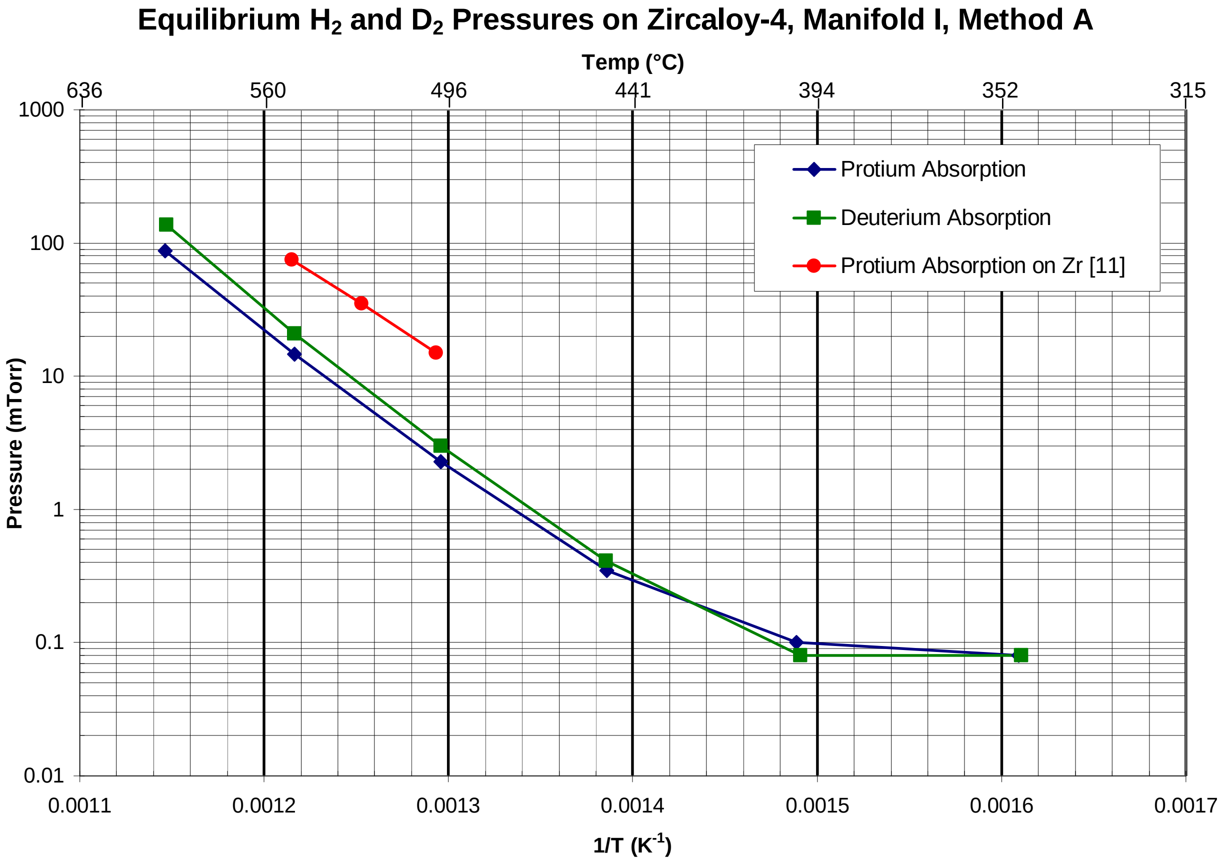

Figure 3. (Color Online) Graphical representation of the equilibrium pressure data for the absorption of H_2 on Zircaloy-4 using Manifold I, Method A for a loading of Q/Zr of 0.5. The literature data is from Reference 11.

Table II: Equilibrium Pressure of Protium over Zirconium from Mueller [11].

Equilibrium Pressures on Zr for Protium			
	Pressure (mtorr)		
Q/M	**500°C**	**525°C**	**550°C**
0.20	12.3	32.7	68
0.50	12.7	33	68
0.80	12.9	33	68
1.10	13	33	80
1.40	30	71	105

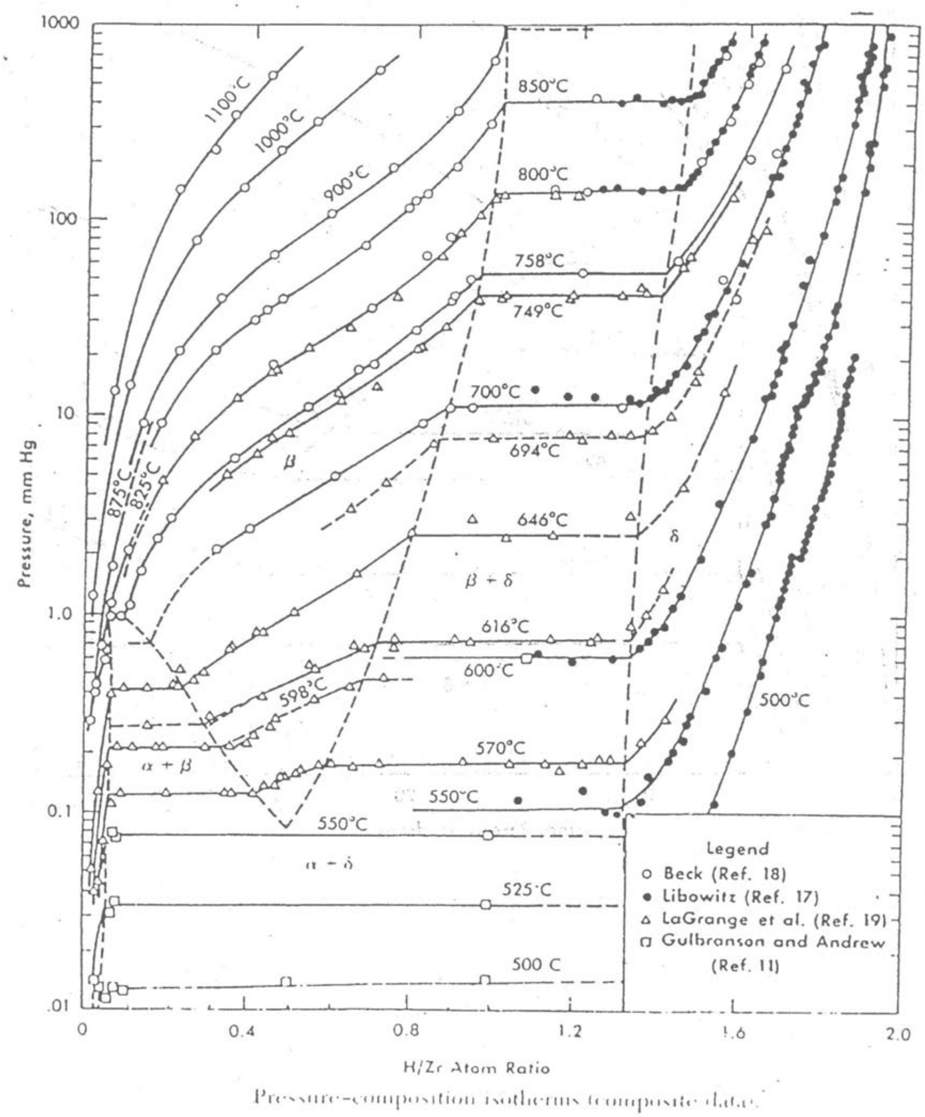

Figure 4. Reference data for equilibrium pressure of H_2 on zirconium. Taken from Ref. 11.

Manifold II: Zircaloy-4

Manifold II was used to determine the equilibrium pressures of H_2 absorbed on Zircaloy-4 with both Method A and Method B. The data are presented in Table III and Table IV, respectively, and graphically in Figure 5. It is apparent from the data that values above about 400°C yield linear data with increasing temperature. This result is consistent with the results obtained from the testing completed on Manifold I, which showed similar behavior and a significant deviation from linearity at the lower temperatures, which can be attributed to inleakage and offgassing.

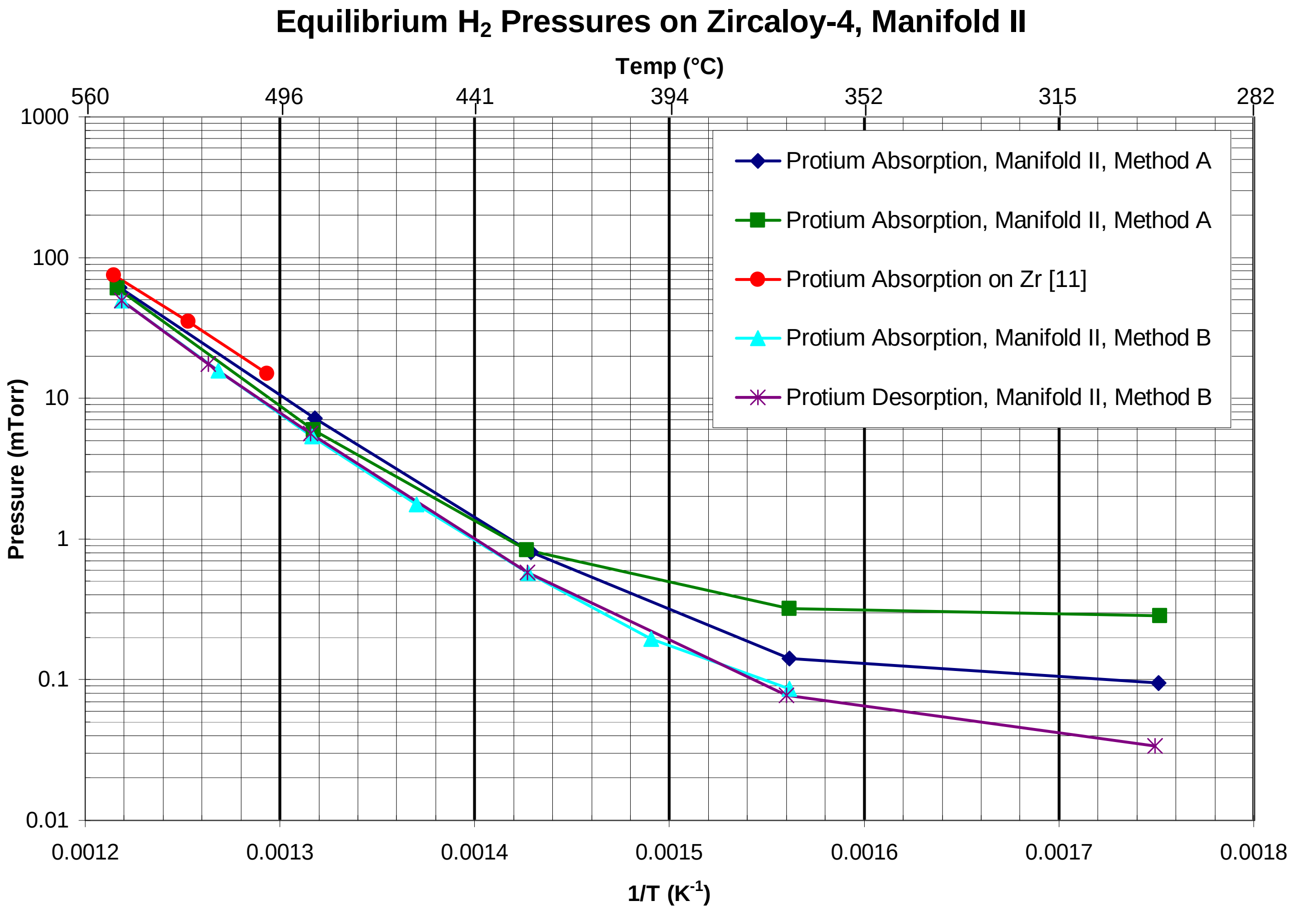

Figure 5. (Color Online) Graphical representation of the equilibrium pressure data for the absorption of H_2 on Zircaloy-4 using Manifold II, Methods A and B for a loading of H/Zr of 0.5.

From these results, it can be determined that Manifold II yields linear data down to ~375°C, which is ~75°C lower than where the data from Method A deviates from linearity. The equilibrium pressures measured using Method B are also lower than the equilibrium pressures measured using Method A. At 550°C, the measured equilibrium pressure using Method B was roughly 19% lower than similar data using Method A and at 425°C the data measured using Method B was 28% lower than the corresponding data point using Method A. It is also interesting to note that there is very little hysteresis between the desorption and absorption data when Method B is used. The absence of hysteresis between the absorption and desorption of hydrogen can possibly be a characteristic of a low pressure hydride material. There is very little literature evidence on the isothermal absorption and desorption on getter type hydride materials and no evidence to support or refute the claim regarding the absence hysteresis. It is also possible that there could be some hysteresis between the hydrogen absorption and desorption data and that it is within the noise of the pressure measurements and is therefore not detectable.

Table III: Equilibrium pressure for the Absorption of H_2 on Zr-4 Using Manifold II, Method A with a loading of 0.5 H/Zr.

Equilibrium Pressures for Protium Manifold II		**Equilibrium Pressures for Protium Manifold II (Re-test)**	
Temperature	**Pressure**	**Temperature**	**Pressure**
(°C)	**(mtorr)**	**(°C)**	**(mtorr)**
548.08	61.611	548.94	60.253
485.74	7.227	486.12	5.931
426.73	0.808	427.76	0.839
367.18	0.141	367.17	0.322
297.85	0.095	297.70	0.286

Table IV: Equilibrium pressure for the Absorption of H_2 on Zr-4 Using Manifold II, Method B with a loading of 0.5 H/Zr.

Zircaloy-4 H/Zr = 0.5, Method B					
Temperature	**Pressure**	**Comment**	**Temperature**	**Pressure**	**Comment**
(°C)	**(mtorr)**		**(°C)**	**(mtorr)**	
550.48	62.778	Initial Loading	547.40	49.801	Common Point
298.56	0.034	Desorption	515.40	15.767	Absorption
367.91	0.077	Desorption	486.55	5.351	Absorption
427.54	0.581	Desorption	456.78	1.763	Absorption
486.94	5.644	Desorption	427.36	0.569	Absorption
518.54	17.474	Desorption	397.71	0.196	Absorption
547.40	49.801	Desorption	367.26	0.086	Absorption

Manifold II: Pure Zirconium

Pure zirconium strip samples were loaded to a protium to zirconium ratio of 0.5. The equilibrium pressures were determined using Method B. The measured equilibrium pressures are presented in Figure 6 and Table V. These data indicate very little hysteresis between the absorption and desorption data. The data are also slightly lower than the literature values.

Table V: Test results from loading Zr strip to an H/Zr ratio of 0.5 with results from Manifold II, Method B.

Pure Zr H/Zr = 0.5			**Pure Zr H/Zr = 0.5**		
Temperature	**Pressure**	**Comment**	**Temperature**	**Pressure**	**Comment**
(°C)	**(mtorr)**		**(°C)**	**(mtorr)**	
547.83	58.145	Initial Loading	547.01	55.404	Common Point
298.49	0.041	Desorption	516.72	18.661	Absorption
370.03	0.082	Desorption	487.10	6.256	Absorption
398.01	0.196	Desorption	457.70	1.995	Absorption
427.95	0.622	Desorption	427.17	0.623	Absorption
457.64	1.994	Desorption	399.00	0.202	Absorption
487.21	6.193	Desorption	368.30	0.078	Absorption
516.96	18.269	Desorption	332.74	0.042	Absorption
547.01	55.404	Desorption	297.99	0.036	Absorption

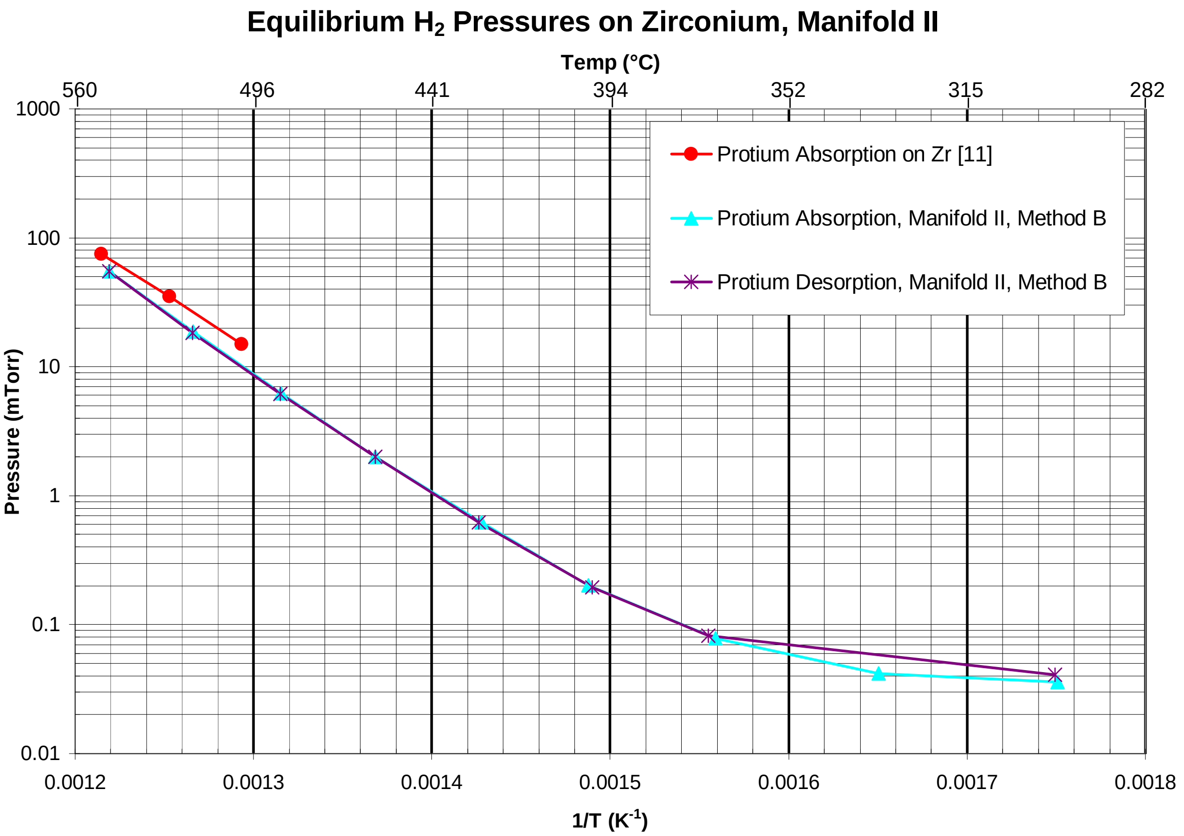

Figure 6. (Color Online) Graphical representation of the equilibrium pressure data for the absorption of H_2 on zirconium using Manifold II, Method B for a loading of H/Zr of 0.5.

SUMMARY OF ALL RESULTS

All of the data that has been collected on Zircaloy-4 and zirconium using Manifold I and II (Methods A and B) is graphically displayed in Figure 7. In all cases the equilibrium pressures measured on Zircaloy-4 and pure zirconium are lower than the previous measurements reported by Meuller.[11] At least two possibilities exist, one is that the alloying effects on the Zircaloy-4 could suppress the pressures and the second is that the new data represents an improvement in the test technique with better manifold materials and instrumentation. The data collected on Manifold II is much closer to the literature values reported by Mueller[11] than the data collected on Manifold I.

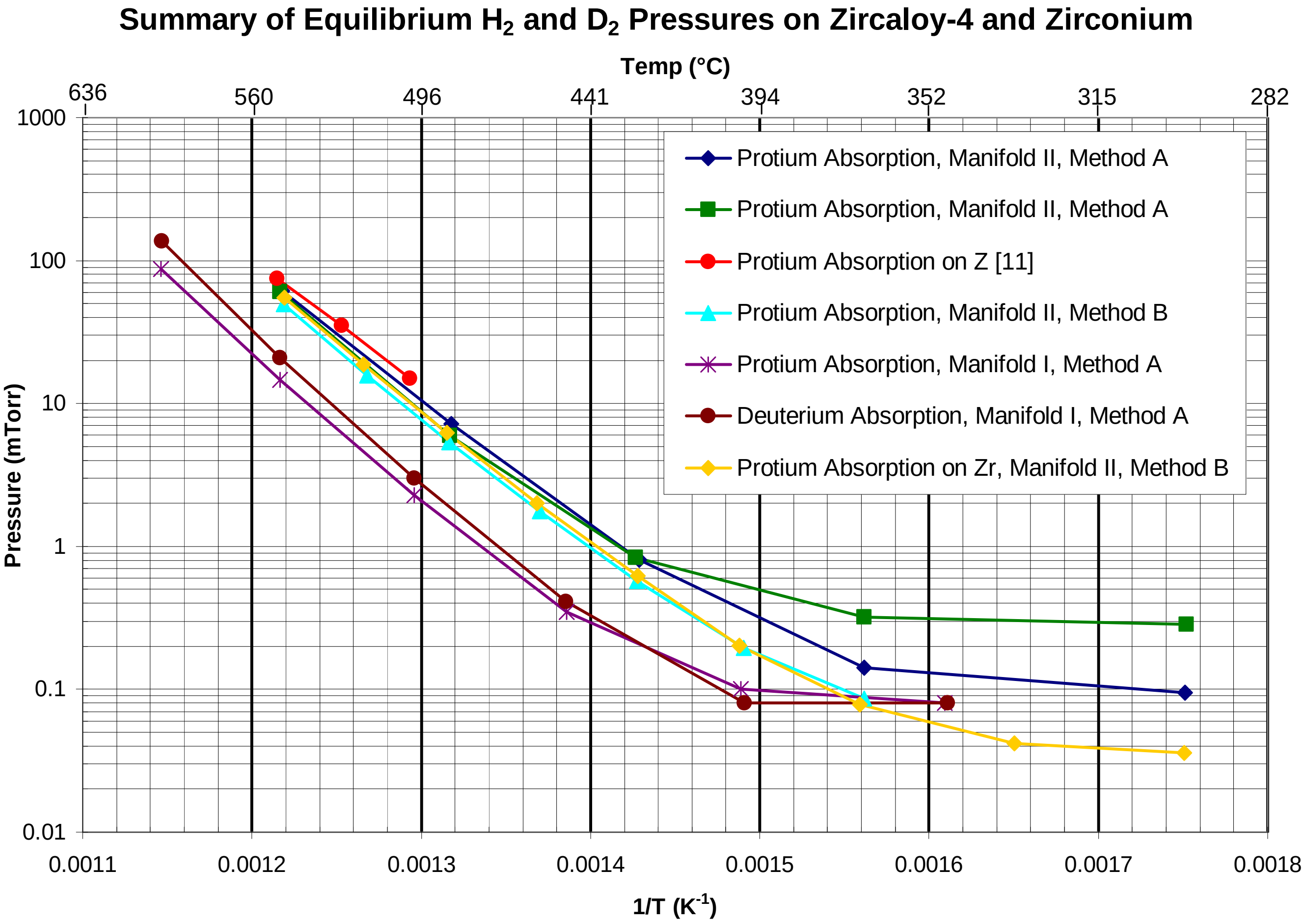

Figure 7. (Color Online) Summary of equilibrium pressure for H_2 and D_2 Absorption on Zircaloy-4 and Zirconium using Manifolds A and B.

The lower equilibrium pressure measured on Manifold I can possibly be attributed to less off-gassing and potential contamination from the manifold. Manifold I has been in service for a significantly longer period of time than Manifold II and has been evacuated for much of that time. The continual evacuation of Manifold I likely has resulted in a reduction in the level of off-gassing and impurities coming from the walls of the manifold. Manifold II was constructed of cleaned stainless steel for this work and was also vacuum degassed in a furnace prior to assembly. Even though these precautions were taken, it is still possible that the various components of Manifold II are the source of small amount of off-gassing and contamination, resulting in a slightly higher equilibrium pressure.

The zirconium surface is very prone to surface oxidation regardless of the type of oxidant (oxygen, water, water vapor, CO, etc.)[13]. Due to the diffusivity of oxygen in zirconium[14,15] and due to the chemical affinity of Zr for oxygen, the formation of the oxide occurs immediately upon contact even at the lowest pressures of the oxidant. Given this information it is imperative to evacuate the zirconium and Zircaloy-4 samples as soon as possible following the mechanical abrading. The pressure in the sample cell should be as low as possible prior to heating the sample to the activation temperature. Ideally a pressure $<5\times10^{-6}$ torr is necessary before heating the sample to the activation temperature. Additionally, it has been determined that a step-wise heating of the sample may be necessary (depending on the pumping speed of the system) to maintain the pressure in the system below 0.5 mtorr.

SUMMARY AND CONCLUSIONS

A manifold was designed, built, proof-tested, and utilized to obtain equilibrium pressure data over Zircaloy-4 and pure zirconium. These getter materials offered significant challenges to overcome given the low hydrogen equilibrium pressure in the temperature range of 400°C to 600°C. Previously zirconium hydride data was available down to only 500°C and results are reported here for temperatures down to 400°C. The H_2 equilibrium pressure on Zircaloy-4 was measured to be 0.1 mtorr at 400°C. In order to obtain equilibrium pressures for hydrogen on zirconium it was necessary to minimize the surface oxidation by evacuating the sample to $<5\times10^{-6}$ torr prior to heating the sample. In addition it was also necessary to minimize the pressure increase in the system during the heating of the sample. This can be accomplished by heating the sample incrementally and allowing the pressure to return to the base level before increasing the temperature.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Jody Dye and James Klein of Savannah River National Laboratory, Donna Hasty of the Savannah River Site, and Dave Senor of Pacific Northwest National Laboratory for their support of this work. The manuscript has been prepared for the U.S. Department of Energy under Contract Number DE-AC09-08SR22470.

1. K. Ojima and K. Ueda, *App. Surf. Sci.*, **165**, 149 (2000).
2. C.S. Zhang, B. Li, and P. R. Norton, *Surf. Sci.*, **346**, 206 (1996).
3. J. A. Llouger and G. N. Walton, *J. Nuc. Mats.*, **97**, 185 (1981).
4. M. Yamamoto, S. Naito, M. Mabuchi, and T. Hashino, *J. Phys. Chem.*, **96**, 3409 (1992).
5. C. S. Zhang, B. J. Flinn, K. Griffiths, and P. R. Norton, *J. Vac. Sci. Tech. A*,, **10**, 2560 (1992).
6. G. R. Corallo, D. A. Asbury, R. E. Gilbert, and G. B. Hoflund, *Langmuir*, **4**, 158 (1988).
7. G. G. Libowitz, J. Nuc. Mats. **5**, 228 (1962).
8. R. D. Penzhorn, M. Devillers, and M. Sirch, *J. Nuc. Mats.*, **179-181**, 863 (1991).
9. Y. Naik, G. A. Rama Rao, and V. Venugopal, *Intermetallics*, **9**, 309 (2001).
10. K. A. Terrani, M. Balooch, D. Wongsawaeng, S. Jaiyen, and D. R. Olander, *J. Nuc. Mats.*, **397**, 61 (2010).
11. W. M. Mueller, J. P. Blackledge, G. G. Libowitz, Metal Hydrides, Academic Press, New York, 1968.
12. G. C. Staack and J. E. Klein, *Fus. Sci. Tech.*, **60**, 1479 (2011).
13. R. A. Causey, D. F. Cowgill, and R. H. Nilson, “Review of the Oxidation Rate of Zirconium Alloys,” Sandia Report, SAND2005-6006 (2005).
14. A. Grandjean and Y. Serruys, *J. Nuc. Mats.*, **273**, 111 (1999).
15. R. A. Perkins, *J. Nuc. Mats.*, **68**, 148 (1977).