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## **Titanium tritide radioisotope heat source development: palladium-coated titanium hydriding kinetics and tritium loading tests**

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# **Titanium tritide radioisotope heat source development: palladium-coated titanium hydriding kinetics and tritium loading tests**

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## **Abstract**

We have found that a 180 nm palladium coating enables titanium to be loaded with hydrogen isotopes without the typical 400-500 °C vacuum activation step. The hydriding kinetics of Pd coated Ti can be described by the Mintz-Bloch adherent film model, where the rate of hydrogen absorption is controlled by diffusion through an adherent metal-hydride layer. Hydriding rate constants of Pd coated and vacuum activated Ti were found to be very similar. In addition, deuterium/tritium loading experiments were done on stacks of Pd coated Ti foil in a representative-size radioisotope heat source vessel. The experiments demonstrated that such a vessel could be loaded completely, at temperatures below 300 °C, in less than 10 hours, using existing department-of-energy tritium handling infrastructure.

## **ACKNOWLEDGMENTS**

At Sandia National Labs, we thank: David Zanini for building the gas manifold, Miles Clift for performing the Auger depth profiling experiments, and Yon Perras for assisting with the design of the HCRH foil stacks and for assembling many of the vessel prototypes described in this report.

Honeywell Kansas-City-Plant manufactured the heat source vessel prototypes that were loaded at the Savanna River Site. Bruce Alquist of KCP oversaw vessel fabrication.

At Savannah River National Labs, Tom Warren and Bill Rogier assisted with loading process development. Savannah River Site tritium facilities personnel performed the tritium loading tests. Scott McGee was responsible for the loading procedures and operation. Debbie Bryson-Damon made the calorimetry measurements. Chad Sweeney designed the loading/pinch-weld fixture.

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## NOMENCLATURE

$\alpha$	reacted fraction of metal [n/a]
L	initial thickness of metal sheet [m]
$d_h$	mass density of hydride [ $\text{kg/m}^3$ ]
$d_m$	mass density of metal [ $\text{kg/m}^3$ ]
$M_m$	formula weight of metal [kg/kgmol]
$M_h$	formula weight of hydride [kg/kgmol]
$k_D$	pressure and temperature dependent hydriding rate constant [ $\text{m}^2/\text{s}$ ]
t	time that metal has been exposed to hydrogen gas [s]
$x_P$	hydride front displacement into parent metal [m]
$Z_0$	concentration of excess hydrogen dissolved in the hydride (atom H/atom M) [n/a]
Y	lower limit of the single phase region (atom H/atom M) [n/a]
D	diffusion coefficient of mobile hydrogen dissolved in hydride lattice [ $\text{m}^2/\text{s}$ ]
$D_0$	pre-exponential constant [ $\text{m}^2/\text{s}$ ]
$E_D$	activation energy for diffusion [J/atom]
k	Boltzmann's constant [J/K/atom]
T	absolute temperature [K]

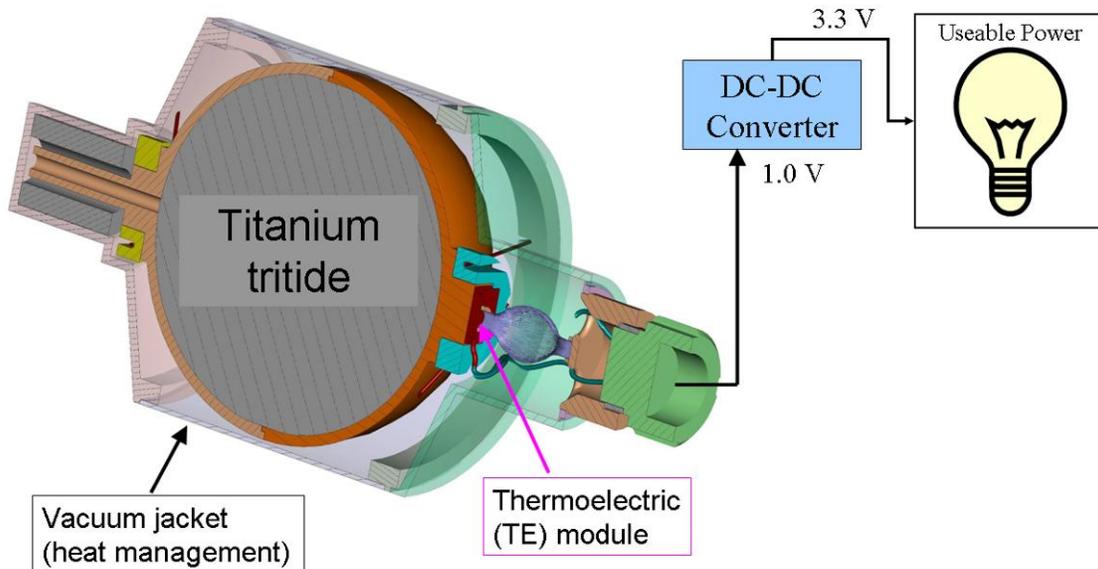
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# 1 INTRODUCTION

Electrical power supplies based on radioactive heat sources (RTGs) have lifetime potential not yet possible with electrochemical battery technology. Such devices have previously been built using plutonium-238 as the heat source material. With a half-life of 88 years and a heat output of 0.56 watts/gram, this isotope is attractive for both large and small scale RTG applications. However, plutonium-238 is an extremely scarce and valuable material.

In hope of developing an RTG based on a more readily available material, Sandia has investigated devices that use tritium as a heat source. We believe a tritium thermoelectric generator (TTG) is a possible alternative to plutonium-238 RTGs for applications that require 5 to 20 mW of electrical power for 10 to 20 years.

The TTG is a stand-alone component; key parts are illustrated in Figure 1.



**Figure 1: Components of a TTG system**

The tritium is stored on a titanium bed. Approximately 80% of the heat generated by tritium decay is directed through a thermoelectric module where a portion is converted into electrical energy. Thermal insulation is provided by a vacuum jacket and low thermal-emissivity coatings. The heat source vessel is suspended on titanium spokes to limit thermal conduction losses. These design features allow the heat source material to be used efficiently. It has been predicted that a TTG producing 5 mW of electrical power for 15 years will only require a 1.39 gram tritium load.

The tritium is mixed with 3.33 g of deuterium and the mixture is stored on a 53.6 g titanium bed. The tritium is diluted with deuterium to delay the onset of rapid helium-3 release from the titanium matrix, which, at room temperature, happens at a  $^3\text{He}/\text{Ti}$  atomic ratio of approximately 0.34 [1-8]. Dilution is an established practice and has been used in the design of titanium-based tritium storage beds [1, 9]. Sequestering the  $^3\text{He}$  in the titanium, instead of containing it in a thick-walled pressure vessel, minimizes heat source size and weight.

Titanium is attractive because it can compactly store tritium at very low gaseous overpressures [10, 11]; two necessary characteristics for the TTG. Low gaseous overpressure eliminates the tritium compatibility issue for all situations – even the highest temperature failure scenarios, where the heat source vessel temperature can approach 300 °C.

Unfortunately, the standard process for loading titanium with hydrogen isotopes complicates the TTG assembly sequence. It is well established that a passivating oxide layer forms on the surface of titanium that has been exposed to air. This can make loading the metal with hydrogen isotopes difficult [12]. Typically titanium metal is heated in vacuum to defeat the oxide layer and expose clean titanium which will then readily absorb hydrogen isotopes. It is understood that heating in vacuum allows the surface oxide to diffuse into the bulk metal, exposing a clean titanium surface [13]. It is accepted that temperatures of 400 to 500 °C, vacuum levels of  $1 \times 10^{-4}$  torr, and process times of 16 to 24 hours are needed to defeat the passivating oxide layer and facilitate hydrogen isotope loading [14, 15]. This is an issue because we would like hydrogen isotope loading to be one of the last steps in the assembly sequence and the maximum temperature of the TTG assembly is limited to less than 300 °C by the thermoelectric module. Consequently, we wanted to develop methods for loading titanium that do not require a 400 to 500 °C activation step.

It is well known that palladium can maintain a sufficiently active surface for hydrogen adsorption even when exposed to air. Palladium coating is commonly used when measuring hydrogen permeation through materials that form passivating oxides when exposed to air. Examples include stainless steels, [16], and zirconium, [17], among others. Palladium coating has also been used to promote hydrogen absorption by bulk samples of: niobium and tantalum [18], vanadium [19], magnesium [20], and titanium [21]. In addition, vacuum deposited palladium coatings have been used on non-evaporable getter materials, [22], to create composite getters that will absorb hydrogen to very low pressures without a thermal activation step.

The mechanism(s) by which palladium promotes bulk absorption are only partially understood and tend to differ between materials. For austenitic stainless steel, it has been proposed that palladium significantly increases the rate of hydrogen adsorption and dissociation, which are thought to be rate-limiting [16]. In contrast, for niobium and tantalum, it is believed that the lower desorption energy of the palladium surface relative to the bulk substrate metal promotes a more equal distribution of hydrogen between the surface (Pd) and bulk (Nb or Ta) sites, keeping the surface free for hydrogen adsorption [18]. In other cases, titanium for example, the mechanism is unknown but significant differences in uptake rates have been observed between palladium-coated and uncoated surfaces [21].

Palladium coated titanium is available commercially. The getter manufacturer, SAES, sells it as a hydrogen getter material. Their high capacity RelHy (HCRH) material is a 125 or 150  $\mu\text{m}$  thick sheet of annealed, grade 2 commercial purity (99% pure), titanium-foil with an approximately 180 nm thick palladium coating. This material will absorb hydrogen at room temperature and does not require thermal activation. To make the product, they sputter etch the titanium foil to remove the native oxide then sputter deposit the palladium onto the clean surface. The cleaning and coating steps are done in one vacuum operation [23].

However, even with an active surface, loading titanium with hydrogen isotopes takes some time. There has been substantial investigation of the kinetics of metal hydride formation. Reference [13] is an excellent review of hydriding kinetics and mechanisms for a number of different metals, including titanium. In Ref. [24], Mintz and Bloch develop a model for the hydriding of metals by hydrogen gas. One form of the model assumes that the rate of hydride formation in a bulk sample is controlled by diffusion of hydrogen through an adherent metal-hydride layer. Efron *et. al* have made measurements on vacuum activated titanium samples which showed that the adherent-layer diffusion limited model is appropriate for the titanium-hydrogen system at pressures between 30 and 450 torr and temperatures between 100 and 250 °C [15].

In this study we conducted hydriding experiments on titanium foil-samples and representative sized heat source vessel prototypes. The purpose of the study was to: 1) understand the kinetics of hydriding titanium; 2) extend the results from Ref. [15] to titanium deuteride; 3) use this information to select a morphology that enables a titanium filled pressure vessel to be fully loaded with a deuterium-tritium mixture, in a few hours, below 300 °C; and 4) demonstrate the loading process on a representative-sized TTG heat source vessel.

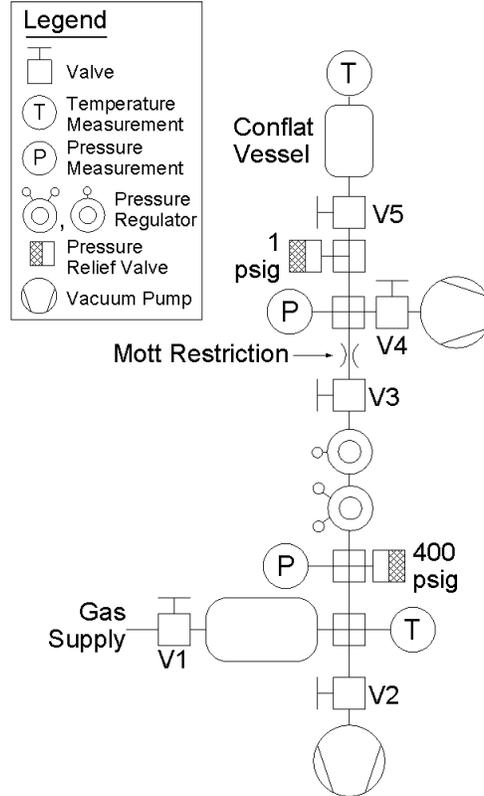
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## 2 HYDRIDING KINETICS EXPERIMENTS

### 2.1 Experimental details

#### 2.1.1 Apparatus

An all-metal hydrogen compatible gas manifold was assembled for the hydriding kinetics investigation.



**Figure 2: Gas supply manifold**

The manifold was assembled from hydrogen compatible materials and components. The gas supply section, between V1, V2, and V3 contained a 1000 cc stainless steel Whitey vessel. Gas pressure was monitored by Teledyne Taber model 209 strain-gauge based transducers. A 50 psia full-scale transducer was used for the hydriding experiments on 0.75×0.75×0.006 inch samples of titanium foil where the pressure drop from hydrogen absorption was approximately 1.8 psia. A 500 psia full-scale transducer was used on the prototype loading experiments where the pressure drop was approximately 350 psia. Gas temperature was monitored by a Type-K thermocouple having an approximately 0.010 inch diameter exposed-junction. A conventional and a special single-stage vacuum pressure regulator were used in series to deliver approximately 5 psia to the inlet of V3.

A Mott 500 sccm rated porous 316L SS flow restriction was placed downstream of V3. It was used in combination with the pressure regulator to control the mass flow rate into the hydride vessel during the large-scale loading experiments. The mass flow rate is controlled to limit the hydriding rate and its corresponding heat generation. A similar flow rate regulation scheme will

be used when loading an actual TTG assembly. In the single-foil loading experiments the rate of hydrogen absorption is sufficiently slow that the flow restriction does not control hydrogen uptake.

The hydride container was an all-metal bakeable stainless steel vessel sealed with 2 ¾ inch Conflat flanges. For elevated temperature experiments, the vessel was wrapped in heat tape and temperature control was provided by an external surface-mounted Type-K thermocouple and an Omega temperature controller. The internal gas temperature was monitored by a 0.020 inch sheathed Type-K thermocouple. The sample assembly was suspended on a 0.040 inch sheathed Type-K thermocouple. Suspending the sample ensured that the thermocouple reading accurately reflected the sample temperature.

Pressure in the hydride vessel and connecting tubing was monitored by a 15 psia full-scale transducer. All pressure transducer and thermocouple signals were recorded by a 16-bit Nicolet Odyssey data acquisition system.

The internal volume of the supply and hydride sections was measured by pressure ratio comparison to a known 148.1 cc volume. The volume of the supply section, between V1, V2, and the first pressure regulator, was found to be 1015 cc. Using the forward-reverse ratio method described in Ref. [25], the volume of the hydride section tubing (between V3, V4, and V5) and the volume of the Conflat vessel were found to be 9.9 and 132.6 cc respectively.

Ultra high purity hydrogen (99.999% H<sub>2</sub>) and chemical purity deuterium (99.7% D<sub>2</sub>) were purchased from Matheson Tri-Gas and used without further purification. The vacuum pump was an Alcatel two-stage rotary vane pump with an ultimate pressure of about 10 mtorr (as read by a thermocouple vacuum gauge located directly upstream of the pump inlet).

The extent of hydriding was computed from a mass balance on the hydrogen gas using the pressures, temperatures, and volumes of the supply and hydride sections.

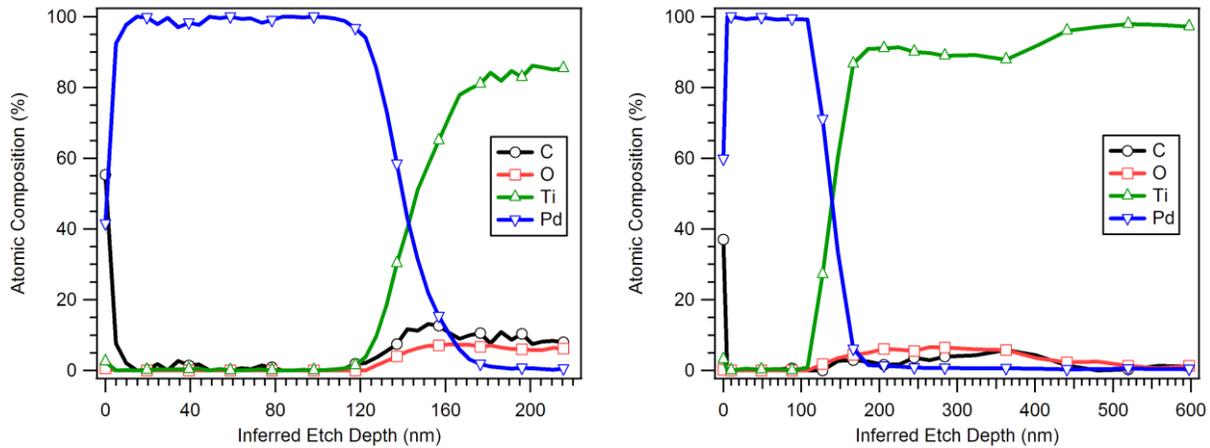
### 2.1.2 Specimens

The foil specimens were either 127 µm thick 99% pure annealed titanium foil purchased from Alfa Aesar or high capacity RelHy (HCRH) material purchased from SAES Getters USA. Both foils were used without modification.

The HCRH foil is sold by SAES as a low-temperature hydrogen getter. It is a 150 µm thick sheet of annealed, grade 2 commercial purity (99% pure), titanium-foil that is sputter etched to remove the native surface oxide then sputter coated with a thin layer of palladium [23].

A sample of HCRH was analyzed using Auger depth profiling. A PHI 680 Scanning Auger Spectrometer and an argon ion sputter gun were used to measure the atomic composition of the palladium coating, palladium-titanium interface, and the titanium substrate as a function of depth. An approximately 1 mm<sup>2</sup> area of a 1 inch diameter HCRH disk was sputter etched with 2 keV argon ions and Auger spectra were taken at regular intervals inside the sputter crater. The Auger analysis area was about 30 nm in diameter. Etch depth was inferred from the etch duration and rate. The etch rate was estimated to be 9.8 nm/min based on an SiO<sub>2</sub> standard.

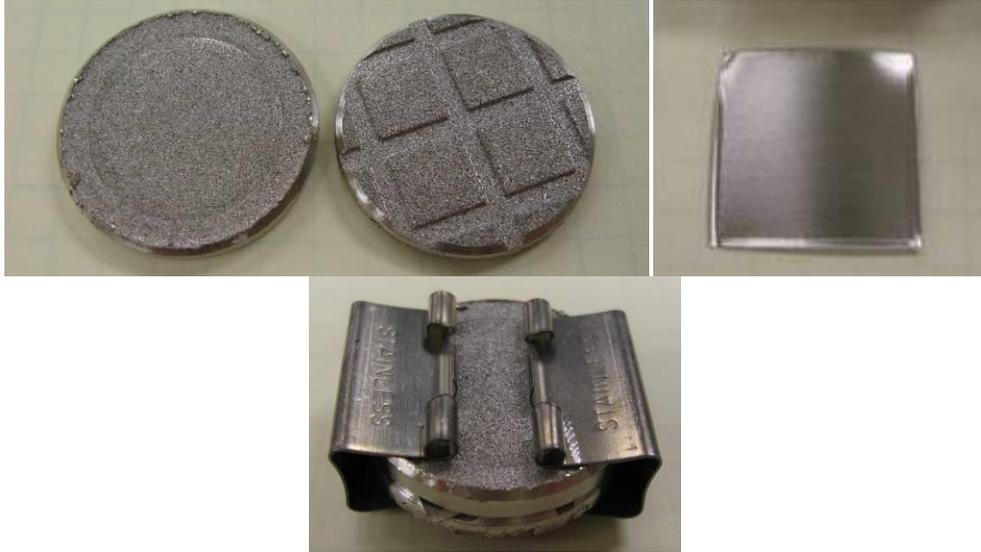
Atomic fractions of C, O, Ti, and Pd were inferred from the Auger spectra. Figure 3 shows the atomic fractions of these four species vs. etching depth.



**Figure 3: Two Auger depth profiles of the same sample of unmodified HRCH. The left profile shows the palladium layer in detail. The right profile extends deeper into the substrate.**

The profiles show: 1) an essentially pure palladium coating approximately 120 nm thick, 2) an interface region, 120-180 nm, where the dominant specie changes from Pd to Ti, 3) a near-interface region where Ti, O, and C, exist, and finally 4) the bulk titanium substrate. These profiles appear consistent with annealed commercial purity titanium that has been sputter etched to remove the surface oxide layer then sputter coated with palladium. It is likely that the oxygen and carbon detected between 125 and 500 nm are near-surface contaminants originally in the annealed Ti foil. It therefore appears that HCRH is simply grade 2 commercial purity (99% pure) titanium-foil that has been sputter etched and palladium coated.

Foil samples were handled in air, cut to size, and put into the test assembly shown below. The 0.75×0.75 inch samples were cut from an approximately 2×2 inch sheet of HCRH using scissors. They were then clamped between two waffle-pattern stainless steel frits made by Mott. A typical assembly is shown below.



**Figure 4: Single-foil test assembly.**

The frits are sintered from 65 to 165  $\mu\text{m}$  304L stainless steel powder to a relative density of 0.70 and have a Darcy's Law permeability of approximately  $3.6 \times 10^{-12} \text{ m}^2$  [26]. The frits are sufficiently open to gas flow so they do not affect hydrogen gas transport to the foil surface. The foil coupons were clamped between two frits using two 304 stainless steel binder clips.

The frits are in close contact with the foil. As mentioned previously, the test assembly is suspended on a thermocouple. The test records indicate that the frits provide sufficient thermal mass to keep foil at an effectively constant temperature during the hydriding reaction. This is important because, without sufficient heat-sinking, self-heating from the hydriding reaction can increase the sample temperature, changing the uptake rate.

### *2.1.3 Hydriding Test Procedure*

To conduct an isothermal hydriding experiment the specimen was weighed on a Mettler-Toledo AE-163 balance having  $\pm 0.0002 \text{ g}$  accuracy and sealed in the Conflat container. The entire system was then evacuated to a pressure of approximately 20 mtorr and all valves and pressure regulators were closed.

The supply section was then filled with hydrogen or deuterium to 30-40 psia then evacuated. After two fill-and-evacuation cycles, the supply section was filled to approximately 40 psia and sealed. The first pressure regulator was set to approximately 35 psia and the second regulator was set to approximately 5 psia.

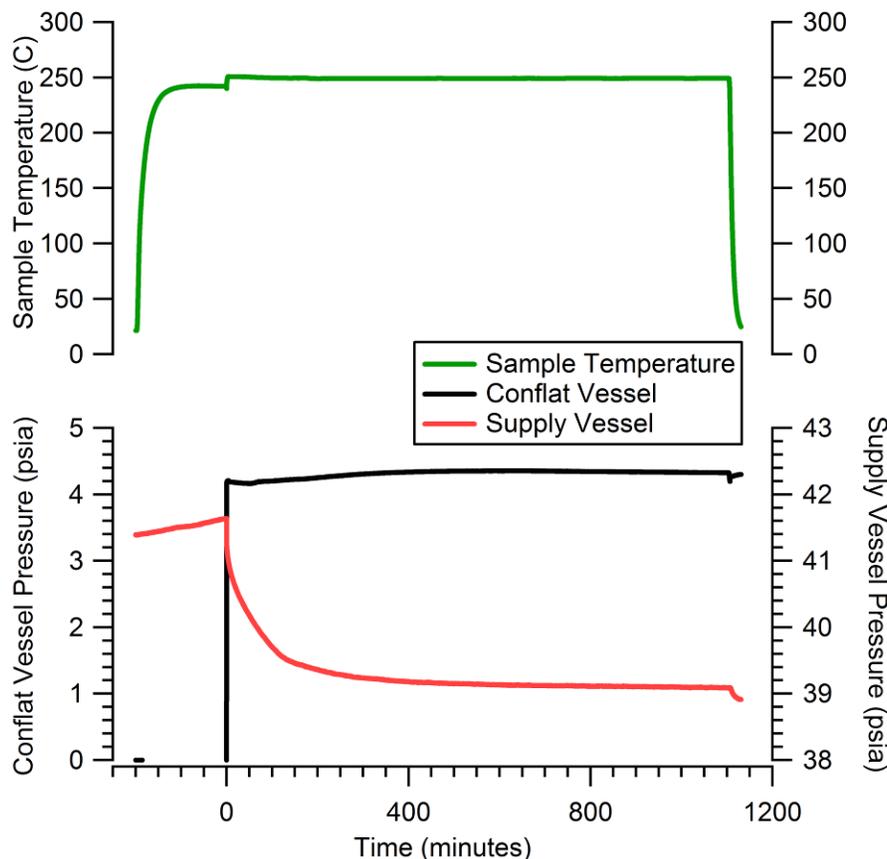
The hydride section was then opened to the vacuum pump and evacuated for 10-20 minutes at room temperature. Following room temperature evacuation, the conflat container was heated to the test temperature under dynamic vacuum. About 2 hours were needed for the container and sample to stabilize at the test temperature. Data acquisition was started just before the heating step.

After the sample temperature had stabilized, the vacuum valve, V4, was closed. This was followed by a few minute wait to check for pressure rise in the hydride vessel indicative of a leak or outgassing. After the wait time, hydriding was started by opening V3. The conflat vessel filled to approximately 5 psia in about 10 seconds. At this point the test was allowed to run unattended. Data was collected for at least 16 and up to 72 hours.

After the test had run for the specified time, the temperature controller was turned off and the vessel cooled to room temperature. At this point the test was complete and data acquisition was stopped. The sample was then removed from the conflat vessel and inspected.

## 2.2 Experimental Results

Figure 5 shows typical pressure and temperature data from an isothermal hydriding experiment. In this case, the specimen was a 0.2536 gram sheet of HCRH foil tested in hydrogen at 250 °C.



**Figure 5: A typical isothermal hydriding experiment.**

The conflat vessel was heated from ambient to 250 °C under a dynamic vacuum of about 20 mtorr. The sample temperature stabilized at a slightly lower value, 242 °C, because of the small amount of heat lost through the suspending thermocouple.

The valve connecting the conflat and supply vessels, V3, was opened at zero seconds. The jump in sample temperature to 249 °C near 0 seconds is from the hydrogen gas addition. The

hydrogen increases heat transfer between the sample and the conflat vessel walls which are held at 250 °C by the temperature controller.

Pressure in the conflat vessel was maintained between 4.17 and 4.35 psia for the duration of the test by the pressure regulator. Hydride formation causes the supply pressure decrease observed over the first 400 minutes. Analysis of the data shows the foil reached an H/Ti of  $2.05 \pm 0.06$ . The temperature controller was switched off at approximately 1100 minutes.

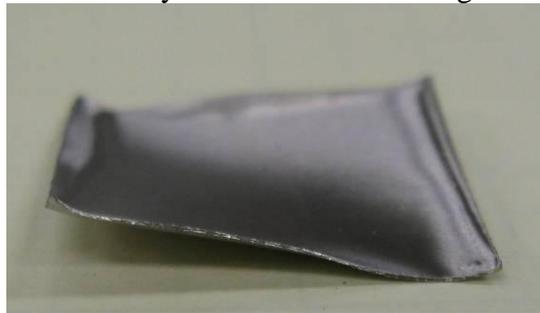
Figure 6 shows the HCRH sample from Figure 5 before and after hydriding.



**Figure 6: HCRH sample before (left) and after hydriding at 250 °C.**

The foil breaks itself up during the test. At these temperatures the HCRH foil is only active for hydrogen absorption on the palladium coated side. According to the adherent-layer hydride model, [24], the hydride phase develops and grows inward from the active surface. There is substantial, about 22%, volume growth during hydride formation which must be accommodated. Unconstrained HCRH foils have been observed to bend and curl dramatically during hydriding and to eventually break into similar sized pieces. The internal stresses that develop in foil combined with the brittleness of the hydride phase ( $\delta$ -phase, Ref. [11]) lead to the fracturing seen in Figure 6.

If the foil is not fully hydrided, then it is predicted that a layered structure of titanium hydride and alpha phase titanium exists [15, 24]. Alpha-Ti is ductile and can accommodate some of the expansion stress by a combination of elastic and plastic deformation. Figure 7 shows a nearly identical piece of HCRH foil that was hydrided to a bulk-average H/Ti of 1.07.

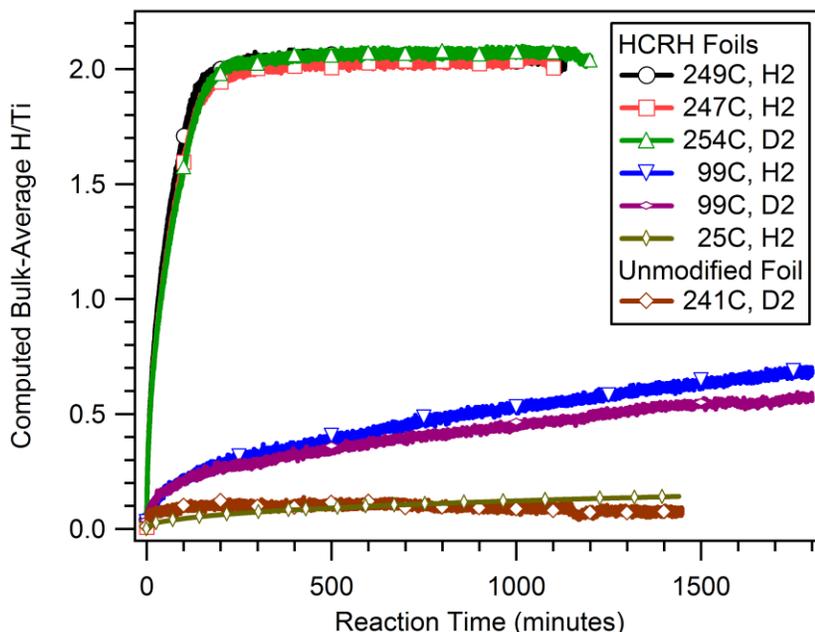


**Figure 7: Sample of HCRH foil hydrided at 100 °C for 75 hours, reaching a bulk-average H/Ti of 1.07.**

The palladium coating is on the bottom surface. This sample was clamped between frits during hydriding. However, it curled noticeably when released from the fixture, presumably due to residual elastic stress. This is consistent with a hydride phase that develops and grows inward

from the active surface in a one-dimensional manner – a morphology assumed by the adherent-layer hydride model discussed in section 2.3.

Samples of unmodified titanium foil and HCRH were tested at Sandia with hydrogen and deuterium gas at temperatures of approximately 100 and 250 °C and pressures of 4 to 5 psia. In addition, HCRH lot acceptance test data was provided by SAES at 25 °C and 0.15 psia in hydrogen gas. Figure 8 shows the computed bulk-average H/Ti for the tests.



**Figure 8: Computed bulk-average H/Ti for unmodified Alfa Aesar titanium foil and SAES HCRH material. The 25 °C data was taken by SAES at a pressure of 0.15 psia. The other tests were done by Sandia at pressures between 4 and 5 psia.**

Figure 8 shows a number of things. First, the unmodified titanium foil has essentially no deuterium uptake at 241 °C; especially when compared to palladium coated HCRH samples. This confirms that an unmodified titanium surface is not sufficiently active for hydrogen absorption at the temperatures of interest for the TTG (around 250 °C).

Second, HCRH foils absorb hydrogen isotopes at all temperatures, however at varying rates<sup>1</sup>. At temperatures near 250 °C, the HCRH attained a bulk-average H/Ti  $\approx$  2.0, as predicted by accepted pressure-composition-temperature correlations [11]. The 100 and 25 °C tests stopped before the foil could reach the ultimate H/Ti of 2.0 that is predicted by thermodynamics.

## 2.3 Discussion

There has been substantial investigation of the kinetics of metal hydride formation and this information can be used to help interpret the experimental results. Our results will be interpreted

<sup>1</sup> Each sample had identical thicknesses (150  $\mu$ m) and nearly the same active surface area (3.7 cm<sup>2</sup>) so the H/Ti data can be compared directly.

using the Mintz-Bloch model, to help understand the temperature and time dependent kinetics, and compared with Efron *et al.*'s work on vacuum activated titanium.

### 2.3.1 Mintz-Bloch Hydriding Model and Efron *et. al* Results

In Ref. [24], Mintz and Bloch develop a model for the hydriding of metals by hydrogen gas. One form of the model has been found by Efron *et. al* to be appropriate for the titanium-hydrogen system at pressures between 30 and 450 torr and temperatures between 100 and 250 °C [15]. This particular form assumes that the rate of hydride formation in a bulk sample is controlled by diffusion of hydrogen through an adherent metal-hydride layer.

This model assumes an adherent, continuous, hydride film forms on the surface of the metal and remains unfractured during the course of the reaction. It is further assumed that the overall reaction rate at the metal-hydride interface is controlled by diffusive transport through the hydride film. In other words, absorption from the gas phase and formation of the hydride at the hydride-metal interface are assumed to be much faster than diffusion through the hydride layer. It is also assumed that hydrogen is accommodated in the interstitial sites of the hydride lattice as a neutral particle. This simplifies the theoretical treatment to diffusion of a single uncharged specie which can be described by a single diffusion equation (for the mobile hydrogen dissolved in the hydride lattice). The treatment of the diffusive flux is further simplified by assuming quasi-steady conditions in the hydride layer (i.e. a linear concentration profile) [24].

For a plane sheet reacting at one surface the following rate law is obtained,

$$\alpha = \frac{\sqrt{2}}{L} \frac{d_h}{d_m} \left( \frac{M_m}{M_h} \right)^{1/2} k_D^{1/2} t^{1/2}, \quad 1$$

where  $\alpha$  is the reacted fraction of metal,  $L$  is the initial thickness of the metal sheet,  $d_h$  is the mass-density of the hydride,  $d_m$  is the mass density of the metal,  $M_m$  is the formula weight of the metal,  $M_h$  is the formula weight of the hydride,  $k_D$  is a pressure and temperature dependent diffusion rate constant, and  $t$  is the time the metal surface has been exposed to hydrogen gas.

The displacement of the hydride front into the parent metal,  $x_p$  is given by the product  $\alpha L$  for a plane sheet. As mentioned previously, the hydride front displacement,  $x_p$ , can be inferred from the bulk-average stoichiometry of a partially hydrided sample if a hydride-layer stoichiometry is assumed<sup>2</sup>.

The pressure and temperature dependent diffusional rate constant,  $k_D$ , is related to the concentration of excess hydrogen dissolved in the hydride,  $Z_0$ , the lower-limit of the single-phase region,  $Y$ , and the diffusion coefficient of the mobile hydrogen dissolved in the hydride lattice,  $D$ ,

$$k_D(P,T) = \frac{Z_0(P,T)}{Y(T)} D(T). \quad 2$$

It should be noted that this is a simplified expression for  $k_D$  where  $Z_1 \ll Z_0$  is assumed and the diffusion coefficient is assumed to be concentration-independent [24].

---

<sup>2</sup> For titanium, we assume the hydride stoichiometry is H/Ti=2.0.

The quantity  $k_D$  is an inherent kinetic parameter that describes the overall hydride reaction. In general it can depend on pressure and temperature but is always independent of sample geometry. The temperature dependence is usually dominated by the temperature dependent diffusion coefficient, which often obeys an Arrhenius relation,

$$D(T) = D_0 e^{-E_D/kT}, \quad \mathbf{3}$$

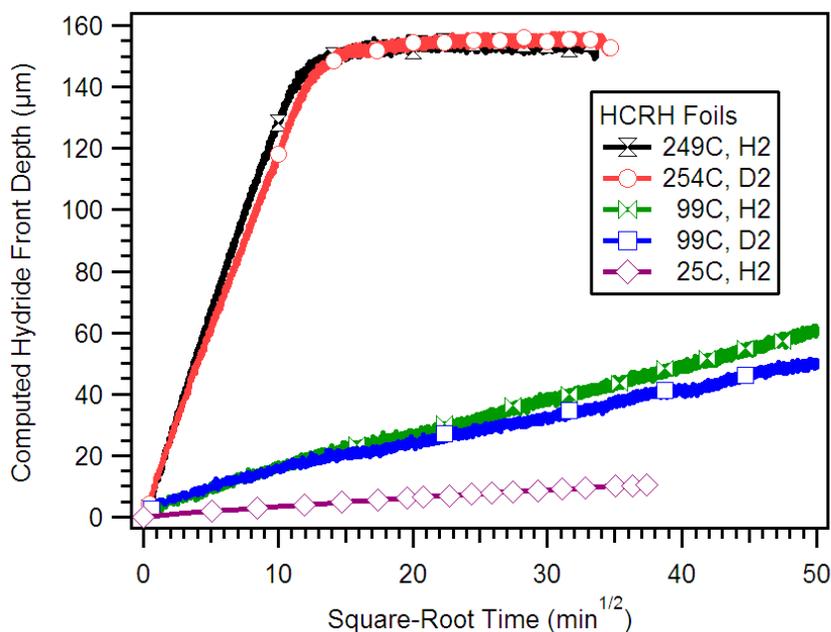
where  $D_0$  is the pre-exponential constant,  $E_D$  is the activation energy,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature.

Equation 1 predicts that the hydride front displacement will have a  $t^{1/2}$  dependence at a particular temperature and pressure and,  $k_D$  can be found from the slope of  $x_P$  vs.  $t^{1/2}$ . Furthermore, if  $Z_0$  and  $Y$  are weakly temperature dependent then an Arrhenius plot of  $\ln(k_D)$  vs.  $1/T$  will give a straight line.

Efron *et. al.*'s experiments on vacuum annealed/activated titanium samples show, fairly conclusively, that the adherent hydride layer diffusion model is appropriate for the titanium-hydrogen system at pressures between 30 and 450 torr and temperatures between 100 and 250 °C [15]. Their experiments also show that  $Z_0$  and  $Y$  are weakly temperature dependent; which is expected given the pressure-composition-temperature characteristics of the titanium-hydrogen system [11]. In addition, they observed that, after some time, the thickening protective hydride layer reaches an apparently constant thickness for diffusion – presumably from cracking at the hydride-gas interface. This constant effective thickness implies a  $t^1$  dependence for hydride front displacement and hence a constant hydriding rate. The maximum thickness is temperature dependent, ranging from about 10  $\mu\text{m}$  at 100 °C to 90  $\mu\text{m}$  at 250 °C [15].

### 2.3.2 Comparison of Results

The first test of the Mintz-Bloch model is to plot the computed hydride front depth against  $t^{1/2}$ . If the hydriding rate follows the derived law, then the data should fall on straight lines (provided the protective hydride layer remains intact). Figure 9 shows the inferred hydride front depth of the HCRH foil samples vs.  $t^{1/2}$ .



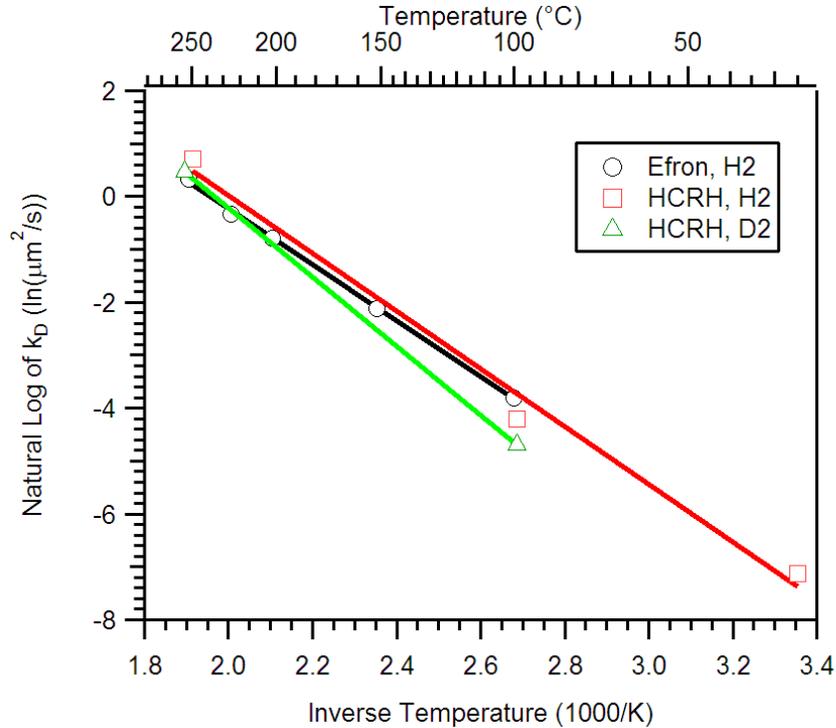
**Figure 9: Hydride front penetration for palladium coated samples plotted against square-root time.**

All of the samples show a hydride front displacement proportional to  $t^{1/2}$  during nearly all of their reaction time. This is strong confirmation that diffusion through an adherent hydride layer controls absorption; just as Efron *et al.* observed for vacuum activated titanium. It therefore appears that hydrogen adsorption and dissociation at the palladium surface, transport through the palladium layer, and transport across the palladium-titanium interface are all significantly faster than diffusion through the hydride layer under all pressure-temperature-time conditions in this study.

In contrast with Efron *et al.*'s results, the HCRC foil data shows no evidence of the assumed hydride layer cracking reported on 1000  $\mu\text{m}$  thick samples in Ref. [15]. At 250  $^{\circ}\text{C}$ , the front depth retains  $t^{1/2}$  dependence for almost the full thickness of the foil (150  $\mu\text{m}$ ). At 100  $^{\circ}\text{C}$  the hydride film still appears to be intact at 60  $\mu\text{m}$ . Reference [15] reports a maximum protective layer thickness of 92  $\mu\text{m}$  at 250  $^{\circ}\text{C}$  and 11  $\mu\text{m}$  at 100  $^{\circ}\text{C}$ . Perhaps the thinness of the HCRH allows the unreacted Ti-metal substrate to accommodate the hydride layer expansion. Further study is needed to explain these observations.

The diffusional rate constants,  $k_D$ , were found by least-squares linear regression of the data in Figure 9. The data points are shown with corresponding least-squares regression lines fit in  $\ln(k_D)$  vs.  $1/T$  space<sup>3</sup>.

<sup>3</sup> Fitting in this coordinate system assumes equal relative uncertainty among points in a particular data set. It therefore gives equal weighting to all  $k_D$  points. This assumption is consistent with our measurement uncertainty and important because, in some cases, the high and low values differ by a factor of nearly 400.



**Figure 10: Arrhenius plot of  $k_D$  vs. temperature comparing data from Ref. [15] with results from palladium coated samples.**

A number of conclusions can be drawn from Figure 10. First, HCRH samples and vacuum activated titanium behave nearly identically. Palladium coating is therefore a very effective method for creating an activation-free hydrogen-adsorbing surface on bulk titanium metal. Second, because  $\ln(k_D)$  vs.  $1/T$  forms a straight line,  $Z_0$  and  $Y$  must be weakly temperature dependent under these conditions – as is expected based on the accepted pressure-composition-temperature relations [11].

Also, HCRH-hydrogen and Efron data show similar activation energies for  $k_D$  and therefore  $D$ . The activation energy is approximately 0.46 eV which corresponds closely to values measured for diffusion of hydrogen in titanium hydride using nuclear magnetic resonance methods, 0.51 eV, [27].

Finally, HCRH deuteriding rate constants are similar to hydrogen with slightly higher activation energy. This gives a very similar  $k_D$  and hence uptake kinetics in the temperature range of interest for heat source loading, 200 to 250 °C. It is therefore reasonable to conclude that loading HCRH with a mixture of deuterium and tritium will proceed at a rate that is very similar to what is observed for pure hydrogen and pure deuterium.

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### 3 HEAT-SOURCE DESIGN AND DEUTERIUM/TRITIUM LOADING

Having measured the hydriding kinetics of HCRH, we then could design a heat source vessel and an experiment to demonstrate the loading process at a configuration and scale appropriate for the TTG component.

In the TTG design, the total stoichiometry of the hydride, (D+T)/Ti, was selected as 1.90. Deuterium and tritium stoichiometries are therefore D/Ti = 1.49 and T/Ti = 0.41. This is high enough to keep the hydride in the single-phase region<sup>4</sup>, (D+T)/Ti ≥ 1.50, for the TTG lifetime, yet low enough to keep tritium overpressure down (eliminating the container-vessel tritium compatibility issue).

A loading time of approximately ten hours was selected for the demonstration. Ten hours balances the production-motivated desire for short loading time with the desire to limit loading temperature to less than 300 °C. More importantly though, a controlled loading time on the order of 10 hours limits hydride-reaction heat generation to about 5 watts. Limiting the heat generation rate will be important when loading a TTG assembly because the heat source vessel is well insulated and we don't want its temperature to exceed 300 °C. Granted, 5 W is significantly more heat than the TTG generates at beginning of life (about 0.45 W) however we believe the heat can be managed because, at this stage of assembly, the vacuum jacket will be filled with gas, significantly increasing its thermal conductance.

Using the hydride model and data in this report, it can be shown that a maximum temperature of 250 °C and 10 hours limits the titanium thickness to approximately 250 μm. Commercially available, 150 μm thick, HCRH was therefore selected as the titanium material. An initial temperature of 230 °C should enable complete hydride of this material in about 6 hours. During loading, a pressure regulator and flow restriction were used to control the D<sub>2</sub> and T<sub>2</sub> inflow rate, lengthen the reaction time to 10 hours, and thereby limit the hydriding heat generation rate.

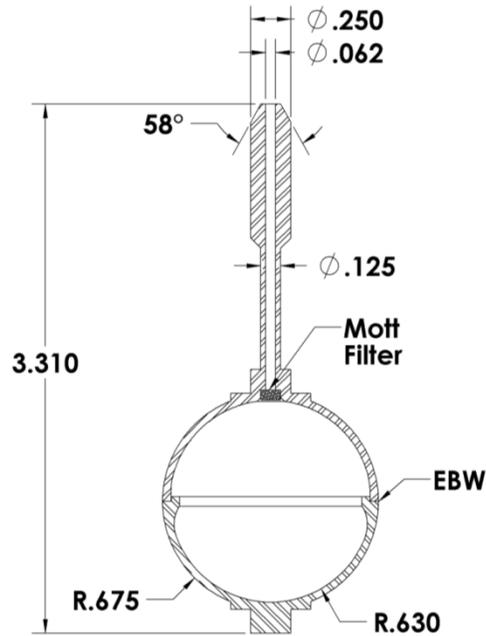
#### 3.1 Prototype Vessel Experiments

HCRH foil is available commercially in convenient 350×220×0.150 mm sheets. Disks can be punched from the sheets and stacked to give a roughly spherical shape with a controlled void fraction, ideal for the TTG assembly.

Full size prototype vessels were machined from weld critical annealed 304L SS barstock. Figure 11 is an assembly drawing of the component.

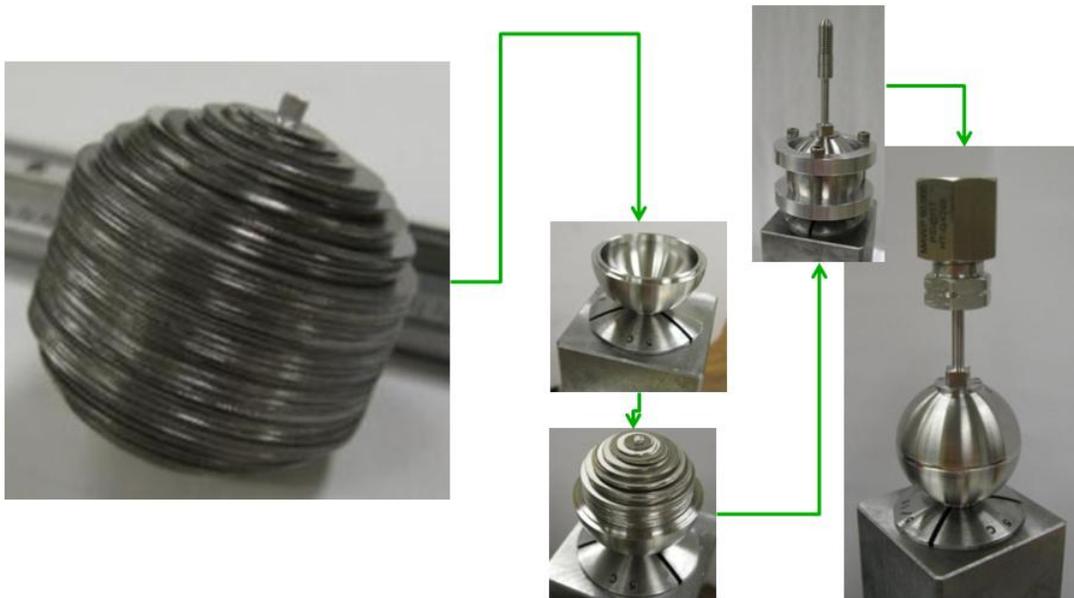
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<sup>4</sup> It seems prudent to keep the hydride in the single-phase region thereby eliminating the internal stresses associated with δ to α phase separation in the hydride matrix.



**Figure 11: Cross-section view of the heat-source vessel assembly (without disk-stack). The Mott filter is a .127-.062-1-20-A-OF 316SS sintered metal frit. Dimensions are in inches.**

Full-size, 350×220×0.150 mm, sheets of HCRH were purchased from SAES and cut into disks using two shim-stock punch and die sets purchased from McMaster Carr. A 0.062 inch diameter by 1.255 inch long 3003 aluminum tube passed through 0.125 inch holes in the disks and bound the stack. The stack was placed inside the vessel halves before they were joined by electron beam welding. Pictures of an assembly are shown in Figure 12.



**Figure 12: Prototype vessel assembly sequence.**

The vessel shells were designed to accommodate the full 53.6 gram titanium load. The vessel cavity included sufficient volume for: 1) the titanium, 11.9 cc; 2) additional free volume to accommodate swelling of the material caused by hydriding, approximately 22% or 2.6 cc; 3) free volume to allow for helium-3 induced swelling of the hydride as the titanium deuterio-tritide ages, estimated to be 12% or 1.7 cc; and finally 4) free volume to accommodate the small fraction of helium-3 that could be released from the titanium over its lifetime. These four contributions add up to the approximately 17.2 cc internal volume of the vessel. It was assumed that the free volume was sufficient to allow free gas passage between the foils, allowing the stack to hydride completely and uniformly. The loading tests described below were done to check this assumption.

### 3.1.1 Pure-Deuterium Process Development Tests

Four vessels were made with three different disk loadings. Table 1 shows the stack configuration in each vessel.

**Table 1: HCRH disk stack configurations for tests 1 through 4.**

Disk Diameter (inches)	Number of Disks (n/a)			
0.250	6	6	6	6
0.375	6	6	6	6
0.500	10	8	8	8
0.625	10	10	10	10
0.750	16	12	12	12
0.875	20	16	18	16
1.000	28	24	26	24
1.125	78	68	71	68
Measured total weight (grams)	53.603	45.816	48.098	46.970

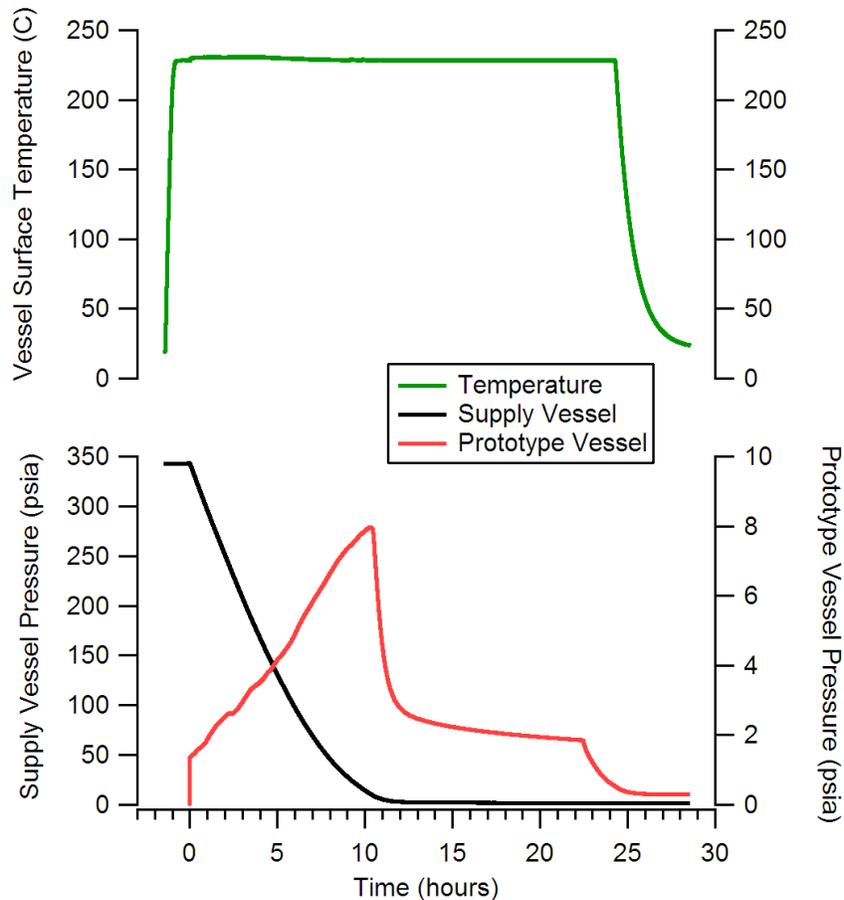
Each vessel was hydrided using the procedure described below.

#### 3.1.1.1 Test Procedure

The hydriding apparatus described in section 2.1.3 was also used for these tests. However, a 500 psia Teledyne Taber model 209 transducer was installed and the supply section fill pressure was increased to between 372 and 330 psia (depending on the titanium load). The vessel temperature was controlled by submerging it in a stirred silicone oil bath held at 230 °C by a hot plate, heat tape, and an Omega temperature controller. A type-K surface mount thermocouple was clamped to the vessel and used to monitor surface temperature. Additional thermocouples measured the bath temperature. The same 500 sccm rated Mott flow restriction was used to control the gas inflow rate; the pressure regulator setting was changed to 10 psia to give an approximately 10 hour load time.

#### 3.1.1.2 Test Results and Discussion

Figure 13 shows the sample temperature and vessel pressures during one of the experiments.

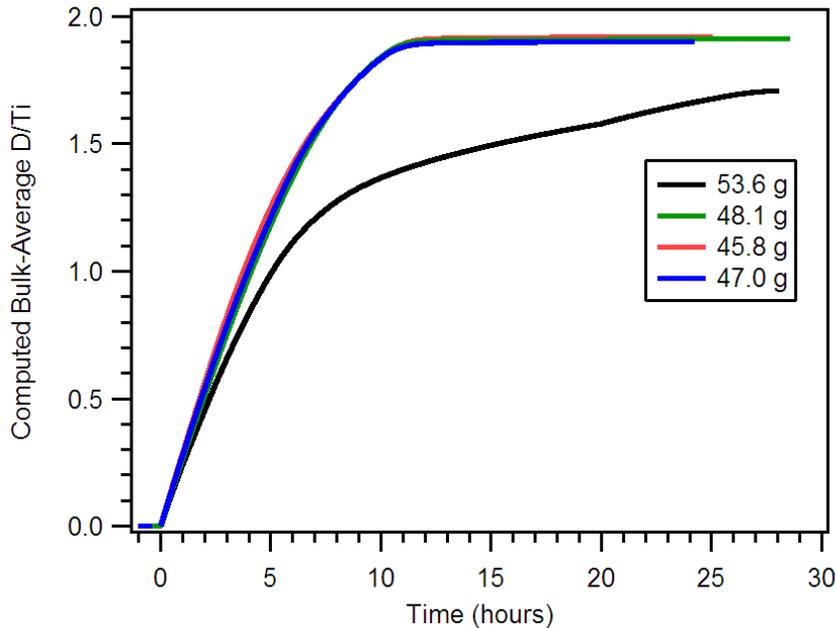


**Figure 13: Sample temperature and vessel pressures during the 48.098 gram vessel loading test.**

After V3 was opened at zero hours, hydriding began immediately. The corresponding heat generation was controlled enough that the vessel surface temperature did not increase by more than a few °C. Hydriding was rapid enough that the uptake was not limited by the kinetics of the reaction but by the conductance of the Mott restriction. This is shown by the prototype vessel pressure trace. The pressure is well below the regulator set-point for the majority of the hydriding reaction. The pressure climbs slowly during the test because the adherent hydride layer thickens which decreases the uptake rate.

The vessel pressure drops sharply at 11 hours because the deuterium in the supply vessel is depleted to below 10 psia, the regulator set point. At about 22.5 hours, the valve connecting the supply and prototype vessels, V3, is closed and the vessel pressure again drops quickly as the HCRH absorbs the deuterium in the ~16 cc receiver plumbing. The HCRH continues to absorb deuterium until the vessel is cooled to room temperature and the test is stopped. The final D/Ti of this sample is 1.91 as inferred from PVT measurements and 1.90 as determined from the vessel's pre and post test weights.

All four tests are compared in Figure 14. It shows the computed bulk-average D/Ti of the foil stacks during the experiment.



**Figure 14: Computed bulk-average D/Ti during the prototype loading tests.**

The 48.1, 45.8, and 47.0 g tests were all successful. The 53.6 g test however, failed. Each vessel was cut open after the test and the hydrided foils were examined. It was clear from the inspection that hydriding was not uniform the 53.6 g test. The foils expanded and moved around enough that parts of a number of the foils were progressively sealed off from deuterium gas as the stack hydrided. This prevented the 53.6 g stack from hydriding to D/Ti=1.90 during the test.

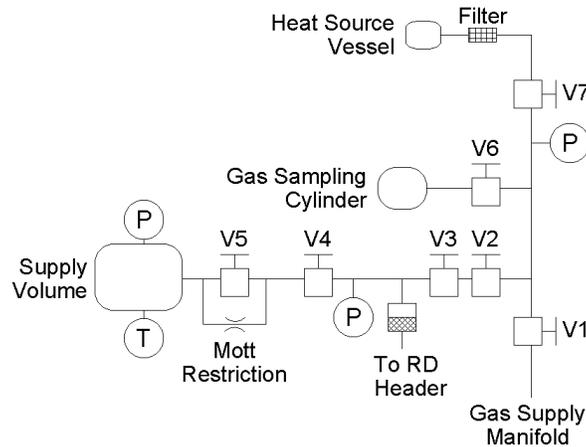
While the 48.1, 45.8, and 47.0 g stacks all loaded fully, we observed that the foils from the 48.1 g test were less uniformly hydrided than the foils from either the 45.8 or 47.0 g tests. The D/Ti and vessel pressure traces don't show much evidence of this but, portions of some of the foils became sealed off during hydriding. Because of this observation, we selected 45.8 grams as the optimal load for the prototype heat source vessels. Future experiments will enlarge the containment vessel proportionally to contain the as-designed titanium load.

### 3.1.2 Tritium Loading Tests

#### 3.1.2.1 Loading apparatus and procedure

Tritium loading was performed at the Department of Energy's Savannah River Site on dedicated tritium handling equipment. As one might imagine, the infrastructure required to prepare, purify, and handle gram-scale quantities of tritium is elaborate. Reference [28] gives an overview of the various processes and systems in-place at SRS. We will limit our discussion to the loading manifold and vessel temperature-control that were used for these experiments.

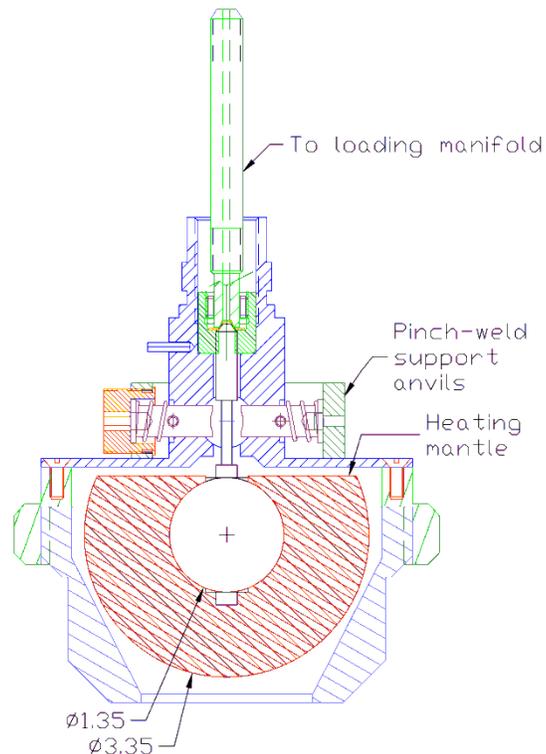
The tritium loading apparatus was similar to the apparatus used at Sandia (Figure 2). However, two important changes were made.



**Figure 15: SRS loading manifold.**

First, unlike in the Sandia apparatus, there are no pressure regulators upstream of the Mott restriction. They were eliminated for simplicity. Instead, the Mott restriction was sized to limit the initial flow rate to approximately 100 std-cc/min (equivalent to 5 W of heat generation from the hydriding reaction) and the supply volume was over-filled with 1.5 times more gas than required to hydride the prototype vessel to  $(D+T)/Ti=1.90$ . The restriction size and overfill ratio were balanced to achieve complete loading in 10 hours. During loading, the supply volume pressure was monitored and V2 was closed when the titanium hydride stoichiometry reached the target value of 1.90.

Second, because loading was done on an SRS production line, inside a tritium-containment glovebox, the silicone oil bath used in the Sandia apparatus was eliminated in favor of the fixture shown below.



**Figure 16: SRS pinch weld fixture. Dimensions are in inches.**

The fixture positions the vessel stem for pinch-weld closure<sup>5</sup> upon completion of the gas load. The vessel is heated by a custom-made Glas-Col heating mantle that surrounds the bottom half of the bottle. The temperature environment provided by this arrangement is less uniform than an oil-bath. Significant development effort went into characterizing and improving vessel temperature uniformity before tritium loading experiments were performed. In the final fixture configuration, surface-mount type-K thermocouple measurements indicate that the temperatures are 220, 230, and 250 °C near the stem-end, at the waist, and at the opposite end of the vessel when the Watlow-F4 temperature controller was set to give a mid-bottle temperature of 230 °C (the corresponding controller set-point and internal mantle-temperature are both 310 °C). While not ideal, this level of temperature stratification was deemed acceptable.

Deuterium/tritium gas mixtures were prepared upstream of the loading manifold; by blending high purity deuterium and tritium gasses in a large mix-tank per established procedures. The mixture was pumped to the loading manifold supply volume by gas compressors similar to the ones described in Ref. [28]. Prior to loading, gas analyses were performed on the mixtures used in both tests; the results are given below.

<sup>5</sup> A special type of resistance welding similar to spot welding

**Table 2: Gas mixture analysis. Quantities are mole-%.**

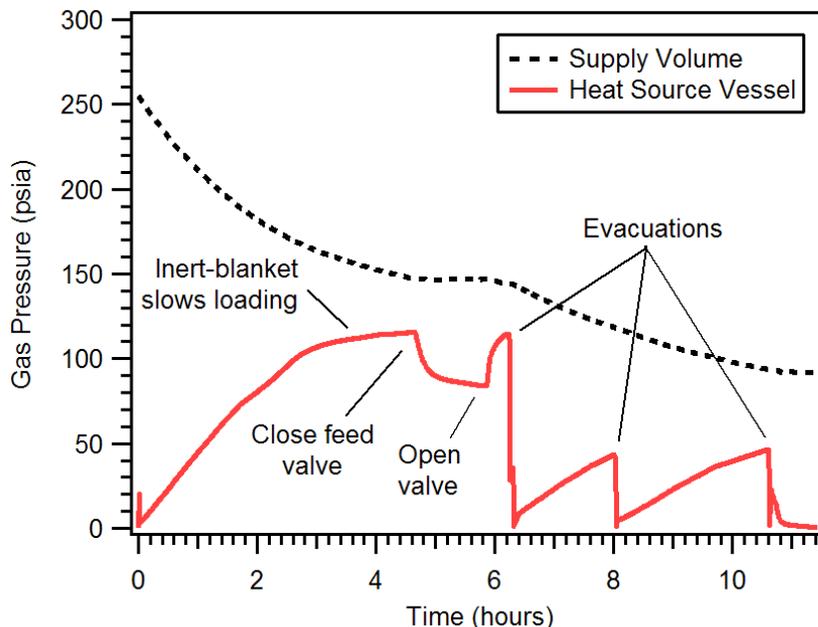
	Load #1 BBN-x1023 (45.600±0.001 g HCRH)	Load #2 BBN-x1024 (45.600±0.001 g HCRH)
Protium (H)	0.132	0.136
Deuterium (D)	78.219	78.290
Tritium (T)	21.490	21.472
Helium-3 (He-3)	0.150	0.094
N <sub>2</sub> /CO	0.009	0.008

At the analysis time, a few hours before loading, the gas mixtures are both approximately 99.9% hydrogen isotopes, 0.1% helium-3, and 0.01% N<sub>2</sub>/CO. The helium-3 impurity forms continuously due to tritium decay. The N<sub>2</sub>/CO impurity is expected to be nearly pure N<sub>2</sub>; as N<sub>2</sub> is used as a purge gas in the loading manifold.

The procedure for loading the vessels was to: (1) place the vessel in the fixture; (2) evacuate and perform rate-of-rise leak tests on the manifold; (3) fill the supply volume with the specified quantity of gas; (4) heat the vessel to a mid-bottle temperature of 230 °C under dynamic vacuum (~100 mtorr) and hold at temperature for two hours; and (5) open the supply volume to the vessel which begins the load.

### 3.1.2.2 Test results and discussion

Figure 17 shows measured gas pressures during load #1.



**Figure 17: Supply volume and heat source vessel pressures for load #1 (BBN-x1023).**

The initial rate of gas absorption for x1023 was 111 std-cc/min. At about 3 hours, the rate of gas absorption slowed noticeably. This was caused by inert (helium) blanketing. The small, yet significant, amount of inert gases present in the supply gas (<sup>3</sup>He 0.150 mole%, N<sub>2</sub>/CO 0.009 mole%) accumulate in the heat source vessel as the hydrogen isotopes absorb into the titanium

foil. As the concentration of inert species in the heat source vessel increases, hydrogen transport to the titanium foil decreases.

To continue loading, V2 was closed and the heat source vessel was evacuated, removing the inert gases from the inner bottle and adjoining piping. The supply volume valve was then opened and loading resumed. This procedure was performed three times with a total gas loss of 0.016 mol. This gas was included in the mass balance used to compute the titanium bed stoichiometry from measured pressure-volume-temperature (PVT) data. The evacuated gas composition was assumed to be identical to the feed gas for this calculation. This is a reasonable assumption because about 80% of the volume between V2 and the heat source vessel is the connection plumbing.

During the second load, BBN-x1022, inert blanketing was better anticipated. The evacuation procedure was performed three times: twice before the rate of absorption had decreased to zero, and a final time prior to the last 30 minutes of the load. This reduced the load-time to less than 8 hours.

During loading the heat source vessel temperature increased; due to the exothermic hydride reaction. Because of radiological waste considerations, the tritium loaded vessels were not instrumented. However, deuterium-only load-development tests performed at SRNL and Sandia indicate that, in the relatively poorly heat-sunk loading fixture, the mean vessel temperature climbs from 230 °C to 285 °C during initial loading; and then slowly returns to 230 °C as loading proceeds (as the hydriding rate decreases). This temperature excursion could be greatly reduced with better heat sinking and improved fixture temperature control.

Calorimetry measurements were used to verify the PVT results and to more directly measure the mass of tritium loaded (tritium-decay is exothermic, producing 0.324 W/g [29]). Calorimetry indicated that BBN-x1023 contained  $1.167 \pm 0.003$  g of tritium at time of measurement ( $1.170 \pm 0.003$  g at time of loading). This is in good agreement with the PVT-derived value, 1.170 g (at time of loading). The level of agreement was similar for BBN-x1022, with  $1.169 \pm 0.002$  g and 1.175 g of tritium for calorimetry and PVT analysis respectively.

Both tests demonstrated that a full scale TTG heat source vessel: could be loaded using existing tritium handling infrastructure, in a reasonable amount of time, and at temperatures that are compatible with current thermoelectric module technology. Additional engineering work is needed to develop fixtures and heat-sinking methods for loading a nearly-complete TTG assembly (in a similar state to that shown in Figure 1).

## 4 CONCLUSIONS

This study has shown that palladium coating allows titanium to be loaded with hydrogen isotopes without requiring a 400 to 500 °C vacuum-activation step. Also, we have found that the hydriding kinetics of commercially available sputter cleaned and Pd-coated titanium can be described by the Mintz-Bloch adherent film model which assumes that the rate of hydride formation is controlled by diffusion of hydrogen through an adherent metal-hydride layer. Furthermore, hydriding rate constants for palladium-coated and vacuum-activated titanium are nearly identical; showing that palladium coating is an effective method for creating an activation-free hydrogen-adsorbing surface on bulk titanium metal. Finally, our measurements provide kinetic data useful for designing Pd/Ti hydrogen getters or storage beds.

Full-scale deuterium and deuterium/tritium loading experiments were done on stacks of commercially available palladium coated titanium foils (SAES HCRH) in a representative-size radioisotope heat source vessel. These experiments demonstrated that a titanium-tritide bed can be loaded completely, at acceptable temperatures (below 300 °C), in a reasonable amount of time (10 hours), using existing department-of-energy tritium-handling infrastructure. Additional engineering work would be needed to develop fixtures and heat-sinking methods for loading a nearly-complete TTG assembly.

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