Method for Measuring Deuterium in Erbium Deuteride Films

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Abstract

Determining the quantity of deuterium in an erbium deuteride (ErD_2) film is essential for assessing the quality of the hydriding process but is a challenging measurement to make. First, the ideal gas law cannot be applied directly due to high temperature (950°C) and low temperature (25°C) regions in the same manifold. Additionally, the metal hydride does not release all of the deuterium rapidly upon heating and metal evaporation occurs during extended heating periods. Therefore, the method developed must provide a means to compensate for temperature inhomogeneities and the amount of deuterium retained in the metal film while heating for a minimal duration. This paper presents two thermal desorption methods used to evaluate the kinetics and equilibria of the deuterium desorption process at high temperatures (950°C). Of primary concern is the evaluation of the quantity of deuterium remaining in these films at the high temperature. A multiple volume expansion technique provided insight into the kinetics of the deuterium evolution and metal evaporation from the film. Finally a repeated pump-down approach yielded data that indicated approximately 10% of the deuterium is retained in the metal film at 950°C and approximately 1 Torr pressure. When the total moles of deuterium determined by this method were divided by the moles of erbium determined by ICP/AES, nearly stochiometric values of 2:1 were obtained for several erbium dideuteride films. Although this work presents data for erbium and deuterium, these methods are applicable to other metal hydrides as well.

Acknowledgments

Contents

Figures

Tables

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Introduction

Erbium films are used for the long term storage of hydrogen isotopes. These films are produced by evaporating erbium under vacuum and at elevated temperature onto molybdenum substrates. The pure erbium film is then loaded with deuterium gas for storage in the stable, dideuteride form. Present applications call for films from one to ten microns in thickness. As a dihydride, these films have a uniform "robin's egg" blue appearance. Despite this visual indication, it is very important to assure that the entire film is in the dideuteride form for long term stability. This paper outlines a procedure that can be used to verify this state.

In order to determine the quality of the hydride film, the quantities of erbium and deuterium must be accurately measured. The essential idea underlying the measurement process is to thermally desorb and measure the deuterium released from the film, followed by a wet chemical analysis to determine the erbium content. The erbium measurement is straightforward using inductively coupled argon plasma atomic emission spectroscopy (ICP/AES). The measurement of the deuterium is more difficult as it must be outgassed from the erbium at elevated temperatures without removing or damaging the erbium. This measurement is further complicated by the temperature and pressure dependence of the gas/solid equilibria in these films[1-13], the kinetics of the desorption process[3,13] and experimental difficulties associated with making measurements at high temperatures.

This paper presents a method for determining the quantity of deuterium contained in an erbium deuteride film that is based on desorption of deuterium during a temperature ramp. Consideration is given to the kinetics of the deuterium outgassing, metal decomposition, and the gas/solid equilibrium. Also noted are the practical considerations that must be evaluated when performing this type of analysis.

Theory

The figure of merit for evaluating the quality of the erbium deuteride film is

$$R = \frac{n_D}{n_{Er}} \tag{1}$$

where R is the ratio of the moles of deuterium atoms, n_D, to the moles of erbium atoms, n_{Er}. A ratio of 2 indicates complete dihydride formation. The moles of erbium atoms are determined by ICP/AES after the moles of deuterium atoms have been determined following high temperature desorption of the deuterium gas from the film.

Since gas/solid equilibrium causes some deuterium to be retained in the metal even at high temperatures, the total number of moles of deuterium atoms is the sum of the moles of deuterium atoms in the gas phase following desorption n_D^{gas} and those retained in the erbium metal n_D^{metal}.

$$n_D = n_D^{gas} + n_D^{metal} \tag{2}$$

Quantitation of the desorbed deuterium will be described below and determination of the deuterium remaining in the metal will be discussed in a later section.

Given pure deuterium loading of the erbium film, gas phase deuterium can be found, in the desorption chamber, as both D_2 and HD (protium-deuteride) due to protium/deuterium exchange reactions at high temperatures. The sources for protium include residual hydrogen outgassed from stainless steel walls and adsorbed water in the system. The moles of deuterium atoms can then be expressed in terms of the total moles of gas in the chamber, n_{total}:

$$n_D^{gas} = n_{total}\left(2X_{D_2} + X_{HD}\right) \tag{3}$$

where the mole fractions of D_2, X_{D_2}, and HD, X_{HD} are determined from mass spectral analysis. The mole fraction for D_2 is multiplied by 2 since two deuterium atoms are obtained from each molecule of deuterium gas. Some deuterium atoms will also be lost from the gas phase to the surface of the manifold. However, the effect is assumed to be small and will be neglected. For the remainder of this paper, moles of deuterium will refer to moles of deuterium *atoms*, not molecules.

It would be desirable to be able to calculate the total moles of gas in the system by using the ideal gas equation:

$$n_{total} = \frac{PV}{RT} \tag{4}$$

where P is the pressure of a gas and V is the volume it occupies, R is the ideal gas constant, and T is the gas temperature. However, while pressure and volume are readily measured, temperature does not have a well defined meaning in the present experiment for several reasons. First, the only temperature reading is obtained from a thermocouple that is external to the sample tube, thus, while useful for controlling the furnace, it does not provide a value that can be directly inserted into the gas equation calculations. More fundamentally, the measurement system is not isothermal, with temperatures ranging from room temperature at the pressure gauge to nearly 1000°C at the sample tube, and thermal steady state is never achieved during the course of the experiment. However, if we make the assumption that the time-dependent temperature distribution within the measurement system will be reproducible for *identical* sets of experimental conditions (equipment configuration, P, V, temperature ramp rates, time-related parameter-switching profiles, etc.), then we can define an operational or effective system temperature T_{eff} at any instant during the experimental run. This is accomplished by loading the chamber with a known quantity n_{std} of nonreactive gas and observing its pressure P_{std}, as a function of time, when subjected to an *identical* experimental profile. T_{eff} is then simply defined as that value of temperature that satisfies the ideal gas law for the given n, P and V at time t during the run:

$$T_{eff}(t) \equiv \frac{P_{std}(t)V(t)}{n_{std}R} \tag{5}$$

where the potential time dependencies are explicitly shown. Equation 5 is general and makes no assumptions about the functional relationships between the individual parameters and time. It can, for example, account for instantaneous changes in system volume as will be shown below for the multiple volume expansion method. For arbitrary experimental profiles, Eq. 5 is most conveniently described and evaluated through the use of lookup tables.

Substituting T_{eff} for T in Eq. 4 and combining with equations 2 and 3, yields the final expression for n_D:

$$n_D = \frac{PV}{R\,T_{eff}}\left(2X_D + X_{HD}\right) + n_D^{metal} \tag{6}$$

Experimental

Figure 1 shows a schematic of the apparatus used to make these measurements. The sample, either pure D_2 gas or the erbium deuteride sample, is introduced into the quartz tube. The volume the gas expands into is labeled V_1 and consists of the quartz tube, manifold, and the pressure gauge. An oven is placed around the quartz tube for heating the sample and the stainless steel manifold is heated to 150°C ±2°C using heating tape to minimize water adsorption. On the outside of the quartz tube is the feedback thermocouple used to measure the indicated temperature and provide temperature feedback to the oven controller. Additional volumes, V_2 and V_3 were installed on the system for the multiple volume expansion experiments described later. The value of each volume is shown in Table 1. Mole fraction measurements were made by directly introducing the gas from V_1 into a calibrated mass spectrometer and measuring the % D_2 and % HD.
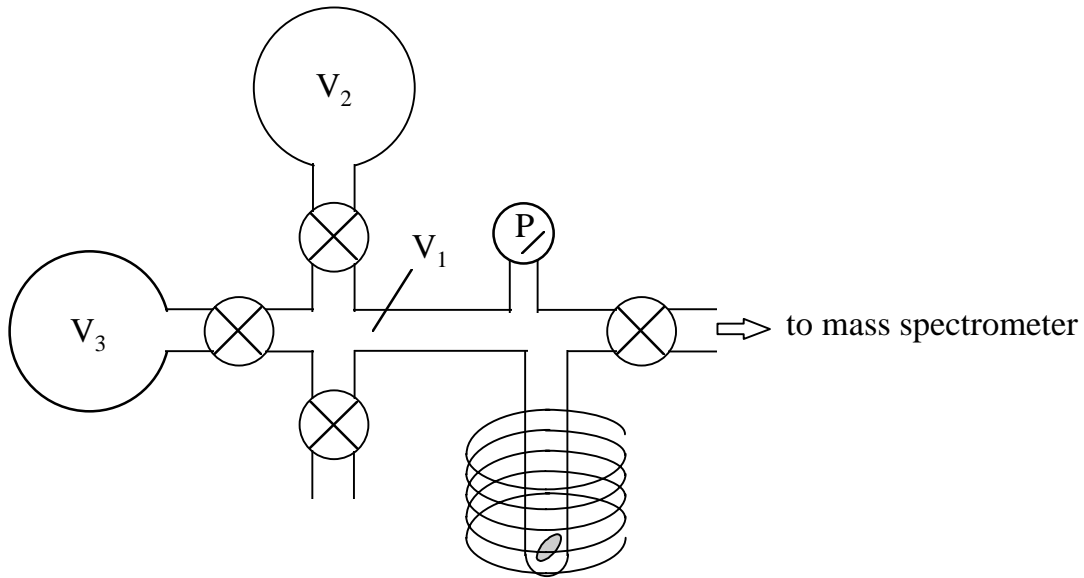

Figure 1. Experimental setup for the hydride outgassing experiments.

Table 1. Values for the calibrated volumes used in experiments.

Volume	Calibration Value (cm³)
V_1 (Repeated Outgassing Experiment)	396.0 ± 2.6
V_1 (Multiple Volume Expansion)	124.4 ± 0.1
V_1+V_2	424.4 ± 2.7
$V_1+V_2+V_3$	737.6 ± 1.0

Determining Moles Evolved from the Metal, n_D^{gas}

In order to maximize the amount of deuterium desorbed from the metal deuteride film while limiting thermally induced metal loss or film damage, a rapid thermal ramp method for determining n_D^{gas} was devised. The number of moles of gas evolved from the metal is determined by ramp heating the sample to a nominal 950°C at 100°C per minute. The sample is placed in the quartz tube, the thermocouple is placed against the outside of the tube and the tube furnace is closed. Next, the manifold is heated to 150°C to help remove moisture and adsorbed gases. The system is then evacuated overnight and the pressure is checked to assure system integrity. All valves to the mass spectrometer and additional volumes are closed. The system is ramp heated while the thermocouple temperature $T_{indicated}$ and pressure P are monitored. As shown in Figure 2, the sample begins outgassing at an indicated temperature of approximately 650° with the highest rate of outgassing occurring near 870°C. Once the system reaches an indicated temperature of 950°C, the heater is turned off and the quartz tube with the sample is allowed to cool as rapidly as possible to room temperature. Cooling is aided by opening the tube furnace. Following this cooling process, a sample of the gas is introduced into the mass spectrometer to determine the percentages of D_2 and HD present in the gas.
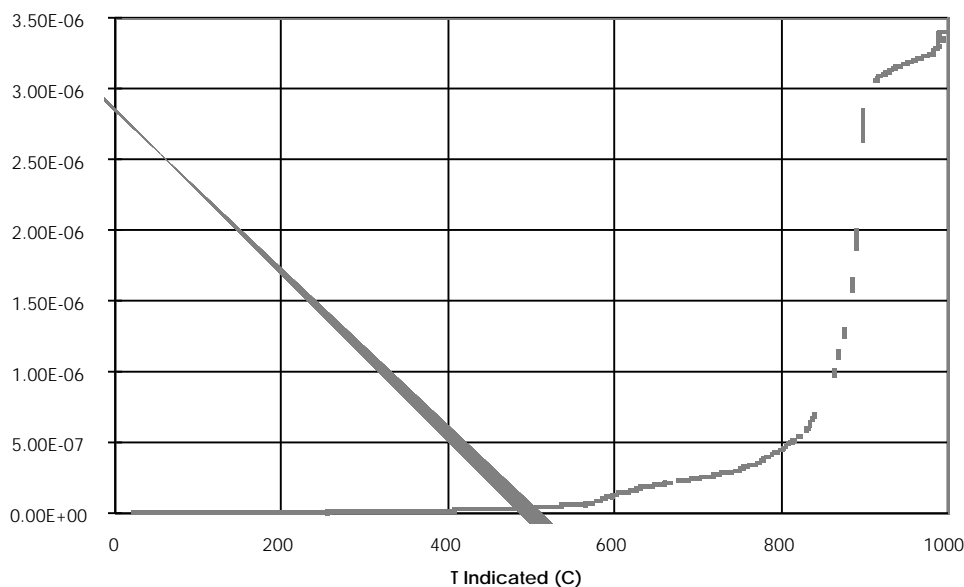
Figure 2. Moles of gas from an erbium deuteride film as a function of indicated temperature.

Since the sample reabsorbs some of the gas during cooling, there was a concern that the percentages of D_2 and HD determined from a gas sample at room temperature might differ from that present at high temperature following outgassing. During development, mass spectrometer analyses were performed at both high temperature ($T_{indicated}$ = 950°C) and at room temperature. This data indicated no significant differences between the compositions of gas samples taken at either temperature.

Calculation of n_D^{gas} also required that T_{eff} be determined for the particular temperature ramp that was used to desorb the deuterium from the film. In the present case, this was accomplished by introducing a known quantity of deuterium into the apparatus at a pressure similar to that which would be generated by an outgassed erbium deuteride sample. This gas sample was then subjected to the previously described temperature program.

Using Equation 5 to calculate the effective temperature, a plot similar to Figure 3 is obtained. The figure shows the effective temperature as a function of time. While the indicated temperature is being ramped, a nearly linear relationship exists between the effective and indicated temperatures.
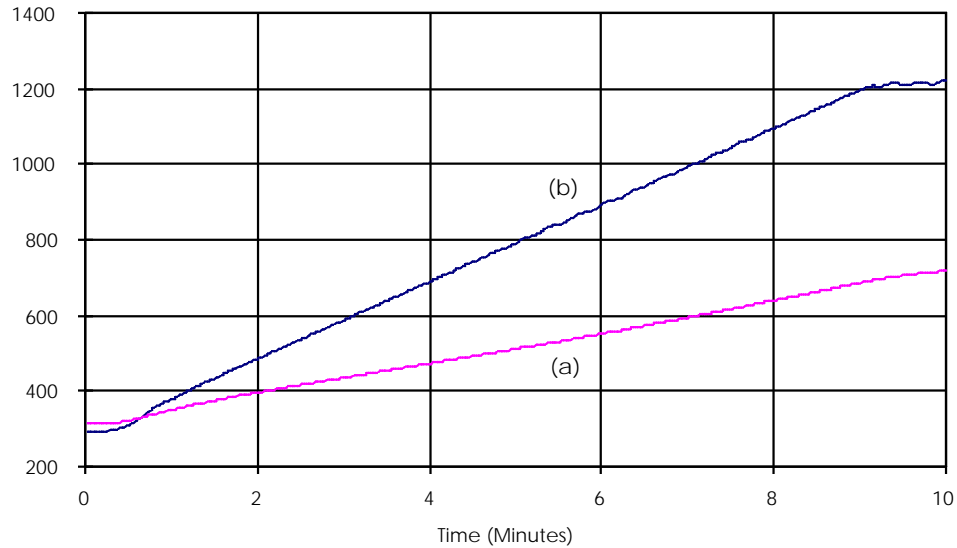
Figure 3. Plot of effective temperature (a) and indicated temperature (b) versus time for the standard deuterium fill for initial ramp.

The reproducibility of this measurement technique was verified by repeating the temperature ramp six times and computing the effective temperature at an indicated temperature of 950°C (1223°K). The results are shown in Table 2.

Table 2. Effective temperature of the manifold at and indicated temperature of 950°C (1223° K).

Run	Effective Temperature, T_{eff}
1	738°K
2	726°K
3	720°K
4	719°K
5	729°K
6	728°K
Average/Standard Deviation	**727 / 6.9 °K**

The data show that the calculated effective temperature was repeatable to within a relative standard deviation of 0.9% for these 6 trials. This means the system reaches, nominally, the same effective temperature each time when the temperature is ramped. Variations in room temperature of ±3°C did not seem to have a detectable impact on the measurement. This is probably due to the fact that the operating temperatures are much higher than 23°C.

Determining Moles Retained in the Metal, n_D^{metal}

The final variable in Equation 2 that must be determined is n_D^{metal}, the number of moles of gas retained by the metal film after the initial temperature ramp. Two methods were devised to characterize the outgassing process and determine the moles of retained deuterium. The first method was based on the working hypothesis that the quantity of deuterium retained in the film is determined solely by a gas/solid equilibrium process and that the desorption kinetics play, at best, a minor role. Under this assumption, it would be expected that the amount of retained deuterium would be a function of the deuterium partial pressure in the gas phase above the metal film, and that in the limit of zero equilibrium partial pressure, no deuterium would be retained. This suggests that it should be possible to decrease the deuterium partial pressure in a step-wise fashion, evolve deuterium to reestablish equilibrium and extrapolate the sum of this incrementally desorbed deuterium to the zero partial pressure limit.

In the present experiment, the pressure in the system was reduced by adding evacuated volumes to the system at specific times. The indicated and calculated effective temperatures are shown for the experiment-specific time/temperature profile in Figure 4, where again, deuterium was used as the calibration gas. The initial ramp to 950°C was followed by a hold at that temperature for approximately 33 minutes. At approximately 25 minutes, the valve to V_2 was opened and the effective temperature (Figure 4,b) dropped as expected (V_2 was at room temperature). At approximately 32 minutes, the valve to V_3 was opened and very little change in the effective temperature was noted. This was probably due to the proportionately small additional volume added.
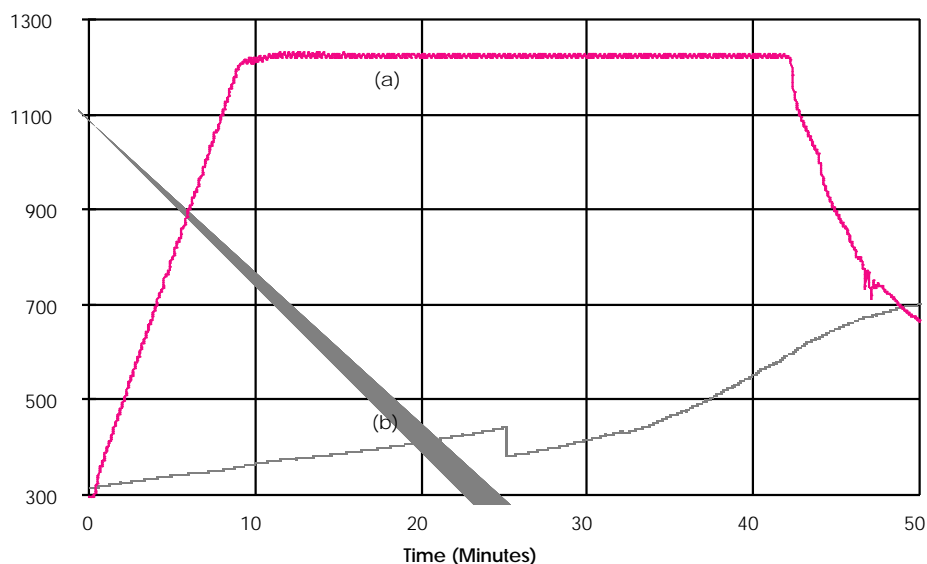

Figure 4. Plot of indicated temperature (a) and effective temperature (b) versus time for the standard deuterium fill for multiple volume expantion.

After determining T_{eff} for this time/temperature/volume profile, the erbium deuteride sample was outgassed using the same profile. The results of this experiment are shown in Figure 5. The majority of deuterium is desorbed in an initial release that occurs at approximately 8 minutes. A small amount of gas continues to be released during the constant temperature hold from 10 minutes to 25 minutes. When the V_2 valve was opened at 25 minutes, approximately 3% more gas was released by reducing the system pressure which shifts the equilibrium. Only a few tenths of a percent more gas was released at 32 minutes when V_3 was opened.
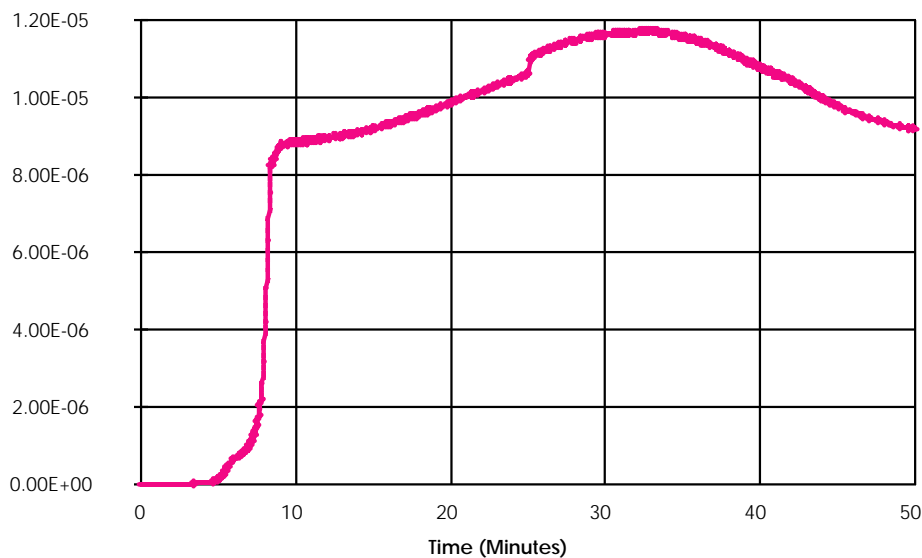

Figure 5. Plot of moles of gas evolved from an erbium deuteride sample versus time.

Although the results of the multiple volume expansion lent a good deal of insight into the desorption process, it also showed that this method was not suitable for making the desired measurement of retained deuterium. Desorption kinetics, for example, were shown to be important. If equilibrium had been quickly reached, the curve of evolved moles of gas as a function of time should have become flat with a slope of zero between volume increments. This was not observed, and gas continued to be evolved. More interestingly, in the region from 32 minutes to 42 minutes, while still maintaining an indicated temperature of 950°C, a *decrease* in the total gas moles was observed. This decrease can be explained by the evaporation and redeposition of the erbium[13] in cooler regions of the manifold. The redeposited erbium can then absorb deuterium which causes the observed decrease. This phenomenon actually has three unfortunate consequences. First, since erbium is acting as both a source and a sink, we can only measure the net change in moles of gas, there is no way to obtain the amount of desorbed deuterium as a separate quantity. Second, as some of the erbium film has evaporated, the subsequent metal analysis will be in error. Finally, and perhaps most importantly, the vacuum system will have been contaminated with a hydrogen getter that will bring into question the results of all future hydrogen analyses.

Taken together, the results of the multiple volume expansion experiment point out the critical need to minimize the time that the metal film is exposed to high temperatures and demonstrate that all of the deuterium can not be desorbed on a time scale that is consistent

with maintaining the integrity of the metal film. In order to minimize the time the sample spends at high temperature, the second method, the repeated outgassing method, was developed.

The repeated outgassing experiment consists of rapidly heating the metal hydride sample to a high temperature, cooling to room temperature, evacuating the manifold to remove the deuterium which was not reabsorbed, and then repeating the previous steps until the moles of deuterium pumped away is insignificant. As with the previous experiments, the chosen high temperature was nominally 950°C since it was above the temperature where the hydride outgasses rapidly.

The number of moles of gas pumped away after the ith outgassing cycle is calculated using the following equation:

$$n_i^{removed} = \frac{P_i V_i}{R T_i}\left(2 X_{D_2,i} + X_{HD,i}\right)$$

(8)

where P_i, V_i, and T_i are the pressure, volume, and temperature after equilibration of the entire volume ($V_i=V_1$ in this case) to room temperature prior to the ith removal of gas. Gas mass spectral analyses were performed at each outgassing cycle to determine X_{D_2} and X_{HD}. The absorbed gas, chemically bound to the erbium, is stable at room temperature so evacuating the volume containing the sample has little or no effect on the deuterium in the metal. The total moles of deuterium in the sample n_D are calculated as the sum of the deuterium gas removed during the evacuations and the deuterium found during the final high temperature outgassing n_k^{gas}.

$$n_D = n_k^{gas} + \sum_{i=1}^{k-1} n_i^{removed}$$

(9)

Figure 6 shows the cumulative amount of deuterium atoms removed during the pump down process. As can be seen from the figure, after about 7 runs very little deuterium remained in the gas phase (most of the deuterium is reabsorbed by the metal) indicating the absorption/desorption of deuterium in the metal film has become nearly reversible.
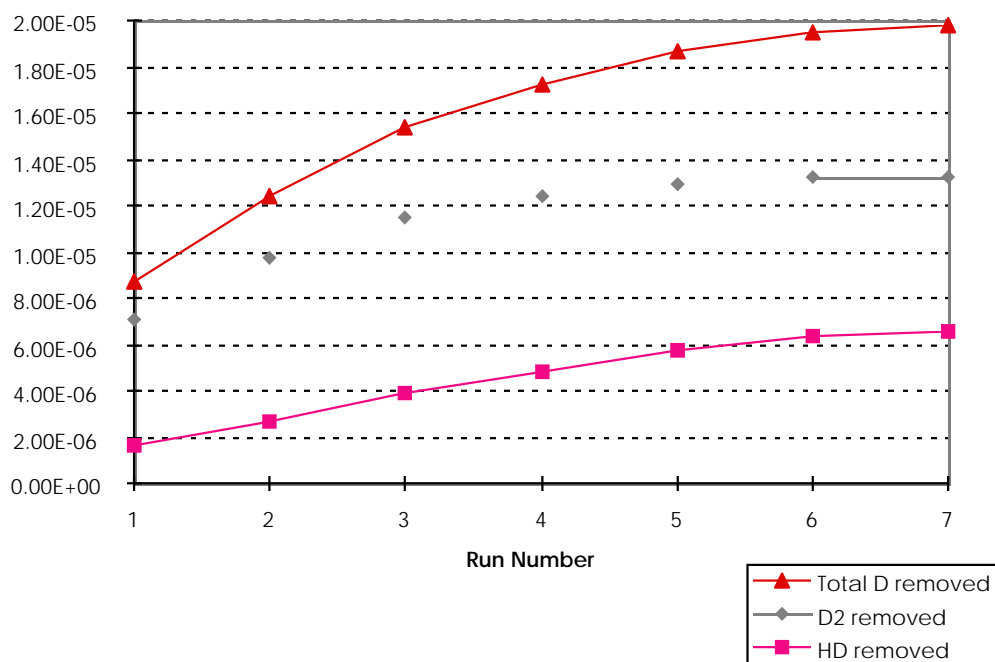
Figure 6. Cumulative amount of deuterium (D$_2$, HD and Total) removed during the pump down process. After about 7 runs very little deuterium remained in the gas phase after cooling.

Table 3 shows the moles of deuterium removed during each run and in the kth analysis, and the cumulative total moles of deuterium in the metal.

Table 3. Results of the repeated vacuum removal of deuterium between heating/cooling cycles. The data shows about 10% of the total moles of gas stored in the metal hydride was not measured (retained in the metal hydride) after the first run

Run No.	Cumulative D removed by vacuum prior to run (moles x 10^{-6})	Gas phase D from sample for each run (moles x 10^{-6})	Cumulative moles of D atoms n_D (moles x 10^{-6})	Amount left in Metal at 950°C (%)
1	-	17.82	17.82	10.7 %
2	8.71	9.79	18.50	9.5 %
3	12.39	6.24	18.63	7.4 %
4	15.36	3.46	18.82	5.6 %
5	17.25	1.90	19.15	4.6 %
6	18.70	0.81	19.51	3.8 %
7	19.50	0.23	19.73	*

*A small fraction of gas remaining in the disk at 950°C was not determined for this last run.

The data shows that, on the first run, approximately 10% of the deuterium was not released from the metal deuteride at an indicated temperature of 950°C. Thus, a significant portion of the total deuterium can be easily overlooked by not determining the amount of deuterium remaining in the metal.

To make this method useful for routine analyses, an assumed constant, K, can be calculated by dividing the total number of moles of deuterium atoms, n_D, by the number of moles of deuterium atoms outgassed on the first run, n_1^{gas} (or equivalently, n_D^{gas} in Eq. 2) . Therefore, the total number of moles of D can be determined by outgassing the sample once and multiplying the result by K.

$$K = \frac{n_D}{n_1^{gas}} \qquad \therefore \qquad n_D = K \bullet n_1^{gas} \qquad\qquad (10)$$

Results

Deuterium to Erbium Ratio

Metal analysis data was combined with the gas analysis data to determine the deuterium to erbium ratio (Equation 1) in Table 4. The results for several samples indicate that a nearly stoichiometric ratio of 2:1 (D:Er) was obtained in each case.

Table 4. Summary of results obtained for the ratio of deuterium to erbium for a series of samples.

Sample ID	Moles D	Moles Er	Ratio (D/Er)
Er/D$_2$ #163	1.85E-05	9.34E-06	1.98
Er/D$_2$ #164	2.08E-05	1.04E-05	2.00
Er/D2 #165	1.86E-05	9.38E-06	1.99
Er/D2 #166	2.04E-05	1.03E-05	1.98
Er/D2 #167[*]	1.97E-05	9.66E-06	2.04

*metal and gas analysis performed on sister samples

Conclusion

Accurate analyses of deuterium in erbium deuteride films can be made using a rapid ramp outgassing technique. The method is based on high temperature desorption of deuterium from the film with quantitation of the gaseous deuterium being accomplished through the application of the principles underlying the ideal gas law. It was also shown that a significant fraction of the total deuterium is retained in the film under the experimental conditions employed in this study, and a method was presented to account for this retained deuterium. A key result that enabled the use of gas law calculations to quantitate the deuterium, even in the case of a non-isothermal, non-steady-state measurement system, is the demonstrated ability to calibrate the effective temperature of the system for a particular time/temperature profile by subjecting a known quantity of a non-reactive gas to the identical profile.

During the course of this investigation, it was shown that both desorption kinetics and gas/solid equilibria influence the deuterium measurement process. As the effects of both of these factors can be varied by changing experimental conditions, temperature ramp rates and sample chamber volumes, for example, the specific results obtained here are applicable solely to the specific apparatus used to make these measurements. The methodology, however, should be generally applicable and should allow other users to perform a thorough evaluation and calibration of their own systems. Finally, the critical importance of minimizing time that the metal film is exposed to high temperature was demonstrated. The effects of such exposure times must be a major consideration in designing any similar high temperature measurement technique.

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