SANDIA REPORT

SAND2008-2578

Unlimited Release

Printed May 2008

Summary of Sandia Research on Metal Tritides: FY 2007

Clark S. Snow, Loren I. Espada, Robert M. Ferrizz, Daniel R. Kammler, Mark A. Rodriguez,
Ryan R. Wixom, and James F. Browning

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of Energy's
National Nuclear Security Administration under Contract DE-AC04-94-AL85000.

Approved for public release; further dissemination unlimited.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: <http://www.osti.gov/bridge>

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online ordering: <http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online>

Summary of Sandia Research on Metal Tritides: FY 2007

Clark S. Snow, Loren I. Espada, Robert M. Ferrizz, and Daniel R. Kammler
Applied Science and Technology Maturation

Mark A. Rodriguez
Materials Characterization

Ryan R. Wixom
Energetics Characterization

Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185

James F. Browning
Oak Ridge National Laboratory
Oak Ridge, TN 37831

Abstract

Sandia National Laboratories has cradle to grave responsibility for all neutron generators in the US nuclear weapons stockpile. As such, much research effort is exerted to develop a comprehensive understanding of all the major components of a neutron generator. One of the key components is the tritium containing target. The target is a thin metal tritide film. Sandia's research into metal tritides began in the early 1960's with a collaboration with the

Denver Research Institute (DRI) and continues to this day with a major in house research effort.

This document is an attempt to briefly summarize what is known about the aging of erbium tritide and to review the major publications conducted at Sandia in FY 07. First, a review of our knowledge of helium in erbium tritide will be presented. Second, executive summaries of the six major SAND reports regarding neutron tube targets published in FY07 by Department 2735, the Applied Science and Technology Maturation Department, and research partners are presented.

Acknowledgment

Over the past five years a major demographic change has occurred amongst the researchers responsible for the science and technology of neutron generators. The seasoned researchers have given way to a newer generation. This work would not have been possible without the effort of the earlier generation who exhibited tremendous insight and technical capabilities. Their measurements and work form the basis of what we are trying to accomplish. Of necessity the early work was phenomenological, simply attempting to categorize the nature and magnitude of the effects of tritium in metals. With this understanding in place and with modern characterization techniques we are now able to begin unraveling the fundamental physics and chemistry of this complex field. We dedicate this work to them, the pioneers of metal tritide science.

The format of this report is based on information found in [14].

Contents

Preface	13
Nomenclature	14
1 Introduction	15
Overview of problem	15
Purpose of this SAND report	16
2 A Review of Historical Data of Sandia Research on Helium in Metals	
<i>C. S. Snow and J. F. Browning</i>	17
Overview of Helium Release	17
Reporting Helium Release Numbers	18
Measuring Helium Release	22
Tube Puncture Method	22
Helium Release Tree	22
Optical Detection of ^3He	23
Helium Release from Metal Tritides	26
Helium Release from Er, Sc, Ti, and Zr Tritides	26
Effect of Stoichiometry on Helium Release from Erbium Tritide	27
Helium in Metal Tritide Films	30
Helium Bubbles	30
Helium Bubble Growth in ErT_2	31
Helium Bubble Denuded Zone	31

Review of Cowgill Model	33
The Cowgill model	33
Implications of Cowgill Model	36
Missing pieces in Cowgill Model	36
Effect of Hydrogen Isotope Ratio	36
Metal Tritide Storage and Handling	38
3 Helium release and microstructural changes in $\text{Er}(\text{D,T})_{2-x}\text{He}_x$ films	
<i>C. S. Snow, L. N. Brewer, D. S. Gelles, M. A. Rodriguez, P. G. Kotula, J. C. Banks, M. A. Mangan, and J. F. Browning</i>	41
Effect of Film Thickness on ERF	41
Presence of oxygen in films	41
4 Erbium Hydride Decomposition Kinetics	
<i>R. Ferrizz</i>	45
5 Erbium Hydride Thermal Desorption: Controlling Kinetics	
<i>R. Ferrizz</i>	47
6 Evaluation of Diffusion Barrier Materials to Inhibit Mixing between Kovar and Erbium Hydride	
<i>D. R. Kammler, L. A. Walla, W. Buttry, H. C. Peebles, C. A. Mehrhoff, M. J. Courtney, L. I. Espada, C. R. Tewell, S. H. King, R. G. Tissot, L. N. Brewer, R. S. Goeke, and R. S. Herrick</i>	49
7 Mechanisms governing D loss in ErD_2 films on kovar with and without a Mo diffusion barrier	
<i>D. R. Kammler, W. R. Wampler, S. B. Van Deusen, S. H. King, R. G. Tissot, L. I. Espada, and R. S. Goeke</i>	53
8 First principles site occupation and migration of hydrogen, helium, and oxygen in beta-phase erbium hydride	

<i>R. R. Wixom, J. F. Browning, C. S. Snow, D. R. Jennison, and P. A. Schultz</i>	55
References	59
 Appendix	
A Publications and Presentations	61
A.1 External Publications	61
A.2 SAND Reports	61
A.3 External Presentations	61
B Hydrogen and Helium Isotopes in Materials Conference	63
C Key Historical Publications on ^3He in Metals	65

List of Figures

2.1	RF _i vs. He:M ratio for ErT ₂ films.	18
2.2	Plot of difference in ARF and IRF helium release numbers as a function of T _{coll}	21
2.3	Finnegan MAT 271 Mass Spectrometer.	23
2.4	Picture of helium release tree.	24
2.5	Optical transitions and data for ³ He and ⁴ He.	25
2.6	Plot of Instantaneous Release Fraction (IRF) vs. He/M for ErT _{1.9} , ScT _{1.9} , TiT _{1.9} , and ZrT _{1.5}	26
2.7	CaF ₂ FCC crystal structure of ErH ₂ , Space Group Fm $\bar{3}$ m, # 225.	27
2.8	³ He instantaneous release fraction (IRF) as a function of helium to metal ratio for ErT _x powders of various stoichiometries.	28
2.9	Onset of critical release for ErT _x powders and 5μm thick films.	30
2.10	TEM micrograph of ErT ₂ and ZrT _{1.9} films showing the different bubble shapes present in the two systems.	31
2.11	Change of helium bubble length with time for ErT ₂ films.	32
2.12	TEM image of ErT ₂ showing the helium bubble “denuded zone”.	32
2.13	Computed bubble nucleation pulse in palladium tritide at 300K.	34
2.14	Dependence of onset of critical helium release on bubble density.	35
2.15	Computed depth profiles of mobile helium and helium bubbles in PdT _{0.65}	37
2.16	Computed He release versus time for a 1 μm thick PdT _{0.65} film.	38
3.1	³ He average release fraction (ARF) as a function of film thickness.	42
3.2	TEM Micrographs and SAED patterns of large oxide particles found in the Er(D,T) _{2-x} ³ He _x films.	43

3.3	SAED pattern showing primary spots from the $\langle 110 \rangle$ and the $\langle 111 \rangle$ zone axes of $\text{Er}(\text{D,T})_2$ and secondary spots of unknown origin.	44
4.1	D_2 thermal desorption spectra.	46
5.1	D_2 thermal desorption spectra ($1.0\text{ }^\circ\text{C/s}$) for $\text{ErD}_2/\text{Mo/Si}$ for samples with two different growth conditions.	48
6.1	Sputter Auger spectra of various ErHD /diffusion barrier/Kovar films.	50
7.1	RBS and NRA spectra for isochronal anneals at several temperatures for three different ErHD /interlay/Kovar films.	54
8.1	Climbing-image nudged elastic band (CINEB) data for hydrogen migration in $\beta\text{-ErH}_2$	56
8.2	Climbing image nudged elastic band data for 3 possible oxygen migration mechanisms.	57
8.3	Climbing image nudged elastic band data for He migration in ErH_{2+x}	58

List of Tables

2.1	ERF and critical release point for $\text{ErT}_{1.9}$, $\text{ScT}_{1.9}$, $\text{TiT}_{1.9}$, and $\text{ZrT}_{1.5}$	26
2.2	Site preferences for hydrogen, oxygen, and helium in $\text{ErH}_{2.0}$	28
2.3	^3He concentration for rapid release as a function of stoichiometry from ErT_x powders.	29
2.4	^3He concentration for rapid release as a function of stoichiometry for ErT_x $5\mu\text{m}$ thick films.	29
5.1	Average desorption peak maximum temperatures (T_P) and activation energies (E_A) for samples A and B.	47
5.2	Average desorption peak maximum temperatures (T_P) and activation energies (E_A) for samples A and B.	48

Preface

As all of us newer researchers have entered the field of metal tritide science we wished that the vast accumulation of knowledge could be had in one place. A few short books have been written but lack the specific knowledge that we are seeking. It is our desire that this report will help, in part, to establish a baseline for research at Sandia National Laboratories. Further, it is hoped that every year a new report will be written summarizing research in the exciting field of metal tritides.

Nomenclature

ARF Average Release Fraction

ERF Early Release Fraction

IRF Instantaneous Release Fraction

Protium (H) commonly called Hydrogen

Deuterium (D) isotope of hydrogen with two neutrons

Tritium (T) isotope of hydrogen with three neutrons

ErH₂ Erbium Di-Hydride

ErD₂ Erbium Di-Deuteride

ErT₂ Erbium Di-Tritide

IBA Ion Beam Analysis

TEM Transmission Electron Microscopy

XRD X-Ray Diffraction

VASP Vienna ab-initio Simulation Package- a code to calculate the electronic structure of materials

SeqQuest an ab-initio electronic structure code

Chapter 1

Introduction

Overview of problem

The design and production of neutron generators has been an important part of Sandia's mission since the 1950s. Neutron generators can be considered to be made of two parts, a power supply and a neutron tube. A neutron tube is essentially a small electrostatic accelerator with an ion source on one end and a target on the other. In order to produce neutrons the deuterium-tritium reaction is utilized. The physics of the reaction is

$$D + T = {}^4\text{He} + n + 17.6\text{MeV}. \quad (1.1)$$

where D is deuterium, T is tritium, ${}^4\text{He}$ is the mass 4 isotope of helium, and n is a neutron. The ion source produces either deuterium or tritium ions while the target contains the opposite atom. While the design has evolved considerably since those early days the basic idea is still the same, ions are accelerated inside a vacuum envelope and made to impinge on a target material. The neutron tubes that will be discussed in this paper are of the type where the ion source produces deuterium ions and the target contains tritium.

Although a neutron generator is simple to describe it is in fact a complicated piece of science and engineering. This report focuses on the tritium containing target. Two important factors dictate how the tritium containing target will perform. First, it must be able to store the necessary amount of tritium for a long period of time. The thermodynamics of erbium tritide guarantees a high density of tritium while the desorption kinetics determine if the tritium will remain in the film during processing and over time. Second, the target needs to retain the helium produced through the radioactive decay of tritium. Tritium decays with a half-life of 12.32 years[16] by the following process

$$T = {}^3\text{He} + \beta^- + \bar{\nu}. \quad (1.2)$$

Much research is still left to be done on both of these important factors. We still do not know the thermodynamics and kinetics of erbium hydride metal films. Further, although the amount of helium released from several metal tritide films have been measured, we still do not know the fundamental mechanisms governing helium release.

Purpose of this SAND report

The purpose of this SAND report is three fold. One, to summarize in one place much of what is known regarding helium in metal tritides. Two, to provide executive summaries of work on metal tritides and helium in metal tritides performed at Sandia in Fiscal Year 2007. Three, to motivate scientists and management that research in metal tritides needs to continue.

Chapter two summarizes key historical results on helium release, both experimental and theoretical. The subsequent chapters are executive summaries of SAND reports published by Department 2735, the Applied Science Technology Maturation Department, and research partners from around Sandia National Laboratories. Appendix A contains lists of all publications, both internal and external, given by members of Department 2735. Appendix B contains a short description of the Hydrogen and Helium Isotopes in Materials conference held annually in February and hosted by Sandia National Laboratories and Department 2735. Appendix C is an incomplete list of key historical publications where future researchers will want to begin their studies.

Chapter 2

A Review of Historical Data of Sandia Research on Helium in Metals

C. S. Snow and J. F. Browning

Overview of Helium Release

The radioactive decay of tritium into ^3He produces an interesting materials problem, the gradual replacement of a very reactive element, H, with an inert one, He. What happens to the inert gas in the metal tritide has been studied for many years. As mentioned in Chap. 1, Sandia is responsible for the design and construction of neutron generators of which metal tritide target materials play a key role. Because of this responsibility, Sandia has been interested in this topic for well over 30 years now. Several aspects of the problem are of interest in neutron generators. One, since neutron generators are vacuum devices the majority of the helium needs to be retained in the metal tritide or else the vacuum will be lost. Two, the film needs to retain the hydrogen over the lifetime of the tube. Mechanical degradation can not lead to hydrogen loss or else the tube will not function. This chapter will focus on the first problem, the amount of helium released from the film and what we have learned about the helium that is stored in the film.

Figure 2.1 shows a typical plot of the amount of helium instantaneously released from an Erbium Di-Tritide (ErT_2) film vs. the ratio of helium to metal atoms (He:M) in the film. The He:M ratio can simply be considered a normalized time axis. Helium release breaks down into two regions, an “early release” period characterized by a constant, and small release fraction (see Section 2 for definition of release fraction) and a “critical release” period where the helium release fraction approaches unity.[2] This chapter will present an overview of what is known about helium in metal tritides. The focus will be on erbium tritide films.

Figure 2.1. Plot of the instantaneous release fraction (RF_i) vs. time for erbium tritide films (see Section 2 for a definition of RF_i). The region where the release fraction is small is labeled the “early release period” while the region where the release fraction is unity is labeled the “critical release period”. This data was taken using the “helium release tree” shown in Fig. 2.4 below and described in detail in Section 2.[2]

Reporting Helium Release Numbers

There currently exists two major methods of determining and reporting the amount of helium released from a metal tritide. Each has merits, the choice between the two is generally determined by the experimental apparatus available and the intended end use of the data. The two methods are an instantaneous release fraction (IRF), also written RF_i and an average release fraction (ARF). The names are rather self-explanatory. Mathematically they are defined as follows

$$IRF(T) = \frac{\text{Rate of } ^3\text{He Desorption}}{\text{Rate of } ^3\text{He Generation}} \Big|_{t=T}. \quad (2.1)$$

and

$$ARF(T) = \frac{\text{Total } ^3\text{He Released}}{\text{Amount } ^3\text{He Generated}} \Big|_{t=T} = \int_0^T IRF dt. \quad (2.2)$$

In the ARF method the neutron tube (or any vacuum envelope containing a tritiated material) is sealed and the helium is allowed to accumulate in the vacuum space. After a pre-determined time period the neutron tube is punctured or opened and the total amount of helium is measured. This is most accurately done using a Finnegan Mass Spectrometer but can also be done using a simple quadrupole mass spectrometer calibrated for ^3He , the latter technique has much larger error bars. If time dependent effects are not important then the ARF method is sufficient.

In the IRF method the vacuum envelope is opened to a ^3He calibrated quadrupole mass spectrometer or other suitable detector and the current of ^3He is measured. This is the method that was originally employed on the “Helium Release Tree” (see below).[3] This method can also be made to be quite accurate. A negative of this technique is that during measurement the tritiated material is repeatedly exposed to a vacuum system. If the vacuum system is not clean or if the tritiated material is very reactive, then the IRF measurement will be influenced by the vacuum environment. This is something that is not a problem in a one time ARF measurement. However, the cost of a one time ARF measurement and sample to sample variability in a one time ARF measurement also need to be considered before a helium release measurement technique is decided upon.

The IRF can be measured in two methods, an exact IRF and an average IRF. The exact IRF is called that because a steady state flow is measured and divided by the rate of ^3He generation. The rate of ^3He generation is also called the Instantaneous Generation Rate (IGR) and is calculated by knowing the initial amount of tritium, N_0 in the sample, the tritium decay constant λ , and the amount of time since tritiding, T , and is given by the following equation

$$IGR = \frac{d}{dt}N_0(1 - \exp(-\lambda t)) = N_0\lambda \exp(-\lambda t). \quad (2.3)$$

The average IRF measures the Average Release Rate for a specified time interval, typically one month, and divides by the IGR. The “Helium Release Tree” discussed below can be configured to measure both an exact IRF and an average IRF, but is currently configured to measure the average IRF.

As the two most common measurements are the average IRF, measured on the helium release tree, and the ARF, measured by the tube puncture technique, it is important and instructive to compare the two measurement techniques and determine the differences of the two reported numbers.

To begin with we recast the average IRF and ARF equations into forms that are easier to compare.

$$IRF_{avg}(t = T) = \frac{\frac{Qty. \text{ } ^3\text{He collected}}{T_{coll}}}{IGR} = \frac{Qty. \text{ } ^3\text{He collected}}{T_{coll}N_0\lambda \exp(-\lambda T)} \quad (2.4)$$

and

$$ARF(t = T) = \frac{\text{Total } ^3\text{He collected}}{\text{Total } ^3\text{He Generated at } t = T} = \frac{\text{Total } ^3\text{He collected}}{N_0(1 - \exp(-\lambda T))} \quad (2.5)$$

where T_{coll} is the time elapsed since last measurement which is the amount of time that ^3He has had to collect inside the sample chamber. To compare the ARF and average IRF we divide equations 2.5 and 2.4 giving

$$\frac{ARF}{IRF_{avg}} = \frac{\text{Total } ^3\text{He collected}}{N_0(1 - \exp(-\lambda T))} \frac{Qty \text{ } ^3\text{He collected}}{T_{coll} N_0 \lambda \exp(-\lambda T)} \quad (2.6)$$

$$= \frac{T_{coll}(\text{Total } ^3\text{He collected})\lambda \exp(-\lambda T)}{(Qty. \text{ } ^3\text{He collected})N_0(1 - \exp(-\lambda T))} \quad (2.7)$$

where T is the time since tritiding. In order to finish the comparison a final assumption needs to be made. We will assume that the fraction of helium released from the film, the RF, is constant over the entire early release period. With this assumption then we can write that

$$\frac{\text{Total } ^3\text{He collected}}{Qty. \text{ } ^3\text{He collected}} = \frac{N_0(1 - \exp(-\lambda T))RF}{N_0[(1 - \exp(-\lambda T)) - (1 - \exp(-\lambda(T - T_{coll})))]RF} \quad (2.8)$$

Combining eqns. 2.10 and 2.7 gives the final equation relating ARF and IRF_{avg} .

$$\frac{ARF}{IRF_{avg}} = \frac{T_{coll} N_0 \lambda \exp(-\lambda T)}{N_0(1 - \exp(-\lambda T))} \frac{1 - \exp(-\lambda T)}{(1 - \exp(-\lambda T))(1 - \exp(-\lambda(T - T_{coll})))} \quad (2.9)$$

$$= T_{coll} \lambda \frac{\exp(-\lambda T)}{(1 - \exp(-\lambda T)) - (1 - \exp(-\lambda(T - T_{coll})))}. \quad (2.10)$$

We will now analyze two distinct cases. Case one will demonstrate when the average IRF and ARF are nearly identical and case two, will demonstrate when they are not.

In case one, consider a sample volume that has been sealed for two years and never measured where $T_{coll} = T = 2$ years. In this case

$$\frac{ARF}{IRF_{avg}} = \frac{T \lambda \exp(-\lambda T)}{1 - \exp(-\lambda T)} \quad (2.11)$$

$$= 0.9446, \quad (2.12)$$

or in other words, they are six percent different. This condition is met when two similarly aged tubes are taken and for one the average IRF measured on the tree and for the remaining the ARF is measured.

In case two, consider a scenario where a film is two years old and the IRF_{avg} has been measured every month since tritiding. For this situation $T_{coll}=1$ month and $T=2$ years, i.e., the sample is measured every month and the film is two years old. In this case the ratio becomes

$$\frac{ARF}{IRF_{avg}} = \frac{1 \text{ mo. } \lambda \exp(-\lambda 24 \text{ mo.})}{(1 - \exp(-\lambda 24 \text{ mo.})) - (1 - \exp(-\lambda(24 \text{ mo.} - 1 \text{ mo.})))} \quad (2.13)$$

$$= 0.9976 \quad (2.14)$$

This condition is what happens if the average IRF of a tube has been measured every month and then a sister tube, same age and amount of tritium, is measured using the ARF method. These two numbers are essentially identical. Fig. 2.2 plots the ratio of ARF/IRF as a function of varying T_{coll} , i.e., how frequently a sample is measured to determine the IRF.

Figure 2.2. Plot of difference in ARF and IRF helium release numbers as a function of T_{coll} .

Obviously, one needs to be careful when comparing data taken and reported by either the IRF_{avg} or ARF methods. The amount of variation in the two methods depends exclusively on the time between sampling because in the IRF_{avg} technique you divide by the IGR which

becomes more accurate the more frequently you sample. One caveat to the above analysis is that we assumed a constant release of helium from the earliest time. This may not be true, in fact, a model proposed by Cowgill and discussed below suggests that more helium is released early in life and then the release evens out.[7]

Measuring Helium Release

There are two main methods used at Sandia for measuring the amount of helium released from a metal tritide film, the tube puncture method and the helium release tree. Other methods have been or are being developed but have not reached the level of precision as the two mentioned above.

Tube Puncture Method

The tube puncture method is a true measure of the Average Release Fraction (ARF) of a metal tritide. The tube puncture method is just what the name implies. A vacuum envelope, usually a neutron tube, is placed in a special fixture designed to puncture a small hole in the copper tubulation used to evacuate the envelope. The fixture and tube are placed on an inlet system connected to a Finnegan MAT 271 Mass Spectrometer. The Finnegan 271 is specially designed to yield high resolution of low-mass atoms. The Finnegan is a magnetic-sector mass spectrometer with high magnetic field stability due to its use of a feedback Hall probe sensor. The lens following circuitry optimizes electrostatic focusing for maximum ion transmission as a function of field strength. These key features yield a resolution greater than 1500, with a measurement uncertainty of ± 2 percent. The measurement range covers 1-150 amu with a dynamic range of 10^9 . The instrument is shown in Fig. 2.3, they are a unique asset to the US DOE NNSA complex.

Helium Release Tree

The “Helium Release Tree” is a vacuum device used to measure the amount of helium released from a metal tritide. The reason for the name “tree” becomes apparent at first glance at a picture of the device, shown in Fig. 2.4. The tree contains 48 ports for mounting various sample holders ranging from small Molybdenum domes to neutron tubes in the tube puncture fixtures used in the tube puncture method discussed above. The tree can be operated in two modes measuring an ARF and an IRF (see Section 2). In the ARF method the valve separating the sample from the tree is opened, pumping is blocked by closing a valve isolating the tree from the pump, and the ^3He partial pressure is allowed to increase until a steady state is reached. The ^3He partial pressure is measured with a calibrated Residual Gas Analyzer. Knowing the volume of the tree, the total number of ^3He atoms can be calculated and knowing the initial amount of tritium in the sample, the ARF can be

Figure 2.3. Finnegan MAT 271 Mass Spectrometer.

calculated. In the IRF method, the valve separating the tree from the sample is opened but the tree is not isolated from the pump. The gas is instead fed through a known conductance path and the leak rate from the sample is determined.[3] Again, knowing the tree volume the amount of ^3He atoms flowing through per second can be calculated and an IRF can be calculated. The tree shown in Fig. 2.4 is already 30 years old. A new tree is being designed and constructed which will take advantage of advances in vacuum technology to improve the measurement. Currently, the error is estimated to be 20-25 percent. It is anticipated that the new tree will approach an error of 10 percent and will expose the sample to a much cleaner vacuum environment during measurement.

Optical Detection of ^3He

Another method that is being pursued is to use the optical properties of helium to detect and quantify the amount of ^3He released from a metal tritide. The ground state of Helium is the 1^1S_0 state, with quantum numbers $n=1$, $l=0$, $J=0$, and $S=0$. In order for an optical transition to occur the helium atom is excited from its ground state into the next excited state, which is the 2^3S_0 state. If light is tuned to the proper energy then the atom will absorb the light which will cause a transition to a higher energy level. For light about 1083 nm the transitions will be to the 2^3P_J levels where $J=0,1$, or 2 . [1] The 2^3P_J level is split into three “fine-structure” levels by the spin-orbit interaction, $\mathbf{H}=\mathbf{L} \bullet \mathbf{S}$. This is the explanation for the three optical transitions shown in Fig. 2.5 for ^4He , the allowed transitions from the 2^3S_0 to the three 2^3P_J states.[4] The situation gets a bit more complicated when ^3He is considered. The nuclear magnetic moment, $\mathbf{I}$, is $1/2$ for ^3He and 0 for ^4He . This difference

Figure 2.4. Picture of helium release tree. Metal tritides are stored under vacuum in individual containers which are sequentially opened and the amount of helium measured.

is significant because the energy levels of ^3He are split by the hyperfine splitting $\mathbf{F}=\mathbf{I} \bullet \mathbf{J}$, where $\mathbf{J}$ is the electron spin. For ^3He the splitting causes the ground state to split in two along with the 2^3P_1 and 2^3P_2 states, yielding nine possible transitions.[10]

The potential benefit of the optical detection scheme is the unambiguous nature of the optical spectra. The spectra for ^3He is different from ^4He , which are both different than the hydrogen isotopes, H,D, and T. The difficulty lies in the quantification, a scheme for which still needs to be worked out.

Figure 2.5. Optical transitions and data for ^3He and ^4He . These results are from Bohler and Martin.[4]

Helium Release from Metal Tritides

Helium Release from Er, Sc, Ti, and Zr Tritides

Figure 2.6. Plot of Instantaneous Release Fraction (IRF) vs. He/M for $\text{ErT}_{1.9}$, $\text{ScT}_{1.9}$, $\text{TiT}_{1.9}$, and $\text{ZrT}_{1.5}$. [2] The dashed lines are averages of the data set which constitutes results from multiple films.

The data presented in Fig. 2.6 shows the IRF for four metal tritides that were evaluated for use in neutron tubes. The $\text{ErT}_{1.9}$, $\text{TiT}_{1.9}$, and $\text{ZrT}_{1.5}$ metal tritides all show a similar release pattern, characterized by a flat, constant IRF followed by a dramatic increase in the IRF at a specific He/M ratio. [2] The constant IRF period is termed the Early Release Fraction (ERF) while the point at where the IRF increases is called the Critical Release point. Interestingly, $\text{ScT}_{1.9}$ is an anomaly and does not exhibit a readily defined ERF or critical release point. It should be noted that other data taken by Perkins *et al.* does not show any anomalous helium release behavior for ScT . [9] The ERF and critical release point for these metal tritides is summarized in Table 2.1. One important difference between the

Table 2.1. ERF and critical release point for $\text{ErT}_{1.9}$, $\text{ScT}_{1.9}$, $\text{TiT}_{1.9}$, and $\text{ZrT}_{1.5}$. [2]

Material	RFi	Critical Release (He/M)
$\text{ErT}_{1.9}$	0.002	0.30
$\text{ScT}_{1.9}$	NA	NA
$\text{TiT}_{1.9}$	0.0001	0.40
$\text{ZrT}_{1.5}$	0.0001	0.48

various tritides is that $\text{ErT}_{1.9}$ and $\text{ScT}_{1.9}$ have a cubic crystal structure while $\text{TiT}_{1.9}$ and

Figure 2.7. CaF_2 FCC crystal structure of ErH_2 , Space Group $\text{Fm}\bar{3}\text{m}$, # 225. The large grey spheres represent the Erbium atoms and the small white sphere represent the Hydrogen atoms.

$\text{ZrT}_{1.5}$ have a tetragonal crystal structure. Why the helium release properties are better for a tetragonal crystal structure than a cubic structure needs to be investigated. Further, the processing conditions which may impact grain size, sample impurities, etc., are not known.

Effect of Stoichiometry on Helium Release from Erbium Tritide

The crystal structure of erbium di-hydride is shown in Fig. 2.7. In the CaF_2 structure of $\text{ErH}_{2.0}$ the erbium atoms form an FCC lattice with the hydrogen atoms residing in the eight tetrahedral sites. Of necessity, in the super-stoichiometric condition the hydrogen atoms must begin to occupy the six octahedral sites. It is shown in Chapter 8 that when helium is produced in the radioactive decay process of tritium, it initially prefers to reside in the octahedral sites of the lattice. An interesting question to consider is the impact of stoichiometry on helium release. Is helium release impacted if most of the octahedral sites are already occupied by hydrogen atoms so that the helium atoms must reside in an unstable tetrahedral site? Would the helium and hydrogen atoms swap places? Is helium able to migrate in a lattice where the octahedral sites are already occupied? An early study by Beavis on ErT_2 powders began to answer this question.[2] Powders of ErT_2 with the following stoichiometries were produced, $\text{ErT}_{1.85}$, $\text{ErT}_{1.95}$, $\text{ErT}_{2.06}$, $\text{ErT}_{2.11}$, and $\text{ErT}_{2.15}$. The stoichiometries were produced by loading a film with excess tritium, i.e., to 2.15, and then heating the sample to outgas the desired amount of tritium gas. The exact stoichiometries were determined destructively on small amounts of the powder in a mass spectrometer. Figure 2.8 shows the data on the five powdered samples. The data is reported in the figure is “instantaneous release fraction” (IRF).

The point where the IRF becomes greater than 0.01 is defined by Beavis as the beginning of critical release. Analysis of Figure 2.8 shows though that the IRF curves of the 2.15

Table 2.2. Site preferences for hydrogen, oxygen, and helium in $\text{ErH}_{2.0}$. Top line indicates atomic species.

	Tritium	Oxygen	Helium
$\text{ErT}_{2.0}$	Tetrahedral		
$\text{ErT}_{2.0}\text{O}$	Octahedral	Tetrahedral	
$\text{ErT}_{2-x}\text{He}_x$			Tetrahedral
$\text{ErT}_{2-x}\text{He}_x\text{O}$	?????	?????	????

Figure 2.8. ^3He instantaneous release fraction as a function of helium to metal ratio for ErT_x powders of various stoichiometries, $\bullet=1.85$, $\times=1.95$, $\circ=2.06$, $\triangle=2.11$, and $\square=2.15$.

and 2.11 samples hardly resemble typical IRF curves, for example like the one shown in Figure 2.1. Table 2.3 compares the onset of critical release for the various stoichiometries from powders and Table 2.4 shows results for 5 μ m thick films.

Table 2.3. ^3He concentration for rapid release as a function of stoichiometry for ErT_x powders.

Stoichiometry	He/M
1.85	0.221
1.95	0.200
2.06	0.147
2.11	0.048
2.15	0.030

Table 2.4. ^3He concentration for rapid release as a function of stoichiometry for ErT_x 5 μ m thick films.

Stoichiometry	He/M
1.90	0.28
2.0	0.16
2.13	0.12

The results from Tables 2.3 and 2.4 are summarized graphically in Figure 2.9.

The implication from this data is that as the number of octahedral sites are filled with hydrogen that either the number of nucleation sites for helium bubbles are reduced or that the density of helium inside the bubbles is reduced. This statement is made because the data shows that most of the helium is released from the film and not retained in it like is the case for the lower stoichiometry powders. Unfortunately, a TEM was not available to analyze this set of powders to determine the behavior of the helium bubbles as a function of stoichiometry. The reader should remember some important differences do exist between this data on powders and target films in neutron tubes. One, the surface area of the powders is many orders of magnitude greater than for the films. Two, it is unknown how much oxygen is in the powders and as it will be shown in Chapter 8, the effect of oxygen on helium can be significant. A study is planned to answer these questions and to verify this data. If this data is accurate and can be applied to films, then the implications for how critical the tritium loading parameters are is obvious.

Another complicating point is the interaction of oxygen in this process. It is shown in Chapter 8 that oxygen prefers to reside in the tetrahedral site of the lattice which forces the hydrogen to reside in the octahedral site. The site preferences for hydrogen, helium, and oxygen are summarized in Table 2.2. Helium, although an inert gas, is mobile in a metal lattice and it is shown below that at sufficient helium densities helium bubbles will

Figure 2.9. Onset of critical release for ErT_x powders (■) and $5\mu\text{m}$ thick films(○).[2]

form along the (111) planes in ErT_2 . This leads to an interesting question, when oxygen, hydrogen, and helium are all present in a lattice, what affect does this have on the helium mobility and hence its ability to nucleate and form helium bubbles. A study by Schober and Trinkaus on $\text{NbO}_{0.015}\text{T}_{0.01-x}\text{He}_x$ suggests that oxygen acts as trapping sites for helium and suppresses ^3He bubble formation[18].

Helium in Metal Tritide Films

The previous sections dealt with measuring the helium that evolves from a metal tritide. The corollary of this problem is what happens to the helium that remains inside the metal tritide. In this section we will review what is known about the helium that resides in the metal lattice. It is hoped that this information will give us a better understanding of neutron tube targets.

Helium Bubbles

When helium, or any other inert gas, accumulates to a high enough density the helium aggregates into bubbles. Major differences in helium bubble shape exist for the $\text{ErT}_{2.0}$ [8] and $\text{ZrT}_{1.5}$ systems.[17] Fig. 2.10 shows lenticular, or plate-like helium bubbles, growing

Figure 2.10. TEM micrograph of an (left) ErT_2 [8] and (right) $\text{ZrT}_{1.9}$ film.[17] In the ErT_2 system the bubbles are lenticular and grow along the crystallographic (111) planes while for $\text{ZrT}_{1.9}$ the bubbles are spherical.

along the crystallographic (111) planes in ErT_2 system while more spherical bubbles grow in the $\text{ZrT}_{1.5}$ system. As mentioned above, a significant difference is the cubic crystal structure of the ErT_2 system and the tetragonal crystal structure of the $\text{ZrT}_{1.5}$. As seen in other systems like SiC, plate-like bubbles will form when there is significant elastic anisotropy.[6] Unfortunately, measurements of elastic constants in thin films are extremely difficult although modern first principles calculations allow fairly accurate calculations to be made. This line of study needs to be pursued to quantify the degree of elastic anisotropy in both the ErT and ZrT systems.

Helium Bubble Growth in ErT_2

A study was undertaken by J. Browning and G. Bond to systematically track the growth of helium bubbles in the ErT_2 system as a function of time.[5] The results of this study are shown in Fig. 2.11. The films were 100 percent tritium loaded to near a stoichiometry of ErT_2 . The earliest time analyzed was 62 days where the average bubble size 8 nm long. As the time progresses the average bubble length increases to 15 nm for the oldest sample, 547 days.

Helium Bubble Denuded Zone

One feature observed in ErT_2 films is the absence of helium bubbles near the surface. This region has been termed a “denuded zone” or “bubble free zone”. The thickness of this region appears to be constant, at about 150 Å.[8] The role that the denuded zone plays

Figure 2.11. Change of helium bubble length with time for ErT_2 films. Results determined from TEM images taken and analyzed by G. Bond.[5] n is the total number of helium bubbles measured for that particular time. The x-axis shows the bubble length in nanometers.

Figure 2.12. TEM image of ErT_2 showing the helium bubble “denuded zone”.

in helium release is still an active area of research. As discussed below in Section 2, the denuded zone plays a prominent role in the model developed by Cowgill.[7]

Review of Cowgill Model

The Cowgill model

In this section we will briefly review a helium release model proposed by D. F. Cowgill.[7] In this model the following series of rate equations is solved.

$$\frac{dc_1}{dt} = g - 2p_1s_1c_1^2 + 2q_2c_2 - p_1s_2c_1c_2 - p_1s_Bc_1c_B \quad (2.15)$$

$$\frac{dc_2}{dt} = p_1s_1c_1^2 - p_1s_2c_1c_2 - q_2c_2 \quad (2.16)$$

$$\frac{dc_B}{dt} = p_1s_2c_1c_2 \quad (2.17)$$

where p_1 is the atomic He hop rate (jumps/second) between interstitial sites, s_N is the number of trapping sites around species N, q_N is the N-species dissociation rate (the rate at which a cluster of N He atoms dissociates), g is the atomic He generation rate. In the equations above then q_2 is the pair dissociation rate, and s_1 , s_2 , and s_B , are the number of trapping sites for a He atom, He pair, and He bubble of radius r respectively. This model is quite generic and can be applied to any crystal lattice. Primarily, the hop rate will change with the energetics of the crystal and the number of interstitial trap sites, which is dependent on crystal structure and impurities that may be filling those sites.

Equations 2.15 - 2.17 when solved for time $t=0$ to $t=8$ days with parameters appropriate for PdT_{0.6} gives Figure 2.13. Importantly, note the initial pulse around one day when the mobile helium and small helium clusters have their largest concentration. The asymptotic behavior of the helium bubbles indicates that virtually all of the helium bubbles (bubbles are defined here as a cluster of 3 or more helium atoms) are nucleated after 5 days. This is a hypothesis that can be tested by careful TEM observations of helium bubble behavior immediately after tritiding, a study that was not possible before the target loading mission transferred to Sandia.

Once the helium bubbles are nucleated they are fed by the generation of helium atoms within a certain source radius of the bubble. As shown in Figure 2.13, the model predicts that the bubble density should be nearly constant with time after $t=5$ days. With n_B constant, the helium source volume can be written as

$$(4/3)\pi R^3 n_B = f_p \quad (2.18)$$

Figure 2.13. Computed bubble nucleation pulse in palladium tritide at 300K. Note that the asymptotic value of c_B was adjusted to match the TEM measured bubble density.

where f_p is the packing fraction and R is the source radius. The packing fraction can be calculated for different bubble array geometries. While the bubble density may not grow significantly with time, the bubble size is growing as more and more helium atoms are generated and trapped by the neighboring helium bubbles. When the bubbles are of sufficient size they begin to interact causing inter-bubble fracturing of the metal lattice to occur. It is hypothesized that when this inter-bubble fracture occurs that a pathway to the surface is opened up allowing the helium in the bubbles and all subsequently generated helium to find its way to the surface. This is the microscopic definition of “critical helium release” as shown in Figure 2.1. Figure 2.14 shows how the continuum model predicts the dependence of the onset of critical helium release on bubble density, signifying that a competition exists between more but smaller bubbles, and fewer but larger bubbles. An optimum bubble density and hence bubble size exists where the inter-bubble fracture mechanism is delayed in time. While not explained in this short overview, the bubble density is dependent on material properties such as the shear modulus and surface energy. Interestingly, the observed helium bubble density of $\text{PdT}_{0.65}$ is at the peak of the predicted maximum critical helium release time.

Figure 2.14. Dependence of onset of critical helium release on bubble density.

The helium bubble depth concentration can be modeled by adding a diffusive term to equations 2.15-2.17 such that

$$\frac{dc_1}{dt} = -D \frac{d^2 c_1}{dx^2} + g - 2p_1 s_1 c_1^2 + 2q_2 c_2 - p_1 s_2 c_1 c_2 - p_1 s_{BC} c_1 c_B \quad (2.19)$$

The result of solving the set of equations is shown in Figure 2.15a and b. Figure 2.15a shows the computed mobile Helium concentration, c_1 , as a function of depth at various time steps. Note that there is always a large concentration of atomic helium near the surface of the film. This atomic helium concentration is the helium that contributes to the Early Release Fraction (ERF). Conversely, Figure 2.15b shows the computed helium bubble concentration, c_B , showing that there exists a concomitant lack of helium bubbles near the surface. This lack of helium bubbles is the “denuded zone” shown in Figure 2.12. Interestingly, the “denuded zone” correlates with the large concentration of atomic helium. This correlation between the “denuded zone” and early helium release has not been conclusively demonstrated experimentally.

Equations 2.19 can be integrated with respect to film thickness to calculate the amount of helium released at a specific time. The curve is quite similar to what is observed for many typical helium release curves. One feature that is predicted by the model that has not yet been conclusively observed experimentally is an initially high ERF followed by a decrease.

Implications of Cowgill Model

Missing pieces in Cowgill Model

As constituted in Reference [7], the Cowgill model is directed at helium in PdTx and is lacking in a few important parameters in order to be applicable to ErT. One, the impact of the oxide layer. The oxide layer as it grows will eat into the tritiated layer and may enhance or inhibit helium diffusion. Second, the anisotropy of materials. The anisotropy of a material is seen in the shape of the helium bubbles. While the model assumes an anisotropic material which works well for the PdTx system it is not appropriate for the ErT system. Third, the phase stability of a material. Again, this is not a problem for PdT which requires an over-pressure of hydrogen in order to retain its hydrogen. The ErT system however, over time loses up to 75 percent of its tritium which may push the system into an unstable phase regime. This effect may be important and should be addressed. Four, the detailed microstructure of the system. The microstructure probably plays a key role in the number and nature of the defects which trap helium. As the model predicts, the helium release is dependent on the number of helium bubbles so that the microstructure should play a significant role.

Effect of Hydrogen Isotope Ratio

The continuum model proposed by Cowgill has a number of implications where it comes to tritiding a target. One general assumption of the neutron generator community has been that studies of ErT₂ can simply be scaled to systems with other isotopic ratios. For example, it was assumed that ErT₂ could be easily scaled to Er(D_{0.5}T_{0.5})₂ by simply multiplying the

Figure 2.15. Computed depth profiles of (a) mobile He showing high near-surface concentration and (b) bubble concentration showing near-surface denuded zone.

Figure 2.16. Computed He release versus time for a 1 μm thick $\text{PdT}_{0.65}$ film.

time scale by a factor of two. However, the continuum model of Cowgill does not support this assumption. First, if there is less tritium to generate helium then the model predicts that there will be fewer helium bubbles. The lower helium bubble density will then significantly impact the onset of critical release as seen in Figure 2.14. Second, the effective helium jump rate will be less for the $\text{Er}(\text{D}_{0.5}\text{T}_{0.5})_2$ than for the ErT_2 system as the system ages more hydrogen remains to continue to occupy the tetrahedral lattice sites.

The effect of hydrogen isotope ratio on helium release and the implications of the Cowgill model need to be addressed experimentally. This is an ongoing research area in the neutron generator science and technology department.

Metal Tritide Storage and Handling

The continuum model also makes some suggestions on how to handle and store tritided targets. First, the model obviously suggests (see Figure 2.15) that the surface and near-surface region of any tritided material is critical to the ERF. Care must be taken to minimize the oxidation of the surface. It is known that a metal tritide surface will continually oxidize and not self-passivate. It is best practice to limit the exposure of metal tritides to air, this generally means vacuum storage. Second, the model also suggests that it may be better to wait a number of days for the predicted initial burst of helium to be expelled before a

target is built into a neutron generator. Third, the number and type of impurities may have a significant impact on the number and type of trapping sites. This change in trapping sites may alter the predicted critical helium release point, for the better or worse.

Chapter 3

Helium release and microstructural changes in $\text{Er(D,T)}_{2-x}\text{}^3\text{He}_x$ films

C. S. Snow, L. N. Brewer, D. S. Gelles, M. A. Rodriguez, P. G. Kotula, J. C. Banks, M. A. Mangan, and J. F. Browning

Executive Summary of SAND2007-7983

Effect of Film Thickness on ERF

As a method of determining where in the film the helium evolving from the film early in life is coming from, a series of films of thickness 5000Å, 4000Å, 3000Å, 2000Å, and 1000Å were grown and tritided. These films were built into neutron tubes and their ARF (see Section 2) was measured after approximately two years. The results of this set of experiments is shown in Figure 3.1. What this data implies is that the majority of the helium released from the films early in life is originating from the near surface region. If the helium was simply diffusing to the surface from throughout the film, then the ARF would be independent of film thickness (or in other words, the total amount of helium evolved would increase linearly with increasing film thickness). This is clearly not the case. The curve fitted to the data in Figure 3.1 is an inverse thickness function. A simple mathematical model can be used to model a two layer system where in the top layer the helium is allowed to be released from the film while in the bottom layer all of the helium is trapped. This model predicts an ARF that should vary inversely proportional to thickness.

Presence of oxygen in films

TEM images of these films showed two features that are related to oxygen contamination. First, large erbium oxide particles were found in practically every image for all film thicknesses except the 5000Å film (see Fig. 3.2). Many of these particles span the entire depth of the film. The origin of these large particles could not be determined in this study.

Figure 3.1. ³He average release fraction as a function of film thickness, time ~ two years. The inset shows the partial pressure of ³He versus film thickness. Three to four tubes were built and punctured for each film thickness.

Figure 3.2. Figure a) is a TEM Micrograph of large oxide particle in the 200 nm film. Figure b) compares two Energy Dispersive Analysis (EDX) spectrum taken in the middle of the particle and outside the particle in the $\text{Er(D,T)}_{2-x}\text{He}_x$ film. The excess amount of oxygen is clearly present from the increased peak intensity of the approximately 0.5 keV oxygen peak. Figures c) and d) are Selected Area Diffraction patterns at different sample tilt angles. Figure c) is a diffraction pattern along the [110] zone axis with the arrows showing the indexing to the Er_2O_3 unit cell. Figure d) is a diffraction pattern along the [211] zone axis.

Second, secondary spots in the TEM diffraction images were shown to come from nano-precipitates of erbium oxide evenly disbursed throughout the film(see Fig. 3.3). This fits Ion Beam Analysis results which consistently indicate oxygen in the film at the 2-3 % level.

Figure 3.3. SAED pattern showing primary spots from a) the $\langle 110 \rangle$ and b) the $\langle 111 \rangle$ zone axes of Er(D,T)_2 and secondary spots of unknown origin. The d -spacings associated with g_1 and g_2 are 0.73 nm and 0.74 nm, respectively.

Chapter 4

Erbium Hydride Decomposition Kinetics

R. Ferrizz

Executive Summary of SAND2006-7014

Thermal desorption spectroscopy (TDS), also known as temperature programmed desorption (TPD), is a powerful tool to study the kinetics of reactions. The hydriding reaction is one of the most complex because it potentially involves many steps, any one of which may be a rate-limiting step.

The most often used equation to analyze TDS spectra is that of Redhead[15]

$$r_D = -\frac{d\Theta_a}{dt} = k_D\Theta_A^n \quad (4.1)$$

where r_D is the rate of desorption of species A and is a function of the surface coverage Θ_A and a rate constant for desorption k_D . Importantly, the rate constant varies according to the Arrhenius expression

$$k_D = k_0 \exp\left(\frac{-E_A}{kT}\right). \quad (4.2)$$

For simple reactions, combining the two equations allows the important activation energy of the reaction to be determined. The situation is more complicated for ErD_2 because it is most likely a multi-step reaction process.

A typical TDS spectra for an ErD_2 film is shown in Fig. 4.1. Two features immediately become apparent, the large peak at roughly 540°C and the smaller peak near 350°C . A statistical analysis of four identical samples yielded an average desorption temperature for the large peak of 534.1°C and for the smaller peak of 344.6°C which associated activation energies of 54.2 and 41.2 kcal/mol respectively. The larger peak at 534°C clearly is related to the decomposition of the erbium hydride. However, the origin of the smaller peak is not easily determined. Further studies are needed to determine the exact origin of this smaller peak.

Figure 4.1. D₂ thermal desorption spectra from a typical ErD₂ film.

Chapter 5

Erbium Hydride Thermal Desorption: Controlling Kinetics

R. Ferrizz

Executive Summary of SAND2007-2659

Chapter 4 outlined the details of thermal desorption spectroscopy (TDS) along with showing a typical TDS spectra from an ErD_2 film. This report summarizes preliminary attempts to control the kinetics of ErD_2 films through changing various processing parameters.

Two samples were deposited at different deposition rates and substrate temperatures. Fig. 5.1 shows the spectra from two samples each of sample A, 10 Å/s and 500°C, and sample B, 200 Å/s and 200°C. The results are summarized in Table 5.1. The result for sample B is similar to what was shown in Chapter 4. The mechanism for the shift in sample A up to 656C is not known but will be the focus of further study.

Table 5.1. Average desorption peak maximum temperatures (T_p) and activation energies (E_A) for samples A and B.

	Sample A 10 Å/s, 500 °C	Sample B 200 Å/s, 200 °C
$T_p(\text{C})$	656.5	592.5
E_A (kcal/mol)	61.4	57.1

Another study examined the impact of hydriding parameters on TDS results. Table 5.2 summarizes the results of this study. Several interesting trends are observable in the TDS spectra. One, for those samples with G:M significantly higher than 2.0, the peak near 350°C is large, indicating the presence of ErD_3 . This conclusion is also supported by X-Ray Diffraction results. Comparing TDS spectra it appears that the presence of tri-hydride domains decreases the thermal stability of beta-phase di-hydride. Two, the higher the activation energy the more stable the erbium hydride film. This result needs to be verified and studied to fully understand the reason why this is the case.

Figure 5.1. D₂ thermal desorption spectra (1.0 °C/s) for ErD₂/Mo/Si for samples with two different growth conditions.

Table 5.2. Average desorption peak maximum temperatures (T_p) and activation energies (E_A) for samples A and B.

Act Temp (°C)	Load Temp (°C)	Load Press (Torr)	$T_{peakmax}$ (°C)	G:M
300	300	10	582.4	2.160 ± 0.035
300	300	500	551.4	2.389 ± 0.082
500	300	500	559.3	2.423 ± 0.078
300	600	500	585.1	1.956 ± 0.032
500	600	500	695.3	2.018 ± 0.023
400	450	500	575.1	2.000 ± 0.017
400	300	150	587.6	2.027 ± 0.027
400	450	150	599.9	1.968 ± 0.005
500	450	150	589.0	1.985 ± 0.009
400	600	150	592.3	NA
300	450	150	580.0	2.005 ± 0.007
500	300	10	NA	2.066 ± 0.014
300	600	10	603.3	1.947
500	600	10	NA	1.931
400	450	10	NA	2.005

Chapter 6

Evaluation of Diffusion Barrier Materials to Inhibit Mixing between Kovar and Erbium Hydride

D. R. Kammler, L. A. Walla, W. Buttry, H. C. Peebles, C. A. Mehrhoff, M. J. Courtney, L. I. Espada, C. R. Tewell, S. H. King, R. G. Tissot, L. N. Brewer, R. S. Goeke, and R. S. Herrick

Executive Summary of SAND2006-5864

Chromium(Cr), Tungsten(W), evaporated Molybdenum (Mo), sputtered Mo, and TiN were evaluated as material candidates to inhibit intermixing between ErHD and kovar at temperatures of interest for neutron tube processes. Erbium/diffusion barrier/kovar specimens were HD loaded and annealed to simulate the exhaust process. Data from the gas laboratory was combined with auger depth profile analysis (see Fig. 6.1), XRD, and in some cases additional SEM and TEM data to characterize the effectiveness of these barrier materials. Several conclusions can be made from the above data:

1. Intermixing between kovar and ErHD does occur at temperatures relevant to neutron tube processing. Auger depth profile data (see Fig. 6.1d) shows clear evidence of Ni, Co, and Fe from the substrate in the Er hydride film and Er in the kovar substrate.
2. Chromium does not appear to be an effective diffusion barrier. Auger depth profile data (see Fig. 6.1a) shows Er has diffused through the Cr and into the substrate and Fe, Ni, Co have diffused through the Cr into the ErHD film.
3. Tungsten appears to be a more effective barrier since no second unidentified phases were observed in the XRD pattern. Auger depth profile data (see Fig. 6.1b) indicate that Er did not diffuse through the tungsten barrier. The Fe, Ni, and Co in the kovar substrate did not diffuse through the tungsten into the Er hydride film either. However, the amount of Er recovered after desorbing annealed ErHD/W/kovar specimens for the G:M measurements was significantly smaller than that recovered from the other specimens. SEM EDS analysis of the kovar substrate and W film following the Er acid etch showed evidence of ~ 2 atomic percent of Er in the W film. This suggests the G:M and D:M numbers for these specimens may not represent the true stoichiometry of the erbium hydride film in these specimens.

Figure 6.1. Sputter Auger spectra for (a) ErHD/Cr/Kovar, (b) ErHD/W/Kovar, (c) ErHD/TiN/Kovar, (d) ErHD/Kovar, (e) ErHD/Mo e-beam/Kovar, (f) ErHD/Mo sputtered/Kovar films. All films had 2000 AA of diffusion barrier material and 5000 AA of ErHD film.

4. TiN deposited via reactive sputtering appears to be more effective than no barrier or Cr. There is, however, some evidence of a reaction between the TiN and the ErHD film. XRD data taken from a ErHD/TiN/kovar specimen subjected to a 2 hr. 564 °C anneal showed evidence of a weak unidentified peak which might be ErN. Auger depth profile data from this specimen show no evidence for diffusion of Er through the TiN into the kovar or vice versa.

5. Molybdenum deposited via electron beam evaporation appears to be an effective barrier. There is no evidence of reaction products between the ErHD, Mo, and kovar in specimens of ErHD/Mo(e-beam)/kovar subjected to a 2 hr. 564 °C anneal. Auger depth profile data(see Fig. 6.1e) from this specimen show no evidence of intermixing between the elements in the ErHD/Mo(e-beam)/kovar film stack. STEM-EDX spectrum image analysis revealed 10-20 nm thick reaction layers between the ErHD and Mo film and between the Mo and kovar substrate.

6. Molybdenum deposited via sputtering appears to be more effective than Cr or no barrier material but shows signs of failure after being subjected to a 564 °C 2 hr. anneal. XRD data from ErHD/Mo(sputtered)/kovar specimens subjected to this anneal did not show evidence of additional phases which might be reaction products between the ErHD, Mo, and kovar. However, there was evidence of hexagonal Er metal (which may well have been a solid solution of H in hexagonal Er metal) in the XRD pattern which suggests the ErHD films started to unload. Auger depth profile data(see Fig. 6.1f) from the same specimen show no evidence of intermixing between elements in the ErHD/Mo(sputter)/kovar film stack. STEM-EDX spectrum imaging again showed a 10-20 nm reaction layers at the Mo/kovar and Mo/ErHD interfaces. These data also show diffusion of Er along grain boundaries of the columnar Mo grains toward the kovar substrate beneath.

The importance of processing was illustrated by the differing abilities of the sputtered Mo and e-beam evaporated Mo film micro-structures to resist Er diffusion under the same annealing conditions. This suggests process variables may impact the level of uncertainty between the data captured in the G:M measurement and the true stoichiometry in the Er hydride film. Process differences may also impact erbium hydride film characteristics such as texture and background oxygen contamination level. In this study, the erbium hydride films grown on kovar capped with W, TiN, e-beam evaporated Mo, and sputtered Mo were found to have a strong (111) texture while those grown on kovar and kovar with a Cr cap were found to have more random textures. All the annealed ErHD films examined with XRD appeared to have some level of Er₂O₃. Auger depth profile data showed oxygen concentrated at the ErHD/kovar and ErHD/evaporated Mo interfaces. In contrast, oxygen appeared to be distributed more evenly throughout the ErHD films on top of Cr, TiN, W, and sputtered Mo. The initial choice of diffusion barrier deposition parameters has yielded films that in some cases (e.g. e-beam evaporated Mo) appear to dramatically reduce inter-diffusion relative to what is observed in a control specimen after identical anneals. Additional process optimization may yield films which perform significantly better than those produced in this study. The impact of process variables such as substrate cleaning procedure, substrate temperature during deposition, deposition rate, film thickness, crucible preparation (for e-beam

evaporation), and the composition of the background ambient need to be characterized and understood for e-beam evaporation, sputtering and perhaps other methods that were not evaluated in this study. In the case of sputtering additional process variables include the use of a substrate bias, varying the sputter deposition pressure, composition of the sputter gas, and the use of a sputter pre-clean. Without a systematic investigation of this process space it is premature to conclude whether sputtering, evaporation, or some other deposition method is truly superior once a material is selected.

Chapter 7

Mechanisms governing D loss in ErD_2 films on kovar with and without a Mo diffusion barrier

D. R. Kammler, W. R. Wampler, S. B. Van Deusen, S. H. King, R. G. Tissot, L. I. Espada, and R. S. Goeke

Executive Summary of SAND2006-5699

Intermixing between a kovar substrate and Er or ErD_2 films with and without the presence of a Mo diffusion barrier was investigated for different times and temperatures in situ using a combination of RBS and NRA ion beam techniques. Substantial intermixing begins between 400 to 450°C for Er/Kovar and 450 to 500 °C for ErD_2 /kovar. Decomposition of the ErD_2 films in this study was found to be driven both by intermixing with components of the kovar substrate (< 500 °C) and simple thermal decomposition (> 500 °C). RBS data collected isothermally at 500 and 550 C have yielded an activation energy of 2.1 eV and a pre-exponential factor of $0.071 \text{ cm}^2/\text{s}$ for diffusion of Er into kovar from ErD_2 . The presence of a Mo diffusion barrier was shown to help reduce diffusion between the ErD_2 film and kovar substrate. Microstructure differences may explain why the E-beam evaporated Mo shows evidence of intermixing between 550-600 °C while the sputtered Mo barrier shows evidence of intermixing between 500-550 °C. Since both processes require optimization it is unclear which method might ultimately yield the best barrier. While a well-engineered Mo diffusion barrier can inhibit the intermixing decomposition mechanism, it cannot suppress thermal decomposition. Therefore, extending the thermal process window beyond 500 °C will require study of the kinetics governing thermal decomposition in addition to process optimization for the Mo diffusion barrier.

Figure 7.1. RBS and NRA spectra for isochronal (20 minutes) anneals at several temperatures for (a) ErHD/Kovar, (b) ErHD/2k Å sputtered Mo/Kovar, and (c) ErHD/2k Å e-beam Mo/Kovar. All films had 5000 Å of ErHD film.

Chapter 8

First principles site occupation and migration of hydrogen, helium, and oxygen in beta-phase erbium hydride

R. R. Wixom, J. F. Browning, C. S. Snow, D. R. Jennison, and P. A. Schultz

Using density functional methods we have calculated the total energy and corresponding equilibrium atomic configuration for the β -phase of ErH_2 . We also investigated several meta-stable configurations including the structure and energy of H occupying the octahedral site—in a 96-atom supercell, 1 H_{Oct} and 1 V_{Tet} separated by more than one nearest neighbor site. The two codes that were utilized were the commercial code VASP (Vienna Ab-Initio Simulation Package[12, 13, 11]) and the Sandia developed SeqQuest[19].

We found that H_{Oct} is unstable by 1.15 eV, but may be trapped in a meta-stable state if no neighboring tetrahedral sites are vacant (see Fig. 8.1). In over-loaded films, H will occupy octahedral sites since there are no tetrahedral sites available. In under-loaded or stoichiometric films, H_{Oct} may exist due to thermally generated $\text{H}_{\text{Oct}} \text{V}_{\text{Tet}}$ pairs or impurities. The specific mechanism for H migration will depend on the H/Er ratio or the existence of H_{Oct} and V_{Tet} . $\text{H}_{\text{Oct}} \text{V}_{\text{Tet}}$ pair formation and H_{Oct} migration (push-mechanism) both proceed by concerted motion. Significant H_{Oct} migration will occur below room temperature. The V_{Tet} mechanism will be active at temperatures near 100 °C. However, substantial thermal generation of $\text{H}_{\text{Oct}} / \text{V}_{\text{Tet}}$ pairs cannot occur until temperatures well over 500°C. This means that in material where the H/Er ratio is very near 2.0, H migration will be minimal unless the material experiences high temperature annealing or impurities are present. In overloaded material, H is free to move even below room temperature.

Oxygen impurities prefer the tetrahedral sites and will force H into a meta-stable H_{Oct} state(see Fig. 8.2). This increases the number of H_{Oct} and will enhance the amount of H diffusion throughout the material. Oxygen will primarily diffuse by making hops between octahedral and tetrahedral sites forcing H, in a concerted motion, out of the way as it proceeds. This process can occur at fairly moderate temperatures (250°C). Although, direct tetrahedral to tetrahedral hops are not energetically favored, this mechanism may become active at higher temperatures. Once mobile, there is a small driving force for oxygen cluster formation—a prediction that is supported by the observation of oxide particles in annealed ErD_2 .

Figure 8.1. Climbing-image nudged elastic band (NEB) data for migration of hydrogen in β -ErH₂. Three possible mechanisms are shown. The dominant mechanism will be determined by the H/Er ratio, which indicates the presence of H_{Oct} and/or V_{Tet}. (a) The barrier and formation energy for the thermal generation of H_{Oct} / V_{Tet} pairs. (b) The barrier for H_{Oct} migration. (c) The barrier for V_{Tet} migration. The open triangle is the final state configuration of path (a) computed with VASP rather than SeqQuest and is typical of the agreement between the two codes.

Figure 8.2. Nudged elastic band (NEB) data for migration of oxygen in erbium hydride. (a) Direct octahedral to octahedral migration. (b) Direct tetrahedral to tetrahedral migration. (c) Migration from a tetrahedral site through an empty octahedral site (path distance of 0.5) and on into another tetrahedral site. For paths b and c the initial and final state have an associated H_{Oct} .

Helium created by tritium decay will seek its ground-state in a vacant tetrahedral site where it will likely be trapped, bound by 0.49 eV. If a connected network of vacant tetrahedral sites exist, helium migration throughout the network will occur at room temperature. Dissociation from this trap has a barrier of 1.31 eV, and the rate limiting barrier for migration beyond this volume is predicted to be 0.88 eV. In order to migrate through the stoichiometric β -phase, helium must move into an empty octahedral site and diffuse by octahedral to octahedral jumps, forcing H_{Tet} temporarily out of the way. At this point, our calculations do not provide a clear mechanism for helium bubble formation, but future calculations are designed to provide insight.

Figure 8.3. Climbing image nudged elastic band data for helium migration in ErH_{2+x} . (a) Direct octahedral to octahedral migration. (b) Concerted-motion from empty octahedral to a filled tetrahedral position (path distance of 0.5) and on to another empty octahedral site. The energy of the tetrahedral site, 0.75 eV, was also calculated with VASP as 0.73 eV. (c) Migration between octahedral and vacant tetrahedral sites. All of the data is arranged such that a path distance of 0 or 1 is an octahedral site. For paths (b) and (c) 0.5 is in the tetrahedral site, while for (a) it is the direct mid-point between two octahedral sites.

References

- [1] A.Kponou and et al. Experiments on the 2^3p state of helium.iii. measurement of the 2^3p_0 - 2^3p_1 fine structure interval. *Phys. Rev. A*, 24:264–278, 1981.
- [2] L.C. Beavis. Metal tritides helium emission. Technical report SAND79-0645, Sandia National Laboratories, Albuquerque, New Mexico 87185 and Livermore, California 94550, 1979.
- [3] L.C. Beavis and W.J. Kass. Room-temperature desorption of ^3He from metal tritides: A tritium concentration effect on the rapid release of helium from the tritide. *J. Vac. Sci. Technol.*, 14:509–513, 1977.
- [4] C. L. Bohler and B. I. Martin. Helium spectroscopy using an indium gallium arsenide laser diode. *Optics Letters*, 19:1346–1348, 1994.
- [5] G. Bond and J. F. Browning. Private communication.
- [6] J. Chen, P. Hung, and H. Trinkaus. Evolution of helium platelets and associated dislocation loops in α -sic. *Phys. Rev. B*, 82:2709, 1999.
- [7] D.F. Cowgill. Helium nano-bubble evolution in aging metal tritides. Technical report SAND2004-1739, Sandia National Laboratories, Albuquerque, New Mexico 87185 and Livermore, California 94550, 2004.
- [8] C.S. Snow et al. Helium release and micro-structural changes in $\text{er(d,t)}_{2-x}\text{He}_x$ films. Technical report SAND2007-7983, Sandia National Laboratories, Albuquerque, New Mexico 87185 and Livermore, California 94550, 2007.
- [9] W. G. Perkins et al. ^3He release characteristics of metal tritides and scandium-tritium solid solutions. Technical report SAND75-0989-2, Sandia National Laboratories, Albuquerque, New Mexico 87185 and Livermore, California 94550, 1975.
- [10] Gerhard Herzberg. *Atomic spectra and atomic structure*. Dover Publications, New York, 1944.
- [11] G. Kresse and J. Furthmuller. *Comput. Mater. Sci.*, 6:159, 1996.
- [12] G. Kresse and J. Hafner. *Phys. Rev. B*, 47:589, 1993.
- [13] G. Kresse and J. Hafner. *Phys. Rev. B*, 49:14521, 1994.
- [14] Tamara K. Locke. Guide to preparing SAND reports. Technical report SAND98-0730, Sandia National Laboratories, Albuquerque, New Mexico 87185 and Livermore, California 94550, May 1998.

- [15] P.A. Redhead. Thermal desorption of gases. *Vacuum*, 12:253–258, 1962.
- [16] C. R. Ridu and K. C. Jordan. Tritium half-life. Technical report MLM-2458, Mound Laboratory Report, Miamisburg, OH 54342, 1977.
- [17] T. Schober and H. Trinkaus. ^3He effects in tritides. In S. E. Donnelly and J. H. Evans, editors, *Fundamental Aspects of Inert Gases in Solids*, pages 83–94, New York, 1991. Plenum Press.
- [18] T. Schober and H. Trinkaus. *Zeit. fur Phys. Chem.*, 183:473–477, 1994.
- [19] P. A. Schultz. Seqquest code (unpublished). <http://dft.sandia.gov/quest>.

Appendix A

Publications and Presentations

A.1 External Publications

M. A. Rodriguez, *et. al.*, “Unit cell expansion in ErT_2 films”, Powder Diffraction **22** (2), pp.118-121, June 2007.

C. S. Snow, *et. al.*, “Helium release and microstructural changes in $\text{Er}(\text{D,T})_{2-x}\text{He}_x$ films”, J. Nucl. Mats. in press.

A.2 SAND Reports

SAND2006-5864 “Evaluation of Diffusion Barrier Materials to Inhibit Mixing between Kovar and Erbium Hydride” by D. R. Kammler, L. A. Walla, W. Buttry, H. C. Peebles, C. A. Mehrhoff, M. J. Courtney, L. I. Espada, C. R. Tewell, S. H. King, R. G. Tissot, L. N. Brewer, R. S. Goeke, and R. S. Herrick.

SAND2006-5699 “Mechanisms governing D loss in ErD_2 films on kovar with and without a Mo diffusion barrier” by D. R. Kammler, W. R. Wampler, S. B. Van Deusen, S. H. King, R. G. Tissot, L. I. Espada, and R. S. Goeke.

SAND2006-7014 “Erbium Hydride Decomposition Kinetics” by R. M. Ferrizz.

SAND2007-2659 “Erbium Hydride Thermal Desorption: Controlling Kinetics” by R. M. Ferrizz.

A.3 External Presentations

R. M. Ferrizz “TDS to Study the Kinetics of Erbium Hydride Decomposition”, Poster presented to the 232nd American Chemical Society National Meeting, San Francisco, CA Sept. 2006.

R. R. Wixom, J. F. Browning, C. S. Snow, D. R. Jennison, and P. A. Schultz, “Fundamental investigation of erbium di-hydride”, Poster presented to the Materials Research Society Fall Meeting, Boston, Oct. 2007.

C. M. Parish, C. S. Snow, J. F. Browning, and L. N. Brewer, “Epitaxial Oxide Growth in ErH_2 Thin Films”, Poster presented to In Microscopy and Microanalysis 2007, Ft. Lauderdale, FL.

J. A. Knapp and J. F. Browning, “Evolution of the Nanomechanical Properties of Aging Erbium Tritide Films”, presented at the Spring Meeting of the Materials Research Society, San Francisco, CA, April 9-13, 2007.

Appendix B

Hydrogen and Helium Isotopes in Materials Conference

B.0.1 Review of February 2007 Hydrogen and Helium Isotopes in Materials Conference

The intent of the Hydrogen and Helium Isotopes in Materials (HHIM) conference is to provide a forum for researchers working in the areas of aging effects in materials comprised of at least one radioactive element, or isotope, as well as radiation effects in storage and containment materials. Specifically, those events that result in the accumulation of helium within the material. These areas of materials research are of interest to neutron generator technology, hydrogen-isotope gas transfer and storage systems, actinide science and fusion science and technology. It is hoped that this forum will stimulate communication and possible collaboration between researchers from these communities. In the past, each of these communities has worked in somewhat of an isolated fashion. Given that the physics and chemistries of aging phenomena associated with each of these areas are the same or similar, it was thought that the HHIM Conference would be beneficial to leverage the knowledge and expertise of workers across these areas in an effort to increase efficiency and reduce the impact of shrinking budgets. Also, given that these areas are not traditional areas of academic research; this forum is intended to bridge the gap between established research programs and aid in training incoming researchers as experienced workers age and retire. It is also hoped to stimulate relationships between academia that may result in the training of graduate students where appropriate.

The February 2007 meeting was the fourth meeting in a three and a half year period. The conference has grown in attendance from 25-30 attendees mostly from Los Alamos National Laboratory (LANL) and Sandia National Laboratories (SNL) to an international gathering of 75 researchers over a two day period with 27 presentations from LANL, SNL, Lawrence Livermore National Laboratory, Oak Ridge National Laboratory, Savannah River National Laboratory, Pacific Northwest National Laboratory, NASA's Jet Propulsion Laboratory, the National Institute of Standards and Technology, the United Kingdom's Atomic Weapons Establishment, the French Ecole Polytechnique, New Mexico Institute of Mining and Technology, and the Georgia Institute of Technology. The feedback from the participants has been highly positive which is reflected in the growth in the number and variety

of institutions involved. This conference will continue to grow as collaborations form and other researchers realize the benefit of the conference to their work. It is anticipated that this conference and the resulting collaborations will yield benefits to the NNSA and its programs.

An archive of the presented talks can be found at <http://www.sandia.gov/tritides/archive.html> along with other information regarding the conference.

The organizing committee was Clark Snow and Jim Browning with administrative assistance from Nicolette Bauer.

Appendix C

Key Historical Publications on ^3He in Metals

J. H. Coon, “ He^3 Isotopic Abundance”, *Physical Review*, **75** (1949) pp. 1358.

D. E. Rimmer and A. H. Cottrell, “The Solution of Inert Gas Atoms in Metals”, *Phil. Mag.*, **23** (1957) pp. 1345-1353.

L. C. Beavis and C. J. Maglionico, “Structural Behavior of Metal Tritide Films”, *J. Less Common Metals*, **27** (1972) pp 201.

W. D. Wilson, M. I. Baskes, and C. L. Bisson, “Atomistics of helium bubble formation in a face-centered-cubic metal”, *Phys. Rev. B*, **13** (1976) pp 2470.

J. H. Evans, “An Interbubble Fracture Mechanism of Blister Formation on Helium-Irradiated Metals”, *J. Nucl. Mats.*, **68** (1977) pp. 129-140.

L. C. Beavis and W. J. Kass, “Room-temperature desorption of ^3He from metal tritides: A tritium concentration effect on the rapid release of helium from the tritide”, *J. Vac. Sci. Technol.*, **14** (1977) pp. 509.

W. J. Kass, “Thermal desorption measurements of helium ion-implanted erbium tritide”, *J. Vac. Sci. Technol.*, **14** (1977) pp. 518.

J. H. Evans, “The role of implanted gas and lateral stress in blister formation mechanisms”, *J. Nucl. Mats.*, **76 & 77** (1978) pp. 228-234.

D. J. Mitchell and R. C. Patrick, “Temperature dependence of helium release from erbium tritide films”, *J. Vac. Sci. Technol*, **19** (1981) pp. 236.

W. D. Wilson, C. L. Bisson, and M. I. Baskes, “Self-trapping of helium in metals”, *Phys. Rev. B*, **24** (1981) pp. 5616.

W. Jager, R. Manzke, H. Trinkaus, G. Crecelius, and R. Zeller, “Density and pressure of helium in small bubbles in metals”, *J. Nucl. Mats.*, **111 & 112** (1982) pp. 674-680 .

M. I. Baskes and W. D. Wilson, “Kinetics of helium self-trapping in metals”, *Phys. Rev.*

B, **27** (1983) pp. 2210.

G. J. Thomas and J. M. Mintz, "Helium bubbles in palladium tritide", J. Nucl. Mats., **116** (1983) pp. 336-338.

G. J. Thomas, "Experimental Studies of Helium in Metals", Radiation Effects, **78** (1983) pp. 37-51.

H. Trinkaus, "Energetics and formation kinetics of helium bubbles in metals", Radiation Effects, **78** (1983) pp. 189-211 .

H. Trinkaus, "On the modeling of the high-temperature embrittlement of metals containing helium", J. Nucl. Mats., **118** pp. 39-49 (1983).

W. G. Wolfer *et. al.*, "Helium equation of state for small cavities: recent developments", J. Nucl. Mats., **122 & 123** pp. 565-570 (1984).

H. Trinkaus and W. G. Wolfer, "Conditions for dislocation loop punching by helium bubbles", J. Nucl. Mats., **122 & 123** pp. 552-557 (1984).

T. Schober *et. al.*, "An electron microscopy study of tritium decay in vanadium", J. Nucl. Mats., **122 & 123** (1984) pp. 571-575.

D. J. Mitchell and J. L. Provo, "Irregularities in helium release rates from metal ditritides", J. Appl. Phys., **57** (1985) pp. 1855.

T. Schober, H. Trinkaus, and R. Lasser, "A TEM study of the aging of Zr tritides", J. Nucl. Mats., **141-143** (1986) pp. 453-457 .

T. Schober *et. al.*, "Swelling of selected metal tritides", J. Less Common Metals, **131** (1987) pp. 293-299.

G. G. Spulak, "On helium release from metal tritides", J. Less Common Metals, **132** (1987) pp. L17-L20.

R. Lasser, K. Bickman, and H. Trinkaus, "X-ray diffraction study of the lattice deformation due to ^3He bubble formation in a tantalum tritide", Phys. Rev. B, **40** (1989) pp. 3306.

T. Schober and K. Farrell, "Helium bubbles in α -Ti and Ti-tritide arising from tritium decay: a TEM study", J. Nucl. Mats., **168** (1989) pp. 171-177.

G. C. Abell and D. F. Cowgill, "Low-temperature ^3He NMR studies in aged palladium tritide", Phys. Rev. B, **44** (1991) pp. 4178.

T. Schober and H. Trinkaus, " ^3He effects in tritides", Fundamental Aspects of Inert Gases in Solids, Edited by S. E. Donnelly and J. H. Evans, Plenum Press, New York (1991) pp 83.

- B. N. Singh and H. Trinkaus, "An analysis of the bubble formation behavior under different experimental conditions", J. Nucl. Mats., **186** (1992) pp. 153-165.
- T. Schober and H. Trinkaus, "Suppression of ^3He Bubble Formation by Impurities in Tritides: Swelling of the Dilute Alloy $\text{NbO}_{0.015}\text{Ti}_{0.01-x}\text{He}_x$ ", Zeit. für Phys. Chem., **183** (1994) pp. 473-477.
- A. I. Vedeneev, A. N. Golubkov, and I. A. Abramov, "Helium-3 Release from Vanadium Tritide", Russian Metallurgy, **3** (1998) pp. 127-130.
- J. Chen, P. Jung, and H. Trinkaus, "Evolution of Helium Platelets and Associated Dislocation Loops in $\alpha\text{-SiC}$ ", Phys. Rev. Letters, **82** (1999) pp. 4475.
- M. Hartmann and H. Trinkaus, "Evolution of Gas-Filled Nanocracks in Crystalline Solids", Phys. Rev. Letters, **88** (2002) pp. 055505.
- B. A. Kalin *et. al.*, "Effect of doping on helium behavior and bubble structure development in nickel and vanadium alloys", Atomic Energy, **92** (2002) pp. 50.
- R. P. Gupta and M. Gupta, "Consequences of helium production from the radioactive decay of tritium on the properties of palladium tritide", Phys. Rev. B, **66** (2002) pp. 014105.
- A. Fabre *et. al.*, "On the correlation between mechanical and TEM studies of the aging of palladium during tritium storage", J. Nucl. Mats., **342** (2005) pp. 101-107.

DISTRIBUTION:

- 1 Jim Browning
Low-Q Scatering Group
Spallation Neutron Source
Oak Ridge National Laboratory
PO Box 2008, MS 6475
Oak Ridge, TN 37831-6475
- 1 Dave Gelles
Pacific Northwest National Laboratory
PO Box 999, Richland, WA 99352
- 4 MS 0878 Clark Snow, 2735
- 1 MS 0878 Loren Espada, 2735
- 1 MS 0878 Rob Ferrizz, 2735
- 1 MS 0878 Dan Kammler, 2735
- 1 MS 0878 Mike Eatough, 2735
- 1 MS 0878 Juan Elizondo, 2735
- 1 MS 1056 James Knapp, 1111
- 1 MS 1056 James Banks, 1111
- 1 MS 1411 Mark Rodriguez, 1822
- 1 MS 1411 Chad Parish, 1822
- 1 MS 1411 Luke Brewer, 1814
- 1 MS 0886 Paul Kotula, 1822
- 1 MS 0862 Carla Busick, 2713
- 1 MS 0862 Saskia King, 2713
- 1 MS 0871 Cliff Renschler, 2730
- 1 MS 9161 Don Cowgill, 8758
- 1 MS 1455 Ryan Wixom, 2555
- 1 MS 0899 Technical Library, 9536 (electronic copy)