^3He bubble evolution in ErT_2 : A survey of experimental results

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Abstract

For the past several years we have been carrying out a long term experimental study of ^3He in ErT_2 (erbium di-tritide). This study has attempted to answer questions regarding the evolution of helium bubbles in $\text{ErT}_{2-x}\text{He}_x$. ErT_2 samples have been studied periodically over four years using Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), and Nano-Indentation (NI). In $\text{ErT}_{2-x}\text{He}_x$, helium bubbles are plate-like and grow along $\{111\}$ planes. The bubbles grow in three distinct phases. First, they nucleate and grow as “Griffith-cracks” until an age of ~ 0.15 He:M. Second, around 0.15 He:M the diameter stops increasing and instead the bubbles grow in thickness by punching dislocation dipoles. Third, the bubbles grow in size until ~ 0.3 He:M at which point the bubbles begin to link.

1 Motivation

The behavior of inert gases in metals has been actively researched for nearly 60 years.[1,2] The field encompasses research on materials used in nuclear reactor and fusion wall materials along with the need to store the radioactive hydrogen isotope tritium. The most commonly found inert gases in metals are helium, krypton, and xenon. The three main processes in which an inert gas is inserted into a metal matrix are ion implantation, nuclear reactions, and radioactive decay.[2] Each method emphasizes different aspects of the problem of inert

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gases in metals. Ion implantation produces significant damage to the metal matrix and can be used to implant to very high inert gas concentrations.[3,4] The nuclear reactions that can occur generally are through (n,p) reactions and usually don't produce significant lattice damage or high concentrations of inert gas.[5] The radioactive decay methods involve the alpha-decay of uranium and plutonium and the beta-decay of the hydrogen isotope tritium into ^3He . The fission decay products also produce significant lattice damage[6] while the tritium decay process produces no lattice damage but can yield extremely high inert gas concentrations.[7] The wide range of phenomena has made the synthesis of a complete theory of inert gases in metals difficult.

This article will focus on helium introduced into erbium di-tritide (ErT_2) via the beta-decay of tritium. Helium in erbium has many unique features that have not yet been adequately discussed. In what follows we will present the important properties of the erbium-hydrogen system specifically applicable to helium in erbium tritide. Then, we will discuss the results of our recent work and what we have learned regarding helium bubble nucleation, shape, distribution, growth and interaction, and helium release. This paper largely represents a summary, extension, and cohesive analysis of data presented in the following papers: Rodriguez *et al.*, "Unit cell expansion in ErT_2 films";[8], Bond *et al.*, "Development of bubble microstructure in ErT_2 films during aging";[9] and Knapp *et al.*, "Evolution of mechanical properties in ErT_2 thin films".[10] We conclude with comments relating to future research and suggest other experiments that would have an impact on our understanding of ^3He in ErT_2 .

2 Introduction and Background

Helium in metal tritides presents a rather complicated case. The diffusion of helium in a metal tritide is impacted by the stoichiometry of the metal hydride.[11] In order to understand the behavior of helium in the metal it is critical to also understand the behavior of the tritium in the metal. In the next two subsections we will present the necessary background information on erbium hydride (all isotopes including tritium) and the state of knowledge for helium in erbium until the present work.

2.1 Erbium Hydride

Studies on the transition and rare-earth metal hydrides have been ongoing for well over a half-century. Many books have been written focusing on the structural, thermodynamic,[12–19] and metallurgical properties of metal hy-

Fig. 1. A phase diagram for the Hydrogen:Erbium system. This phase diagram is also for the heavy rare earths (Gd to Tm) (RE:H) system. The three important phases are the α -phase where hydrogen is in solution with the erbium metal lattice, the cubic di-hydride β -phase, and the tetragonal tri-hydride γ -phase. The difference between the solid and dashed lines on the β phase boundary represents the stoichiometric deficiency, δ .

drides.[20] Much of the important crystallographic and thermodynamic data needed to understand the ErT_2 system can be found in two excellent review articles by P. Vajda[21] and R. R. Arons.[22]

Lundin performed the first known measurements of the pressure-composition-temperature (PCT) phase diagram on the Er-H system.[23] The reported phase diagram is sketched in Fig. 1.[21] He reported an α phase where hydrogen, up to an H:Er concentration of 0.2, is in solution with the Er metal. Beyond an H:Er ratio of 0.2 a two-phase region occurs separating the α and β phases. Lundin reported that the β phase began near an H:Er ratio of 1.8 and extended up to 2.2.[23] Lundin's work was performed on 3N (99.9% pure) material. Vajda has since demonstrated that in actuality, the phase boundary does not begin until an H:Er (same for the other heavy rare earths) ratio of 2.0.

Fig. 2. a) HCP structure of erbium metal. b) 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 spheres represent the hydrogen atoms.

The discrepancy he ascribes to a “stoichiometric deficiency”.[21] He writes the chemical equation as $\text{H:Er}_{2+x-\delta}$ where the x counts the amount of hydrogen in excess of 2.0 and δ represents the number of RE metal atoms that can’t bond with hydrogen. The theory is that in the hydrided material the RE:H ratio is nearly a perfect 2.0, but that some of the RE material can’t be hydrided but is still measured which drives down the apparent stoichiometry, a stoichiometric deficiency. To support his theory, he measured the beginning β phase boundary on several bulk pieces of rare-earth metals using 3N (99.9% pure) and 4N (99.99% pure) materials. The 4N materials exhibited a β phase that began very close to 2.0 while the 3N materials had a β phase boundary near 1.8. The stoichiometric deficiency derives from impurities, defects, grain boundaries, or any situation where the RE metal can’t bond with hydrogen. For erbium and many RE metals, oxygen is a major contaminant which would contribute to a stoichiometric deficiency.[24] Vajda states that 4N bulk materials with annealing and other treatments can be made to have a δ of 0.01 - 0.04. Fine powders and thin films are expected to have much higher δ values such that a pure di-hydride film, such as that used in this study, could have a measured stoichiometry of 1.8 with a δ of 0.2.[21]

The crystallographic properties of the H:Er system are now well known and understood. Erbium metal forms in the HCP (hexagonal close-packed) structure shown in Fig. 2a. The α -phase of the hydrogen-erbium system has hydrogen atoms occupying the tetrahedral interstitial sites of the HCP metal lattice. This was confirmed by ion channeling and neutron diffraction studies on the analogous systems $\alpha\text{-LuD}_x$ [25], $\alpha\text{-YD}_x$, [26], $\alpha\text{-Tm-D}_x$, [27], and $\alpha\text{-ScD}_x$. [28] The β -phase of the Er:H system is the CaF_2 structure (Space Group $\text{Fm}\bar{3}\text{m}$, # 225), shown in Fig. 2b. In the CaF_2 structure the erbium metal atoms are

arranged in an FCC pattern with the hydrogen atoms occupying the tetrahedral lattice sites.[29] It has been shown, based on thermodynamic arguments and supported by inelastic neutron scattering, that some of the octahedral sites of the β -phase for the RE:H_{2.0- δ} systems are occupied even at room temperature.[30,31] There will also be some site preferences for the different hydrogen isotopes. The thermodynamic arguments have been further confirmed by first-principles Density Functional Theory (DFT) calculations carried out by Wixom.[11] The thermally induced octahedral site occupation effect will be small compared to the stoichiometric deficiency in most materials. It should be noted that if a sample is measured with a super-stoichiometric ratio, i.e., > 2.0 , then the actual x ratio will be higher by the stoichiometric deficiency δ . The occupation of even a small percentage of octahedral sites while some tetrahedral sites are still unoccupied could have a significant impact on helium properties in ErT₂. Octahedral site occupation could change the helium mobility and site binding energies which would change the helium bubble nucleation and growth dynamics.[11,32] Most of the RE metal hydrides, including ErH_{2+x} can accommodate up to $x = 0.20$ of excess hydrogen atoms in the octahedral sites creating a super-stoichiometric compound. These octahedral hydrogen atoms are mobile at room temperature. Using DFT calculations Wixom showed that the octahedral hydrogen move in a *concerted motion* where the octahedral hydrogen diffuse by moving into an occupied neighboring tetrahedral site and displacing the tetrahedral hydrogen into an octahedral site. The energy barrier for this movement is 0.62 eV, which is small enough that significant diffusion will occur at room temperature.[11] The hydrogen in the octahedral lattice sites are not as stable as the hydrogen in the tetrahedral sites. This can be seen from the fact that the equilibrium pressure at the isothermal plateau of the β -phase is low (10^{-6} Torr at 500-600°C). Thus, the octahedral hydrogen can be removed after hydriding a sample into the β -phase simply by holding the sample at elevated temperatures and removing the gas (this also provides a convenient method to determine the stoichiometric deficiency δ). The precise amount of excess gas, x , can then also be controlled by evacuating the hydrogen gas from the sample to produce a near perfect di-hydride and then reintroducing hydrogen gas that will only enter into the empty octahedral sites.[21] It should be noted that in the super-stoichiometric case, the unit cell of the CaF_2 structure decreases with increasing x . This is due to the ionic nature of the hydrogen in the metal lattice.[21] If sufficient hydrogen atoms fill the octahedral sites then a final transformation back to an HCP phase with an RE:H ratio of near 3.0 occurs. The tri-hydride γ -phase has an HCP structure but with a larger unit cell. The γ phase has many interesting properties but is not important for this paper and will not be discussed further.[33]

Erbium readily forms a very stable sesquioxide, Er₂O₃. To give a comparison the heat of formation for Er₂O₃ is -19.67 eV at 25°C while Al₂O₃ is -17.37 at 25°C (for the corundum structure).[34] The oxide surface has a tremendous impact on the kinetics of the hydriding process and also potentially on the

helium release properties.[35] The native oxide thickness of an electron beam deposited erbium film after being exposed to air is around 100 Å.[36] If the air exposed erbium film is then hydrided, the oxide thickness increases, depending on the hydrogen gas purity.[36] While the oxide surface is predominantly Er_2O_3 , the presence of hydroxides has also been detected using XPS.[33,37] Even though the heat of formation for ErH_2 is negative (-2.30 eV/mole),[34] the reaction does not proceed because the erbium oxide layer prevents hydrogen diffusion into the bulk and the H:Er reaction. An “activation” step is needed in order to get the H:Er reaction to happen;[19] however, the activation step is not associated with an energy barrier to the reaction that needs to be overcome. Instead, it has been shown that upon heating erbium films, oxygen is driven into the bulk of the erbium leaving an oxygen deficient $\text{Er}_2\text{O}_{3-x}$ surface that reacts with and permits the diffusion of hydrogen.[33,37] Parish *et al.* showed that oxygen is a very common contaminant in erbium films, forming dispersed erbium oxide nanoinclusions and larger macroscopic particles.[24]

2.2 ^3He in Erbium Tritide

The literature of He in metals is not nearly as extensive as that of metal hydrides, including only a few review articles or books.[2,35,38,39] Of them, the book by R. Lässer on tritium and ^3He in metals is the latest.[35]

Early measurements of $\text{ErT}_{2-x}\text{He}_x$ determined the amount of helium that was retained in ErT_2 films and that the ^3He evolution, or release, from films occurred in two distinct regimes. The ‘early’ release phase is characterized by most of the helium being retained in the film and only a small fraction, 0.01 to 0.1 %, released from the film[40–42]. The measurement of a very small initial fraction of helium released from the film has been corroborated in other measurements on $\text{ErT}_{2.0}$. [43] Snow *et al.* also showed that the total amount of helium released early in life was independent of film thickness which they interpreted to mean that the helium released early in life is coming from the near surface region.[43] A second phase, termed ‘critical’ release is characterized by most of the generated helium being released from the film. The onset of critical release occurs around 0.3 He:M for $\text{ErT}_{2-x}\text{He}_x$, while for $\text{TiT}_{2-x}\text{He}_x$, and $\text{ZrT}_{2-x}\text{He}_x$ it occurs around 0.40 and 0.45 He:M respectively.[42] The differences in critical release between materials is a complicated interplay between fracture mechanics, surface energies, and bubble densities.

Films of metal tritides undergo swelling due to the accumulation of helium in the metal matrix. This swelling runs counter to the lattice contraction from the loss of tritium. Measurements of the amount of swelling of erbium, yttrium, holmium, titanium, and scandium tritide films with age, i.e., amount of ^3He in the film, showed a near linear swelling rate with only the slope changing

Fig. 3. Neutron reflectivity results for two ErT_2 samples. The solid line (sample 1) and dashed line (sample 2) are linear fits to the data in the early release region while simply guides to the eye in the critical release region.[49]

with different materials[44]. The authors used this data to suggest that helium was accumulating in bubbles in these films. Swelling data, when coupled with the Equation of State (EOS) of helium, yields the pressure of the helium in a bubble.[45] Using precision dilatometry Schober studied $\text{NbT}_{0.0253}$, $\text{TaT}_{0.0744}$, and $\text{LuT}_{0.15}$ and reported helium bubble pressures of 8-9, 11-13, and 6-8 GPa, respectively.[46,47] Note that all of these materials are in the alpha phase and not the β -dihydride phase that is of interest to ErT_2 . The swelling of $\text{PdT}_{0.6}$ has also been measured yielding a calculated helium bubble pressure of 3-6 GPa depending on the age of the sample with the older the sample the lower the pressure.[48] The swelling of ErT_2 films were measured by Browning using neutron reflectivity (NR). This technique is very powerful because the thickness and chemistries of all layers in the film can be tracked simultaneously so for example, any growth in the oxide layer will not impact the swelling measurement of the important tritide layer. His measurements yielded helium bubble pressures of 0.9 and 3.0 GPa for two separate samples,[49] the results are shown in Fig. 3 for the swelling of the tritide layer of ErT_2 .

The Transmission Electron Microscope (TEM) has been used to image the he-

lium bubbles in many metal tritide systems and inert gas implanted materials.[43,50–57] As shown in Snow *et al.* and in more detail below, the helium bubbles in ErT₂ are platelets with diameters between 10-20 nm, only a few nm thick, aligned along the {111} planes, and with bubble densities of 1-9x10²³ bubbles/m³. [43] See Fig. 8 for a diagram of a helium bubble and the meaning of the terms diameter and thickness.

Wilson *et al.* first proposed a self-trapping mechanism for helium bubble nucleation in 1981.[58] They calculated the energies associated with mobile interstitial helium moving in a nickel lattice using the embedded atom method. They found a binding energy of only 0.22 eV for two helium atoms in neighboring interstitial sites with no nickel vacancies. This binding energy climbs to 2.02 eV for six helium atoms. As helium atoms join the cluster, nickel atoms are eventually ejected from their lattice site and create a nearby self-interstitial. Five interstitial helium atoms spontaneously produce a single lattice vacancy and self-interstitial, eight helium atoms create two lattice vacancy and self-interstitial pairs, while sixteen helium atoms produce five pairs. An important feature they calculated was that the nickel self-interstitial's prefer to cluster on the same side of the helium bubble which makes the self-trapping of helium energetically favorable.[58] Independent calculations using the same approach confirm the possibility of a self-trapping mechanism.[59,60] In a later paper Baskes and Wilson[61] state that the self-trapping mechanism explains the experiments of low-energy helium implantation by Thomas and Bastasz.[62] Because of the small length scales associated with helium bubble nucleation it is very difficult to observe the nucleation of a helium bubble in a metal tritide. Differences in swelling in oxygen doped samples of NbT (NbO_{0.015}T_{0.01-x}³He_x) suggest that helium bubbles are nucleated around oxygen impurities. In helium implanted at 200 keV into zirconium, the helium was observed to accumulate in oxygen rich regions of the material and that the helium mobility was reduced when oxygen was pre-implanted into the zirconium.[63] Finally, the specific details of helium bubble nucleation is extremely complicated and many questions remain.

Evans calculated the helium bubble pressure necessary to produce inter-bubble fracture in a metal matrix.[64] A gas bubble of internal pressure P and radius r will be in equilibrium when $P = 2\gamma/r$ where γ is the surface tension. If $P > 2\gamma/r$ then there is an excess internal pressure which is defined as $P' = P - 2\gamma/r$. A bubble with excess internal pressure will have a pure shear strain around it with the perpendicular planes to the surface being in tension. If a simple cubic array of spherical bubbles, spaced a distance d apart, is assumed then the average tensile stress, σ , across the plane of bubbles will be

$$\sigma = \frac{P'\pi r^2}{d^2 - \pi r^2}. \quad (1)$$

If P' exceeds the fracture stress, σ_F , of the material then fracture will occur.

Finally, Evans rearranges equation 1 and replaces the bubble spacing d with the bubble concentration C_b , which produces a critical pressure P_F for inter-bubble fracture:[64]

$$P_F = \sigma_F[(\pi r^2 C_b^{2/3})^{-1} - 1] + 2\gamma/r. \quad (2)$$

It is difficult to make an accurate prediction of P_F for ErT_2 because, to our knowledge, there is not a good measurement of σ_F and γ . However, if we make the assumption that the values for erbium metal and ErT_2 will be similar then we can use the experimental values of $\gamma \sim 0.637$ (GPa-nm) and $\sigma_F \sim 4.56$ GPa.[65] An experimental C_b value of $3 \times 10^{23}/\text{m}^3$ along with bubble diameters of ~ 10 nm were measured by Snow *et al.*[43] Putting these values together yields a $P_F = 1.44$ GPa (14.4 kbar), in line with the estimate made by Browning from neutron reflectivity, 0.9 - 3.0 GPa.[49]

3 Sample Details

(100) silicon wafers were used as the substrate material to obtain flat films. A 100 nm barrier layer of molybdenum was deposited to avoid compound formation between erbium and silicon. A 500 nm layer of erbium was deposited by electron-beam evaporation onto the molybdenum layer to produce the sample geometry shown in Fig. 4. The substrate temperature during evaporation was 450°C and deposition occurred at a rate of 1 nm/sec. The erbium films were removed from the evaporator at ambient conditions and then placed in a special tritiding apparatus at the Tritium Science and Engineering facility at Los Alamos National Laboratory in which the samples were brought to an elevated temperature and held there after which the tritium gas was introduced. Three separate load runs were performed with two films pulled from each load run for determination of areal densities of tritium and of erbium. The tritium and erbium concentrations within the films were determined simultaneously by high-energy ion-beam analysis (HE-IBA).[66–69] The measured tritium-to-metal ratio for the three tritiding runs are given in Table 1. Tritiding conditions were chosen to produce a stoichiometry of 2.0. The stoichiometric deficiency of these films is estimated to be $\delta \sim 0.1$. After soaking in the tritium gas at temperature the gas was evacuated while maintaining the samples at temperature, this should have the effect of removing all excess octahedral site tritium atoms producing an $x = 0$. While we think that the x is small, we do not have a way of quantifying it and determining the stoichiometric deficiency δ of the films precisely. Between measurements, all samples were stored in a UHV ($P \sim 10^{-7}$ torr) storage chamber at ambient temperatures. To normalize sample ages due to different tritium content, a helium-to-metal ratio is calculated

Fig. 4. The sample configuration used on all experiments in this paper was a 500 nm layer of erbium, deposited onto a 100 nm molybdenum buffer layer, deposited onto a (111) silicon wafer. The size and shape of the silicon wafer varied depending on the experiment. The silicon wafers were 1 cm x 1 cm, 1.25 cm x 1.25 cm, and larger 2.54 cm x 5.08 cm silicon bricks.

Table 1

Tritium-to-metal ratios measured for two samples from each of the three load runs. The spread in the T:Er ratio for each load run is thought to be real because the deviation falls outside of that expected based on the accuracy of the HE-IBA technique and is probably indicative of differences in native oxide thickness amongst the various samples.

Load Run	T:Er
1	1.844
1	1.927
2	1.842
2	1.987
3	1.851
3	1.909
Average	1.893
Standard Deviation	0.058

from the ^3He generation rate $G(t)$, which is given by

$$G(t) = N'[1 - \exp(-\lambda t)] \quad (3)$$

where N' is the original amount of tritium and λ is the tritium decay constant ($t_{1/2} = 12.3$ years).

Fig. 5. Left) TEM image showing helium bubbles for a sample that is at 0.018 He:Er. Right) TEM image showing helium bubbles for a sample that is at 0.031 He:Er. The helium bubbles are the platelet inclusions which lie on $\{111\}$ planes.

4 Results and Discussion

4.1 Helium Bubble Nucleation

It is estimated that only 6 helium atoms are needed to begin the nucleation of a helium bubble, making the nucleation process difficult to probe experimentally.[58] While the data in this paper did not directly probe helium bubble nucleation it did shed some light on the mechanisms and dynamics involved in the process.

TEM images as early as 0.018 He:Er (58 days after the samples were tritided), shown in Fig. 5, show that helium bubbles have already formed.[9] As mentioned above, the helium bubbles in $\text{ErT}_{2-x}\text{He}_x$ are platelets and grow along the $\{111\}$ planes (see Sections 4.2 and 4.3, respectively for more details). The average diameter for a He:Er ratio of 0.018 (58 days) is 6.8 nm[9] which means that the average bubble already spans more than 10 ErT_2 unit cells.

Wixom *et al.* performed first principles Density Functional Theory (DFT) calculations on the $\text{ErT}_{2-x}\text{He}_x$ system.[11] As mentioned above in Section 2.1 and shown in Fig. 2, ErT_2 forms in the CaF_2 structure with the metallic erbium atoms forming an FCC structure and the tritium atoms residing on the eight tetrahedral sites. Using the base CaF_2 structure they calculated the migration paths and energy barriers for helium diffusion in three different stoichiometries of ErT_x where x was 2.0, < 2.0 , and > 2.0 . The majority of the helium born through tritium decay is created on the tetrahedral sites, only in a scenario with excess tritium, i.e. the >2.0 stoichiometry, will helium be created on octahedral sites. Wixom's calculations showed the following:

- ^3He is more stable in the tetrahedral site. Furthermore, ^3He is not even

locally stable in the octahedral site unless all of the neighboring tetrahedral sites are filled. It is bound to the tetrahedral sites by 0.49 eV, and must overcome a 1.31 eV barrier to dissociate from the tetrahedral vacancy and travel beyond the neighboring octahedral sites to an octahedral site with no neighboring vacancies. Further, the mean recoil energy of a helium atom created via tritium decay is estimated to be only 0.35 eV[39] such that the average helium atom will not have enough energy to leave the tetrahedral site in which it is created.

- Once ^3He overcomes this dissociation barrier and enters the octahedral sublattice, a 0.88 eV barrier limits diffusion between near neighbor octahedral sites. The mechanism involves motion through a filled tetrahedral site, pushing that tritium atom temporarily to the side. By this mechanism ^3He could travel several μm in an hour at 300°C .
- As more and more tritium decays, the concentration of tetrahedral vacancies will increase. If two of these vacancies are neighboring, ^3He can move between them with a relatively low 0.49 eV barrier. If extended networks of neighboring vacancies exist, this allows for wholesale diffusion throughout the material, even at room temperature.

If helium atoms are trapped on their tetrahedral sites as Wixom’s calculations show, then how do helium bubbles form in the $\text{ErT}_{2-x}\text{He}_x$ system where we know that the helium bubbles form along side the four equivalent $\{111\}$ planes made up of the octahedral sites of the CaF_2 structure? We believe that an energetics type analysis, like the self-trapping mechanism of Wilson *et al.*[58](see Section 2.2 paragraph 5) is appropriate for the ErT_2 system, but the exact energetics and structure of the He-Tritium-Vacancy system in ErT_2 is still unknown. It is further confusing that the energies calculated by Wixom *et al.* show that ^3He born in the tetrahedral sites is not likely to migrate. If Wixom’s calculations of helium migration in ErT_2 are correct then the self-trapping mechanism may not explain helium bubble formation in metal tritides. In our view the nature of helium bubble nucleation in metal tritides is still not answered and is indeed an area of active research.

Regardless of the exact nature of the initial trapping mechanism, it is clear that helium atoms do cluster and form helium bubbles. After the initial nucleation phase, the bubbles grow as “Griffith-cracks” along the $\{111\}$ planes of the ErT_2 lattice (see Fig. 2b). For helium bubbles the tensile stress is normal to the plane of the crack, creating an opening in the lattice (also termed a Mode I crack). The crack will grow as a competition between the surface energy created by the crack and the strain energy relieved by the crack growth.[70] More details on this phase of platelet growth is given in Section 4.4.

4.2 Helium Bubble Shape

The helium bubble shape is one of the most striking features of the bubbles in ErT_2 . The helium bubble is platelet shaped as seen in Figs. 6 and 7. Proof that the helium bubbles are indeed platelets is obtained by tilting the sample and comparing images with and without tilt. The tilt angle is limited due to the imaging condition for TEM, however, it can be seen that the central area of the bubble does indeed begin to enlarge as would be expected for a platelet structure. The thickness of the bubble varies over its life, ranging from a nano-crack to a final thickness averaging 2-5 nm. We should note that the thickness of the bubble was difficult to determine from the TEM images due to the significant strain contrast present in the films. Figs. 6 and 7 reveal that many bubbles can be seen to have ‘ragged’ edges due to fracture growth at the tips, uneven thicknesses, and distortions caused by inclusions or defects. The general platelet shape did not change over the length of this study which lasted until a He:M ratio of 0.42 was reached at which point defining a helium bubble became extremely difficult.

Cowgill analyzed the growth of spherical bubbles in PdT and the platelet bubbles in $\text{ErT}_{2-x}\text{He}_x$. [71] Spherical bubbles grow via dislocation loop punching with a pressure given by Trinkaus as [72]

$$P_{LP} = 2\gamma/r + \mu b/r \quad (4)$$

where γ is the surface energy, μ is the shear modulus in the direction of the Burgers vector b , and r is the bubble radius. The dislocation loop begins on the rim of the bubble and proceeds along its perimeter until a loop is punched. A dislocation dipole forms when dislocation loops are created but remain trapped by the strain field of the platelet. Cowgill calculated the platelet pressure to be

$$\begin{aligned} P_{DE} &= (2\gamma/s)[(2r + b + s)/(2r + b)] + \mu d/(2r + b) \\ P_{DE} &\approx 2\gamma/s + \mu d/2r \end{aligned} \quad (5)$$

where r is the platelets major radius, s is the minor radius, and d is the planar spacing. Since many of the material properties are unknown for the metal hydride, the best estimate is to use the metal parameters, which for erbium are $\gamma = 0.637 \text{ GPa}\cdot\text{nm}$, $\mu = 57.4 \text{ GPa}$, $b = 0.3623 \text{ nm}$, and a Poisson ratio of 0.238. The determination of a bubble shape, whether spherical or platelet, is determined as a competition between surface energy and shear energy. Chen *et al.* analyzed helium platelets in $\alpha\text{-SiC}$ and found that platelets are favored when the elastic energy dominates compared to the surface energy. [57] They further analyzed plates and derived two equations for the pressure p and surface

energy γ . [57]

$$p = \frac{\pi}{2} \frac{\mu}{(1-\nu)} \frac{s}{r} \quad (6)$$

$$\gamma = \frac{\pi}{4} \frac{\mu}{(1-\nu)} \frac{s^2}{r} = p \frac{s}{2} \quad (7)$$

where ν is Poisson's ratio, r is the radius of the long axis, and s is the radius of the short axis. In metal tritides Eqn. 7 is one of the only methods of estimating the surface energy and is an important result. [57] Using the following parameters $s=1.0$ nm, $r = 7.5$ nm, [9] and the Erbium material parameters of $\mu = 57.4$ GPa and $\nu = 0.22$ (where μ is the Shear Modulus and ν is the Poisson ratio) we calculate a bubble pressure of $p_c = 15.4$ GPa. This value is much greater than other estimated bubble pressures, which from swelling was 1-3 GPa and from Evans was 1.44 GPa (Eqn. 1). The same parameters yield a surface energy of 7.7 GPa-nm and as far as we know, no other measurements or calculations have a comparable value. One possible source of error in the bubble estimation is in determining the width of the bubble. The TEM images have strain contrast which makes an accurate width measurement difficult.

Cowgill hypothesizes that all bubbles should follow the same general growth pattern. All helium bubbles begin as nano-cracks, transitioning to platelets, and finally, converting from platelets to spheres. The shear modulus and surface energies determine the point at which each transition will occur. Based on this analysis, Cowgill predicts that dislocation dipoles should begin forming in ErT_2 around 0.14 He:M [71], very similar to inflection points observed in the lattice parameters, moduli, and bubble sizes (more on this will be discussed below in Section 4.4). At the transition from "Griffith-cracks" to dipole expansion, using the listed values for erbium above, the bubble pressure is predicted to be ~ 2 -3 GPa. This value is in excellent agreement with the two previous estimates from the neutron reflectivity [49] (1-3 GPa) and using the Evans criteria for material fracture (1.44 GPa). [64] Cowgill also predicts that the platelet bubbles in ErT_2 should change to spheres when the major radius is ~ 10 nm. As shown below in Section 4.4 the transition from platelet to spherical never occurs in ErT_2 because at the transition pressure the bubbles are no longer independent but are linking and causing material fracture at this point. Cowgill hypothesized that the end state helium bubble shape can be determined by the ratio

$$2\gamma/\mu b \quad (8)$$

where γ is the surface energy, b is the Burger's vector in the growth direction, and μ is the shear modulus in the b direction. If the ratio is low (< 0.1) the bubbles will be platelets and if the ratio is high (> 0.1) the bubbles will be spheres. The relationship holds for many FCC materials, including ErT_2 , ScT_2 , TiT_2 , Ni, ZrT_2 , PdT, and several HCP and BCC materials as well. [71]

Fig. 6. TEM image showing helium bubbles oriented along two equivalent sets of $\{111\}$ planes. Left) is the Selected Area Diffraction (SAD) pattern and Right) is the image for a sample aged to 0.074 He:Er. The helium bubbles are the platelet inclusions shown along the four equivalent $\{111\}$ planes. A measurement of one of the more prominent pairs of bubbles determined the angle between the two to be $\sim 110^\circ$.

4.3 Helium Bubble Spatial Distribution

In ErT_2 the helium bubbles exhibit the following spatial characteristics:

- The helium bubbles exist entirely along the four equivalent $\{111\}$ planes.
- The helium bubbles are uniformly distributed throughout the film with no preference for grain boundaries or other defect structures unless those defects are oriented along one of the four equivalent $\{111\}$ planes.
- The film surface *may* be void of helium bubbles forming an area sometimes referred to as a denuded zone.

The rest of this section will discuss in detail the three findings related to the helium bubble spatial distribution in $\text{ErT}_{2-x}\text{He}_x$.

The theoretical angle between the four equivalent $\{111\}$ planes in an FCC system is 70.53° . The supplemental angle measured between two bubbles in our images was usually between $108-112^\circ$, shown in Fig. 6. Two of the equivalent planes can be seen simultaneously because bubbles are only observed if the electron beam is at a small angle to the planes containing the bubbles. That means that we may be able to see either one or two sets of bubbles on different sets of $\{111\}$ planes, depending on the orientation of the sample with respect to the imaging electron beam. In order to see two sets of bubbles simultaneously, the beam needs to be close to the zone axis of the two sets of planes. There

Fig. 7. Left) TEM image showing helium bubbles for a sample aged to 0.37 He:Er. This image shows an oxide inclusion in the lower left quadrant. The mottled area around the oxide particle is due to a surface effect. The grain boundary running along the upper left of the image and which happens to be parallel to one of the $\{111\}$ planes of the adjacent grain is decorated with helium bubbles. Right) A TEM image of grain boundary for a sample aged to 0.07 He:Er demonstrating that this grain boundary is not decorated by helium bubbles.

is no zone axis for three or more sets of $\{111\}$ -type planes, so it will never be possible to image more than two sets of the bubbles at once.

In many material systems that have been implanted with helium or that have been tritium charged, the helium bubbles decorate grain boundaries or defects. This is very pronounced in tritium charged stainless steels for example.[73,74] ErT_2 is quite different with no observed bubble nucleation preference for grain boundaries or other defects like oxide inclusions. Figure 7 shows two TEM images with grain boundaries and an oxide inclusion. In the figure on the left there do exist some bright features associated mostly with the left hand part of the oxide inclusion, similar contrast can also be seen in adjoining regions of matrix which indicates the contrast results from surface effects. Open areas are sometimes associated with the oxide/matrix interface, but these appear to represent preferential-milling artifacts rather than bubbles. Similar bright features were sometimes observed on grain boundaries in images not presented in this paper. In the figure on the right, a grain boundary is also seen with no noticeable preference for helium bubbles. The only situation where helium

bubbles do decorate a grain boundary is when the grain boundary is parallel to one of the equivalent sets of $\{111\}$ planes in one or other of the adjacent grains. This situation is seen in the left image of Fig. 7 with the grain boundary running along the upper left quadrant of the image being highly covered with helium bubbles. Grain boundary decoration only with preferred grain boundary orientation has been observed in several other images that aren't presented in this paper. It is important to recognize that the bubbles are viewed in kinematical conditions but with a beam direction reasonably close to $[110]$, and there are two sets of $\{111\}$ planes that belong to each $[110]$ zone. Therefore, if the beam direction lies approximately in the grain-boundary plane, there are two sets of $\{111\}$ planes that must be considered in each of the two adjacent grains. This is done by tilting the sample to obtain bubble images for each of the sets of planes in question. It cannot be stated that there is a bubble in an area of a grain boundary that is not nearly parallel to $\{111\}$ planes in one or other of the adjacent grains unless we have looked at all of these sets of planes.

Differences in helium bubble preference for grain boundaries or defects implies a significant difference in material systems where the tritium occupies a distinct lattice site and those in which the helium and or tritium are in interstitial sites. The difference is in helium mobility. Wixom calculated a helium diffusion length in ErT_2 as only 0.17 microns at 25°C after 10 years.[11] In material systems with greater helium mobility, the helium is more likely to find a trapping site, like a grain boundary, than for the ErT_2 system with the lower mobility. Helium atoms born from tritium decay in ErT_2 will only travel to a grain boundary when they happen to be born immediately adjacent to a grain boundary.

A final feature that is observed in many systems with either implanted helium or helium produced from tritium decay is a surface region, often called a 'denuded zone' or 'depleted zone', that is void of helium bubbles. Cowgill uses a continuum model to predict the existence of a 'denuded zone'.[75] He uses a series of rate equations

$$\begin{aligned} dc_N/dt &= p_1 s_{N-1} c_1 c_{N-1} + q_{N+1} c_{N+1} - p_1 s_N c_1 c_N - q_N c_N \\ dc_1/dt &= -D d^2 c_1 / dx^2 + g - 2p_1 s_1 c_1^2 + 2q_2 c_2 - p_1 s_2 c_1 c_2 - p_1 s_B c_1 c_B \end{aligned} \quad (9)$$

where D is the helium diffusion constant, g the helium generation rate, q_2 is the pair dissociation rate, s_N is the number of trapping sites, and p_1 is the hop rate. Solving this system of equations shows that the surface is a sink for helium atoms and that there is an increased concentration of mobile helium at the surface that extends for several nm (Cowgill's calculations were done on Palladium and the increased concentration extends for 6 nm). The increase of mobile helium at the surface then creates an area where helium bubbles are not able to form, creating a 'denuded zone', or if not completely void of

Fig. 8. Two modes of bubble growth in the $\text{ErT}_{2-x}\text{He}_x$ system: a) an initial Griffith crack growth mode, and b) a final dipole growth which dominates until the material between two bubbles fracture causing the two bubbles to link. See Cowgill for a similar drawing.[71]

bubbles at least a ‘depleted zone’ where the bubbles may be small and much less numerous than inside the film. Snow *et al.* observed denuded zones on all of the ErT_2 samples in their study, reporting nearly constant thicknesses of ~ 15 nm.[43] The difference in size between predicted and measured is a factor of 2-3 which may be accounted for that Cowgill’s model was based on spherical Palladium powder and Snow’s results were on ErT_2 films with native oxide layers around 10 nm. Denuded zones have been reported in austenitic stainless steels[76], aluminum irradiated with 600 MeV protons[77], helium-ion implanted niobium monocrystals[78], and α -Ti and Ti Tritide.[53], to just name a few. Interestingly, a denuded zone was not observed in the TEM images taken on the samples described in Section 3 and the focus of this article. A negative result does not imply that denuded zones did not exist in these samples but it does raise many questions. It is possible that the denuded zones were damaged during the sample preparation process or that the surface region of the films was removed during sample preparation. This is unlikely due to the large number of samples, over 50, that were prepared and studied over the many years of this study. The existence and true nature of denuded zones in $\text{ErT}_{2-x}\text{He}_x$ will continue to be an active area of research.

4.4 Helium Bubble Growth and Interaction

Once a helium trap has been established the bubble will continue to grow as long as helium is available in the local environment. As seen in Figs. 6 and 7, the helium bubbles are generally uniformly spaced in the material matrix. The helium source volume for each bubble then is the equally spaced volume surrounding each individual bubble. This reasoning suggests that if there are more nucleation sites and thus more helium bubbles then the source volumes will be smaller producing smaller helium bubbles.

Knapp *et al.* studied aged films using the nano-indentation technique and modeled his results using two growth regions:[10] First, an initial period of “Griffith-crack” [79] nucleation and growth, where the ^3He forces apart $\{111\}$

Fig. 9. a) Plot of yield stress versus age. b) The change in lattice parameter for both the (111) and (200) directions with age. c) Plot of the Young's modulus versus age. d) Table of the change in lattice parameter (in Angstroms) plotted in b). In a), b) and c), notice the inflection that occurs around a He:M ratio of 0.12. The fits listed in a) and c) are for different models of elastic behavior of effective modulus of composite or cracked materials developed by Zhu[82], Christensen[81], Budiansky *et al.*[83], and Walpole.[84]

planes and forms the platelet bubbles. Second, once the bubbles are thick enough, they transition to a dislocation dipole mode, where circular dislocations form around each platelet, further increasing the thickness and lowering the pressure.[32,57,80] The two bubble growth models are illustrated in Fig. 8. The bubbles continue to grow in the dipole mode until they overlap enough that the material fractures between two bubbles. The nano-indentation results are shown in Fig. 9a and c along with different models of effective modulus of composite or cracked materials.[81–84] Using these models an average bubble pressure of ~ 4.7 GPa and ~ 9 GPa are calculated for larger bubbles(after the transition to a dislocation dipole growth mechanism) and smaller bubbles (the “Griffith-crack” regime), respectively.

Rodriguez *et al.* studied the same series of films using X-Ray Diffraction (XRD);[8] his results are shown in Fig. 9b and d. In the XRD data the lattice parameter for the (111) and (200) planes increase with age but interestingly diverge, meaning that the structure is losing its cubic nature. At a

Fig. 10. Plot of mean bubble diameter in nm versus age of film. The dashed lines are guides to the eye. The errors in the measurements are the standard deviation of the mean for each set of measurements.

point near 0.15 He:M, the lattice parameters begin to decrease. This same point, 0.15 He:M is also when Knapp’s mechanical measurements show a change. Knapp *et al.* identify this point as the transition from “Griffith-cracks” to “dipole cracks”. The divergence in the XRD lattice parameters support this contention. The greatest lattice dilation will occur in the “Griffith-crack” regime when the bubble is growing and actively spreading lattice planes. In the “dipole-crack” regime the lattice dilation stops since the stress is relieved with the punching of a dislocation loop, which when punched, restores the lattice to its earlier state.

Bond *et al.* also followed this same sample series using TEM. They meticulously measured the helium bubble diameters of literally thousands of platelets. The result of their work is shown in Fig. 10. A laboratory issue prevented data taking between the 0.15 and 0.37 He:M points. Fig. 10 shows two dashed lines that are simply guides to the eye. Although there is unfortunately no data between 0.15 and 0.37 He:M, it is not improbable that the bubble diameters were beginning to plateau. This same inflection point, 0.15 He:M, was also observed in the mechanical and XRD results shown in Fig. 9. The transition from a “Griffith-crack” to a dislocation dipole where the growth is no longer

Fig. 11. a) TEM image of a large section of an ErT_2 film at 0.416 He:Er. b) Same image but at a higher magnification.

along the $\{111\}$ planes but instead is perpendicular to the platelet diameter fits this data as well. This inflection point also coincides with Cowgill's analysis of bubble pressures using Eqns. 4 and 5, where he predicts that dipole loops should begin to form at 0.14 He:M.[71]

Hartmann and Trinkaus analyzed an analogous situation for SiC which also exhibits platelet helium bubbles upon helium implantation.[80] Their analysis says that the "Griffith-crack" will grow until a loop dislocation at the crack tips is formed which effectively blocks all future bubble growth. At this point the bubble pressure begins to increase as the bubble grows until the pressure reaches some critical pressure and a dipole dislocation is punched around the rim of the helium bubble. The critical pressure for dipole loop punching was given earlier in Eqns. 6 and 7.

The final stage for helium platelets in ErT_2 is when they begin to cause inter-bubble fracture. As discussed earlier in Section 2.2 and given in Eqn. 2, inter-bubble fracture is estimated to occur in ErT_2 near a bubble pressure of 1.44 GPa using Evans criteria.[64] Given the large uncertainties and assumptions in each measurement and calculation, the value of 1.44 GPa for inter-bubble fracture should be considered close to the bubble pressures estimated by Browning (1-3 GPa[49]) and Knapp (~ 4.7 GPa[10]). Figure 11 shows a portion of an ErT_2 film aged to 0.416 He:Er. This image looks very different from the images of the other helium bubbles shown earlier. The amount of strain contrast in the image makes it difficult to even identify bubbles. The bubbles that can be identified are linked and much wider and longer than earlier in life. This configuration of bubbles is what causes the 'critical' release discussed in Section 4.5.

Fig. 12. Measured ^3He content as a function of age, using Elastic Recoil Detection.

4.5 Helium Release

Knapp *et al.* developed a unique ion beam analytical technique to simultaneously measure the amount of ^3He , the three hydrogen isotopes (protium, deuterium, and tritium), and oxygen in metal tritide films with a depth resolution of ~ 40 nm.[85] They were able to measure the fraction of helium in the metal film as a function of time. The data is shown in Fig. 12. The growth in the He:M ratio tracks closely with the expected amount of helium produced by tritium decay, but diverges from the tritium decay curve at a point near a He:M ratio of 0.32. This value is very similar to that reported in other publications[42,43] and is called the ‘critical release’ point. After ‘critical release’ the ErT_2 film stops storing helium and instead releases it into the local environment. This data also demonstrates the tremendous helium storage capacity of ErT_2 films. To within the error of the measurement technique (< 1 at.%),[85] all of the helium generated early in life is stored in the film.

5 Conclusions and Future Work

The $\text{ErT}_{2-x}\text{He}_x$ system offers an interesting case to study the nucleation, growth, and evolution of helium platelets in a metal tritide. We have tracked the same sample series over a period of nearly four years, measuring helium bubble sizes, crystal lattice dilation, mechanical properties, and helium release. We have observed the following properties of helium platelets in $\text{ErT}_{2-x}\text{He}_x$:

- The helium bubbles are aligned along the $\{111\}$ planes. This family of planes accommodates easy-access for He bubble growth from a crystallographic perspective, as it provides the greatest open area.
- The helium bubbles are evenly distributed in the lattice and only decorate defects and grain boundaries when the defects align with crystallographic (111) planes.
- The helium bubble grows in three distinct regimes. First, the helium bubbles begin by creating “Griffith-cracks” and grow until a loop dipole is created at the crack-tip. Second, the helium bubble pressure then begins to increase until a dislocation dipole is created which relieves the pressure. Third, the helium bubble pressure increases until fracture occurs between bubbles. This fracture network increases until it reaches a free surface at which point helium is released rapidly into the local environment. This point is known as critical release.

There exists several key points that are not understood in the $\text{ErT}_{2-x}\text{He}_x$ system. One, a better understanding of the bubble nucleation mechanism in stoichiometric metal hydrides is needed. The principal question is where and what traps the initial 3-5 helium atoms that begin the formation of a helium bubble. It is not clear that Wilson’s self-trapping mechanism is valid for the ErT_2 system. An understanding of helium bubble nucleation must come through both experimental and computational means. Two, what is the relationship between the oxide layer and the bubble ‘depleted’ zone near the surface? Does the TEM sample preparation technique impact the observed thickness? Is the ‘depleted’ zone truly universal and should it be observed in all metal tritide films? Three, many of the parameters used in modeling ErT_2 are taken from Er, such as the surface energies and mechanical properties. It is very difficult if not impossible to make these measurements on multi-grained thin films. This gap can be removed through first-principles modeling.

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$$\begin{aligned}
V = & (22.575 + 0.0064655T - 7.2645T^{-1/2})P^{-1/3} \\
& + (-12.483 - 0.024549T)P^{-2/3} \\
& + (1.0596 + 0.10604T - 19.641T^{-1/2} + 189.84T^{-1})P^{-1},
\end{aligned} \tag{10}$$

where V is given in cm^3/mole and the equation is valid in the region of $2 < P < 20$ kbar and $75 < T < 300\text{K}$. While the Mills EOS for helium is the most widely used, other experimental and theoretical efforts have extended the EOS. On the experimental side see for example the two papers by Mao (H.K. Mao *et al.*, Phys. Rev. Lett., **60**, p. 2649 (1988)) and Loubeyre (P. Loubeyre *et al.*, Phys. Rev. Lett., **71**, p. 2272 (1993)) have extended the EOS for solid He up to 58 GPa and 400K using single-crystal x-ray diffraction techniques. On the theoretical side much work was done by Wolfer *et al.*, which was published in a series of articles (W.G. Wolfer *et al.*, J. Nucl. Mats., **122 & 123** p. 565-570 (1984); M.F. Wehner and W.G. Wolfer, J. Statistical Physics, **42**, p. 493 (1986); M.F. Wehner and W.G. Wolfer, J. Statistical Physics, **42**, p. 509 (1986)). Wolfer developed separate EOS for the fluid and solid phases and has shown that his theoretical expressions provide an excellent match to the later experimental work of Mao (private communication between primary author and W.G. Wolfer). Another interesting point regarding the He EOS is the need for curvature corrections. Wolfer calculated a curvature correction when the helium bubble radius became less than 10 times the atomic radius of the He atom. However, since the actual cavity surface is not spherical but corrugated the curvature correction is most likely not important. This also implies that no corrections to the He EOS need to be made for ErT_2 where the helium bubbles are platelet cavities and not the spherical cavities of many other systems.

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