UNIT CELL EXPANSION IN ErT₂ FILMS

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ABSTRACT

XRD analysis of plasma-vapor-deposited ErT₂ films during aging (T decay to ³He) reveals an hkl-dependent unit-cell expansion in which (200) grains expand out-of-plane as much as 0.01 Å more than (111) out-of-plane grains. Texture analysis of an aged ErT₂ film reveals a bimodal (111)/(200) out-of-plane preferred orientation. Sin²ψ analysis reveals significant in-plane macro-strain due to ³He formation/growth. The mechanistic origins regarding these observations are also discussed.

INTRODUCTION

Metal hydride systems containing tritium, the radioactive isotope of hydrogen, are of interest to the fusion community [1]. Rare earth (RE) tritides have been shown to exhibit favorable properties in regard to the reversible cycling of tritium gas stored in such systems. A common observation in RE-tritides is that, initially, most of the ³He produced via tritium decay is retained within the tritide lattice in the form of high density precipitates or bubbles. The release of ³He during this initial period has been shown to remain constant until some critical concentration of ³He has been achieved within the lattice. Once this critical concentration has been achieved, helium evolves from the tritide at a rate equal to or greater than its generation rate [2–3]. The observed helium release characteristic in the early release period is believed to be governed by near surface conditions within the material, while that observed during the critical release period is believed to be related to changes in the physical characteristics of the ³He bubbles within the lattice.

In order to gain a better understanding of ³He behavior in metal tritides, we have used XRD to monitor how the lattice parameter of a thin film ErT₂ sample changes as a function of ³He concentration. This analysis was performed over a time period sufficient to observe the lattice expansion within the low, constant-fraction regime of ³He emission from the films.

EXPERIMENTAL

Sample Preparation

To prepare thin film specimens, 1 cm² Si (100) substrates were first coated with a Mo (~100 nm thick) buffer layer to prevent reaction of the Er with the Si substrate. Next, 500 nm films of Er (99.95%) metal were deposited by electron-beam Plasma Vapor Deposition (PVD) onto the Mo-coated Si substrates. The Er films were subsequently exposed to T₂ gas at pressure/temperature conditions consistent with the formation of ErT₂ (often referred to as the β-phase in the Er-T phase diagram). The β-phase has a fluorite-type structure (space group Fm-3m) with Er atoms...
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located at the origin and faces of each unit cell, and tritium atoms at the tetrahedral (¼, ¼, ¼) sites. After the films were prepared, they were analyzed using Ion-Beam-Analysis (IBA) to determine the T to Er ratio. From this analysis, a (³He:Er) can be derived based on the well known tritium decay constant. Transmission Electron Microscopy (TEM) was also performed to observe the presence of ³He bubbles. These measurements were performed to supplement the XRD analysis, which is discussed below.

**XRD Data Collection**

X-ray powder diffraction patterns were collected on a Bruker Discover diffractometer equipped with a sealed-tube copper X-ray source having both incident and diffracted beam mirror optics, fixed scatter and receiving slits of 0.6 mm width, and a scintillation detector. This configuration was useful for collection of high quality θ−2θ diffraction patterns. Typical scan parameters were 20 to 80 °2θ, 0.04° step size, and 4 sec count time. Such patterns were collected in approximately 3 to 6 month intervals over the course of two years. The ErT₂ films were stored in vacuum (1 × 10⁻⁷ Torr) when not being analyzed. In addition to standard θ-2θ analysis, a more detailed diffraction analysis was performed after significant tritium decay (³He:Er = 0.179). The more detailed XRD structural characterization was performed with the addition of a 1 mm pinhole snout placed after the incident-beam mirror optic. The use of the snout substantially reduced the beam intensity, but also allowed collection of texture data. The Bruker Discover system, configured with an Eulerian cradle, was programmed to collect θ-2θ diffraction patterns over a 27 to 77 °2θ range, with an approximate ~0.04° step-size and 0.4 sec count time. Each θ-2θ scan was performed at a fixed position of psi (ψ) and phi (φ). ψ and φ angles were incremented in 6° steps with ψ = 0, 6,…72° and φ = 0, 6,…354°. This iterative series of scans resulted in a total of 780 θ-2θ patterns. Total data collection time was ~60 hrs.

**RESULTS AND DISCUSSION**

Figure 1 displays the overlaid sequence of θ-2θ scans as a function of tritium decay. In this figure, the pattern collected in August '04 (only 3 months after tritium loading in May '04) has relatively sharp peak profiles for the ErT₂ phase. Based on the decay rate of tritium, one can predict the ³He:Er ratio, and for this first scan ³He:Er = 0.036 as shown on the plot. Subsequent ³He:Er ratios are listed for the additional scans. There is a clear trend of the ErT₂ (111) and (200) peaks towards lower peak-height maximum and increased FWHM. This observation strongly suggests significant micro-strain broadening of the ErT₂ phase as ³He bubbles form within the film. The obvious ErT₂ peak shifts to lower 2θ (larger d-spacing) also indicate substantial unit-cell expansion of the fluorite lattice with aging. As these data are symmetric θ-2θ scans, the unit-cell expansion is for those grains with their diffraction vector perpendicular to the plane of the film (i.e. out-of-plane grains).The peak shift for the ErT₂ (111) and (200) hkl’s is in stark contrast to the Mo (110) peak of the buffer layer, which remains essentially fixed during the entire aging process. Careful evaluation of the profiles also reveals a subtle asymmetry of the peak shape, slightly skewing the ErT₂ (111) and (200) peaks on the higher 2θ side of the profile. In addition, we observed a weak Er₂O₃ (222) reflection. Presence of Er₂O₃ is persistent and likely has its origins in the presence of soluble oxygen within the Mo buffer layer. This oxygen likely was drawn out of the Mo during the Er-film deposition and subsequent T₂ exposure. IBA results
indicate less than 5 wt% oxygen as Er$_2$O$_3$ and/or soluble oxygen within the ErT$_2$ lattice. The Er$_2$O$_3$ peak location and shape change very little over time.

![ErT$_2$ diffraction patterns](image)

Figure 1. Sequence of ErT$_2$ diffraction patterns during aging process. (see text for details).

Profile-fitting on the ErT$_2$ (111) and (200) reflections was performed and corresponding d-spacing values were quantified from the peak positions. The d-spacing values were then converted to a lattice parameter (a) value based on each hkl, the results of which are plotted in Figure 2. This figure shows the dramatic increase in unit-cell lattice parameter in the 0 < $^3$He:Er < 0.076 range (i.e. the first 8 months of study). During this time, the lattice expands as much as 0.05 Å. However, what is most interesting about this figure is the observation of an hkl dependency for unit cell expansion. The data clearly show that the (200) out-of-plane grains expand more than those of the (111) hkl. This intriguing observation of hkl-dependent lattice expansion in ErT$_2$ infers something about the properties of the fluorite lattice. The graph shows that if ErT$_2$ grains are oriented such that a (200) diffraction vector is perpendicular to the film, they are free to expand to a larger unit-cell value (max. ~ 5.165 Å). In comparison, the (111) grains plateau at a smaller maximum cell dimension (max. ~ 5.155 Å). It is important to mention that we did not obtain a (time = 0) diffraction scan on the tritiated films. Therefore, the initial data point (a = 5.110 Å at $^3$He:Er = 0) that we report was from an identically prepared D$_2$ loaded specimen. This initial data point fits reasonably well with the observed trends, and the d-spacing locations for the (111) and (200) reflections of the D-loaded film predict an identical lattice parameter within the error of the profile refinement. The ErD$_2$ lattice parameter is considered an upper bound for the ErT$_2$ lattice parameter, as it is expected that tritium will further contract the unit cell to a smaller initial lattice parameter than either protium or deuterium [4–5]. The inset in Figure 2 is a TEM micrograph collected on a film from the same lot as those used for XRD analysis. This cross-section micrograph illustrates the appearance of $^3$He bubbles present within
the host ErT$_2$ grains. The bubbles appear as long regions of low contrast. As this specimen is a cross-section of the ErT$_2$ film, one only observes the cross-section of the bubbles. Extensive analysis of these bubbles indicates that they are actually disc shaped, having a large aspect ratio, and that they form along (111) planes within the fluorite lattice (personal communication with G. Bond).

![ErT$_2$ lattice parameter values based on (111) peaks (circles) and (200) peaks (squares) as a function of $^3$He:Er ratio. Inset: TEM cross-section image of an ErT$_2$ grain showing disc-like bubbles.](image)

Our detailed XRD analysis of the ErT$_2$ film with $^3$He:Er ratio = 0.179 (i.e. Dec '05) revealed significant in-plane compressive macro-strain. Figure 3 (left) shows 0-20 scans with varying $\psi$ tilt. The figure shows a significant peak shift to higher 20 as the $\psi$ angle increases. A $\sin^2\psi$ plot using the (220) ErT$_2$ peak positions (Figure 3, right) shows a negative slope (i.e. compressive strain) with a strain magnitude of 0.88%. This very large macro-stain value is associated with the $^3$He bubble formation/growth within the film (it was assumed that the out-of-plane strain for the film was zero). Note that the Mo (110) peak (from the underlying buffer layer) shows a slight shift to lower 20 position as a function of $\psi$ tilt, indicating in-plane tensile strain (estimated at 0.39%). Such measurements are consistent with other ErD$_2$ films that also show in-plane tensile strains of the same order. These results confirm that the strain observed in the ErT$_2$ films is reliable, and not due to misalignment of the instrument. Also, note the variation of the ErT$_2$ (220) peak intensity with $\psi$ tilt. This variation illustrates the textured nature of the film in that the major intensity for the (220) peak is only observed with a significant $\psi$ tilt.
Figure 3. On left, XRD data for ErT$_2$ film with $^3$He:Er ratio = 0.179 showing peak shift of ErT$_2$ (220) as a function of $\psi$ tilt. On right, in-plane strain derived from ErT$_2$ (220) peaks (see text for details).

Figure 4. Pole figures from ErT$_2$ film ($^3$He:Er = 0.179) illustrating bimodal (111) and (200) out-of-plane preferred orientation and in-plane fiber texture.

Confirmation of preferred orientation was obtained with the evaluation of pole figures derived from XRD data on the ErT$_2$ film ($^3$He:Er = 0.179). Figure 4 shows the pole figures from this analysis. The center intensity observed in both the (111) and (200) pole figures indicates that they both show a preference to align their diffraction vectors out-of-plane. The absence of a central intensity for the (220) pole figure confirms the orientation dependence, indicating that although the (111) and (200) grains may align out-of-plane, the (220) grains are nearly all constrained to be tilted in-plane, driven by either the (111) or (200) grain alignment. In addition, the rings observed in all three pole figures indicate an in-plane fiber texture, showing no effective restriction on grain orientation within the plane of the film.

A tentative hypothesis regarding ErT$_2$ expansion can be made based on these initial observations. Figure 2 shows that (200) out-of-plane grains expand more than those of the (111). In addition, TEM demonstrates that the $^3$He bubbles tend to grow along (111) planes. Therefore, bubbles that form in a (200) out-of-plane grain all lie at 54° to the film surface as dictated by
geometry. The (111) out-of-plane grains will have one of the four possible (111) planes oriented parallel the film surface. While this arrangement will allow for easy expansion of the film surface for such grains, it also restricts the other three sets of (111) planes to a 70° in-plane tilt. Constraint of the film in-plane opposes the expansion of the out-of-plane (111) grains. The (200) grains also have a component of the expansion in-plane due to the bubble growth along the (111) planes. However, all four (111) directions present in the (200) out-of-plane grains orient in an identical fashion to the film surface. This fact allows the (200) grains to expand more uniformly, while not experiencing the degree of restriction experienced by the (111) grains. Hence, the (200) out-of-plane grains expand more readily, and to a higher degree over time, than the (111) out-of-plane grain orientations. This model (along with additional mechanistic effects) shall be the subject of a future, more detailed publication.

CONCLUSION

XRD analysis of ErT₂ films during aging (³He decay) indicates significant unit-cell expansion of the fluorite-type lattice. This unit-cell expansion varies with hkl, showing (200) out-of-plane grains to have a larger expansion than (111) out-of-plane grains for a given ³He:Er ratio. Texture analysis on one of the aged ErT₂ films (³He:Er = 0.179) reveals that the film displays a bimodal (111)/(200) out-of-plane preferred orientation and in-plane fiber texture. Sin²ψ analysis of the same sample reveals significant in-plane macro-strain due to ³He formation/growth. This analysis yields significant insight regarding structure/property relationships in ErT₂ films.

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REFERENCES