X-ray and neutron diffraction of Er-hydride films

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Outline

• Structures of hexagonal Er metal, ErH₂ fluorite, Molybdenum

• Texture issues and processing effects

• Idea of pole figure integration

• Promising neutron diffraction work
Structures of target and substrate have high symmetries

- Er metal (HCP)
- ErH₂ Fluorite (FCC)
- Moly metal (BCC)

- Er layers shift from HCP to FCC during loading
- Large void in center of fluorite lattice
Random grain orientation = no texture

**Fiber**
- out-of-plane (YES)
- in-plane (NO)

**Rolling Texture**
- out-of-plane (YES)
- in-plane: 1-dimension of freedom, other fixed

**Bi-Axial**
- out-of-plane (YES)
- in-plane (YES)
Typical $\theta$–$2\theta$ x-ray diffraction patterns reveal out-of-plane texture effects.

ErH$_2$

Calculated

Moly

(110)

(200)

(111)

(220)

45M

144M

Moly

(200)

45M

144M

Intensity(Counts)

2-Theta(°)

x10³
Several processing issues control texture of Er and ErH₂ films

• Er deposition rate and/or temperature
  – Faster deposition rates encourage randomization
  – High deposition temperatures encourage grain growth

• Presence of oxygen
  – O₂ encourages Er (002) out-of-plane texture

• Texture of underlying Moly
  – Can dictate Er and ErD₂ texture via substrate templating
Deposition temperature/rate can dramatically alter resulting Er microstructure

- **200°C, 200 Å/sec**
  - ~random orientation
  - 10-50nm xtal size

- **500°C, 10 Å/sec**
  - Strong (002) texture
  - 100–500nm xtal size

Note: underlying Moly was not strongly textured
Presence of oxygen strongly affects texture of deposited Er film

Sample with oxygen shows strong (002) out-of-plane texture
Substrate etching changes Moly texture - dictates ErD$_2$ grain orientation

**Etched**  
450°C, 200 Å/sec

Moly pole figures (15x random)

ErD$_2$ pole figures (5x random)

**No Etch**

Moly pole figures (10x random)

ErD$_2$ pole figures (5x random)
Can we use XRD data to model Helium in ErT$_2$ lattice?

- Generate calculated pattern with Helium atom present in octahedral (oct) site.
- Perform Rietveld structural-refinement on calculated pattern using fluorite structure (without He addition).
- Perform difference-Fourier analysis to see if He electron density is detectable.

- Correct peak intensities are crucial.
Calculated data for ErH$_2$ with He added at (½ ½ ½) site shows electron density in difference-Fourier mapping.

Rietveld refinement of calculated pattern

$R_1 = 11.27\%$

He detected in oct site via diff-Fourier mapping

Contour plotted at 1.7
He was inserted into the model and refined to ~1 or full occupancy (as expected).

**R₁ = 9.03%**

Significant drop in R value (-1.72%)  

Final difference Fourier map just shows background noise.
Accurate integrated intensities are crucial for He site occupancy measurements with XRD

<table>
<thead>
<tr>
<th></th>
<th>(111)</th>
<th>(200)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ErH₂</td>
<td>100%</td>
<td>48%</td>
</tr>
<tr>
<td>ErH₂He</td>
<td>100%</td>
<td>54%</td>
</tr>
</tbody>
</table>

Biggest change of intensity:
6% increase in (200) with He addition at octahedral site

Challenge for this type of analysis – Texture
ErT$_2$ films on Moly show texture effects that bias intensities in standard $\theta$–2$\theta$ scans.
**Approach**: Collect intensity of hkl in many different orientations (pole figure) to un-bias observed intensities due to texturing.

<table>
<thead>
<tr>
<th>hkl</th>
<th>Obs. RI (%)</th>
<th>Exp. RI (%)</th>
<th>Cor. RI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>34</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>16</td>
<td>14</td>
</tr>
</tbody>
</table>
Pole figures for ErT₂ films show texturing effects and influence of Moly substrate

Bi-modal distribution of ErT₂ grain orientations
Relative intensity ratios derived from ErT$_2$ pole figures are much better estimates than $\theta$–$2\theta$ scans.

<table>
<thead>
<tr>
<th>ErT$_2$ film</th>
<th>$\theta$–$2\theta$ normal scan 200/111 %</th>
<th>Pole integration 200/111 %</th>
<th>$\theta$–$2\theta$ normal scan 220/111 %</th>
<th>Pole integration 220/111 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal</td>
<td>19</td>
<td>41</td>
<td>4</td>
<td>24</td>
</tr>
<tr>
<td>40% Thickness</td>
<td>26</td>
<td>42</td>
<td>3</td>
<td>22</td>
</tr>
<tr>
<td>20% thickness</td>
<td>8</td>
<td>49</td>
<td>4</td>
<td>29</td>
</tr>
<tr>
<td>Calculated (random)</td>
<td>50</td>
<td>50</td>
<td>29</td>
<td>29</td>
</tr>
</tbody>
</table>
Neutron diffraction is being investigated as a diagnostic tool for ErD$_2$ films

• Advantage
  – Unlike x-rays, neutrons scatter well from deuterium (and tritium)

• Disadvantages
  – Need large volume of sample
  – Difficulties for analysis of thin films
  – Limited facilities and beam-time
  – Samples may activate
Recent neutron diffraction experiments at LANSCE/LANL show promise for structural analysis.

- **First attempt: HIPD (2002)**
  - 6 ErD<sub>2</sub> films on moly-coated silicon (ErD<sub>2</sub> = 0.2x10<sup>-3</sup> cc)
  - Result…
    - need more ErD<sub>2</sub> signal, patterns swamped by Si peaks

- **Second attempt: HIPPO (2003)**
  - 80 ErD<sub>2</sub> films deposited on 40 thin Moly foils (ErD<sub>2</sub> = 3x10<sup>-3</sup> cc)
  - Result…
ErD$_2$ phase detected in neutron diffraction measurement: possible sensitivity to oct. site

Refined weight % ErD$_2$ = 2.1(3)%
Expected weight % ErD$_2$ = 2.6 %

Refined ErD$_2$ lattice parameter, $a = 5.126(2)$ Å

Extra density at the $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ site from diff-Fourier
Summary

• ErD₂ and ErT₂ film microstructures are strongly effected by processing conditions.
• Both X-ray and neutron diffraction are being pursued to help diagnose structure/property issues regarding ErT₂ films and these correlations to He retention/release.
• Texture issues are great challenge for determination of site occupancy.
• Work on pole-figure-integration looks to have promise addressing texture issues in ErD₂ and ErT₂ films.
Acknowledgments

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