A Review of Helium Precipitate Evolution in Metal Tritides

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Outline
- Stages of bubble evolution and rate of He release
- Shapes: spheres & platelets
- Effect of bubble density & spacing distribution
- Onset of Rapid He Release: Percolation of inter-bubble fracture condition in a fracture plane
- Testing with data for Pd, Er, & other tritide systems

TEM images by Brewer, Gelles, & Kotula
The evolution of He bubbles/platelets is captured in a model with four distinct stages.

Behavior of spherical bubbles in Pd$T_x$

- Bubble Nucleation
- Bubble Growth
- Inter-Bubble Fracture
- Percolation of the Fracture Condition

The He release spectrum is critically dependent on the bubble shape and spacing distribution.
Bubble nucleation by self-trapping occurs during a short pulse in mobile He concentration

- 3 component model for bulk: mobile He, He-pairs, “bubbles”
  \[
  \frac{dc_1}{dt} = g - 2ps_1c_1^2 - ps_2c_1c_2 + 2q_2c_2 - ps_B(r)c_1c_B
  \]
  \[
  \frac{dc_2}{dt} = ps_1c_1^2 - q_2c_2 - ps_2c_1c_2
  \]
  \[
  \frac{dc_B}{dt} = ps_2c_1c_2
  \]
  
  generation rate, \( g = \lambda (3H/M) \)
  
  jump rate, \( p = 12D_{He}/a^2 \)
  
  pair dissoc. rate, \( q_2 = 2pe^{-E_2/kT} \)

- Triplets are added near surfaces.

- The mobile concentration drops as bubbles produce traps.
  - Nucleation is 90% complete in 2 days.

Using theoretical \( E_2 \) and experimental \( D_{He} \) gives correct \( c_B \).
Nucleation parameters are measured by a He Implant/Re-emission technique

- He re-emission following a short implant pulse is fitted to the self-trapping model.

- This technique produced the first measurements of He diffusion in metals near room temperature.

- Self-trapping energies are determined by varying implant pulse characteristics.
Each bubble’s growth is determined by its He supply rate -- its tritium source volume

• Bubble growth relations:
  - Mass conservation: \( (r/R)^3 f_p = (v_{He}/v_{MH})(He/M) \)
    \( (v=\)molar volume, \( f_p=0.64 \) for random array packing)  
  - Dislocation loop-punching: \( p = \frac{2\gamma}{r} + \frac{\mu b}{r(1+\varepsilon)} \)
    \( (\gamma=\)surface energy, \( \mu=\)shear modulus, \( b=\)Burgers vector) 
  - Bulk He EOS (Mills et al.): \( v_{He}(p,T) \)

• For a given bubble spacing \( R \):
  At each He/M, there is a unique \( r, p, v_{He} \)

**Computed mean He pressure drop agrees with NMR data.**
The bubble spacing distribution in PdTx has been determined by $^3$He NMR

- $^3$He $T_1$ (motion) distinguishes solid bubbles from liquid bubbles.
- Growth relations convert fluid fractions to bubble distributions.

### Graphs

- **Abell & Cowgill**
  - Fluid Fraction vs. $1000/T(K)$
  - Bubble Radius, $r$ (Å) vs. $f(r)$, normalized

- **The Bubble Spacing Distribution**
  - Lognormal (multiplicative central limit theorem)
  - Bubble Half-Spacing, $R$ (Å) vs. $F(R)$, normalized
  - The constant spacing distribution - verifies nucleation has stopped - provides a sensitive test of the nucleation and growth models.
The bubbles cause swelling and lattice stress, which produces a shift in the hydride PCT.

Volume occupied by He bubbles:
\[ dV/V = (v_{He}/v_{MH})(He/M) \]

Plateau pressure:
\[ p_H = p_o \exp(-2\sigma_{hy}v_H/R_gT), \]
hydrostatic stress,
\[ \sigma_{hy} = p_{He}(dV/V) \]

Swelling and PCT data are consistent with the different bubble densities found by TEM (Thomas/Guthrie, 1983 and Thiebaut et al., 2000).
Bubbles are platelet-shaped in some materials

TEM images by Brewer, Gelles, & Kotula

Pd tritide

Spherical bubbles grow by dislocation loop punching

Minimizes surface energy

Platelets are trapped between [111] planes or a dislocation dipole, which expands radially

Minimizes strain energy

2d < s < 3d

What causes the shape difference?
The bubble shape and growth process depend on the tritide’s mechanical properties

- **Dislocation loop punching**
  \[ P_{LP} = 2\gamma/r + \mu b/r \]

- **Dislocation dipole expansion**
  \[ P_{DE} \approx 2\gamma/s + \mu d/(2r+b) \]

- Thin, disk-shaped bubbles are caused by a low surface energy (low \(\gamma/\mu b\)).

<table>
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<tr>
<th>Tritide</th>
<th>(\gamma) (GPa-nm)</th>
<th>(\mu) (GPa)</th>
<th>(b) (nm)</th>
<th>(\gamma/\mu b)</th>
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<td>0.637</td>
<td>57.4</td>
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<td>0.03</td>
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Platelets appear to be the preferred shape in young Pd tritide (<50 days).
The bubbles in fcc materials may evolve from He-filled nano-cracks

- He atoms accumulate in “relatively open” spaces between (111) planes, where they open Griffith-like nano-cracks:

  \[ s < 2d = 0.6 \text{ nm} \]

- When the crack opens to \( s = 2d = 0.6 \text{ nm} \), dislocation loops begin to form, creating a dipole:

  \[ 2d < s < 3d \]

HR-TEM of n-crack in PdT by Thiebaut
Early growth of bubbles in PdT should involve multiple shapes

1. He collects in (111) planes, opening nano-cracks (Griffith):
   \[ P_{nc} = 4\gamma/s, \quad s = 4[\gamma(1-\nu)r/\pi\mu]^{1/2}. \]

2. Dislocation dipole forms when nano-crack gap \( s=2d \).

3. Platelet pressure drops with radial expansion, its thickness slowly increasing to \( s=3d \), where the dipole escapes.

4. [110] loops are emitted as the platelets transition to spheres.

5. Spherical bubbles continue to grow by normal loop-punching.
Rapid lattice dilation in young Pd Tritide shows evidence for platelets

• Bubble pressure is balanced by tensile stress:
  - hydrostatic for spheres
    \[ p_{LP}(dV/V) = B^\star (3 \frac{da}{a})_{LP} \]
  - [111] tension for platelets
    \[ p_{DE}(dA/A) \frac{4/3^{1/2}}{2} = E^\star (\frac{da}{a})_{DE}, \]

• Initial high pressure Griffith crack growth and platelet expansion produce rapid dilation.

• Bubble volumes increase by 8X during the transition from platelets to spheres
  - dilation slows in accordance with loop-punching.
The precipitates in Er tritide remain 2-dimensional platelets throughout life.

- Linking of the platelets occurs prior to their spherical transition.
  - At \( r \approx 25 \text{ nm} \), co-planar platelet area >1 (area projections overlap).
The model accounts for the platelet growth in ErT_x films observed by Bond & Browning

- The calculation uses average platelet density of 5x10^{17} platelets/cm^3.
- The platelet thickness s increases slowly with r: 
  \[ s = \left[ \frac{4\gamma(1-\nu)r}{\pi\mu} \right]^{1/2} \]
  - Predicted thickness appears slightly less than the TEM determination
The bubble shape condition appears to hold for precipitates in fcc, hex, and bcc metals

<table>
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<tr>
<th>Material</th>
<th>$\gamma$(GPa-nm)</th>
<th>$\mu$(GPa)</th>
<th>b(nm)</th>
<th>$2\gamma/\mu b$</th>
<th>shape</th>
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- Surface energy/strain energy ratio for spherical bubbles
- Platelets are preferred for small $r$, where $s/2r > 2\gamma/\mu b$. 
Later in life, bubble interactions assist initiation of loops and lower bubble pressures

• Shear stress is maximum on bubble surfaces adjacent to neighboring bubbles.

• Repeated loop initiation at these surfaces can cause stress-directed growth and bubble coalescence.
The “condition” for bubble linkage examines the tension across a ligament between bubbles.

- As the bubbles grow, tension on the ligament between bubbles increases.
- Evans’ fracture criterion:
  
  For plane through adjacent bubbles, fracture occurs when:
  \[ p_{LP} \text{ (bubble area)} > \sigma_F \text{ (metal area)} \]
  \( (\sigma_F = \text{fracture strength} \approx \mu/4\pi) \)

- Valid when neighboring ligaments fracture simultaneously (i.e., the surrounding lattice provides no support).

Wide-spread fracture should occur “near” the fracture “condition” for bubbles at the mean bubble density.
The condition for inter-platelet fracture uses platelet area projections in a fracture plane

- Equating stresses on the ligament between 3 adjacent platelets:
  \[ p_S (\text{projected platelet area}) = \sigma_F (\text{projected metal area}) \]
  \[ (p_F - 2\gamma/s) (\pi r^2/2) \cos \theta = \sigma_F [3^{1/3}R^2 - (\pi r^2/2) \cos \theta] \]

- IP-Fracture criterion:
  \[ p_F = 2\gamma/s + \sigma_F \left\{ [\pi r^2 n_p^{2/3} \langle \cos \theta \rangle]^{-1} - 1 \right\} \]

- \( \theta \) = platelet angle in fracture plane

- Relative angle between platelets is zero or the angle between [111] directions, 70.5°

- Averaging areas using (100), (110), (111) principle planes and the frequency in each geometry, gives \( \langle \cos \theta \rangle = 0.476 \)
Fracture occurs when the projected area satisfying the fracture condition reaches a critical value

- The projected area in a fracture plane of clusters satisfying the fracture condition increases with He/M:

\[ A_{\text{Fracture}} = \int_{R_o}^{R_{\text{He/M}}} F(R) R^2 \cos \theta \, dR \]

- From classical Percolation Theory, the Critical Area Fraction = .45
In approaching this threshold, the mean diameter of “linked” bubble clusters is increasing

- From classical percolation theory, bubbles linked by satisfying their local fracture condition can be described as a cluster of linked adjacent sites.

- With \( q = \) fraction of sites linked, the linked-area fraction is \( \eta = f_p q \). (Large bubbles are considered as groups of small bubbles (sites) with packing factor \( f_p = 1 \).)

- At \( q = q_c \) (percolation threshold), the clusters are infinite and have a critical area fraction \( \eta_c = f_p q_c \). (At the Critical He/M, \( \eta = \eta_c \) and \( d_c = \square \))

- For \( q < q_c \), 2d dimensional invariants relate \( \eta \) to \( d_c \):
  - the #sites in average cluster, \( s \propto 1/(q_c - q)^{j+1} \)
  - the cluster size, \( d_c \propto s^{1/D} \), (D=fractal dimension),
  - minimum site separation = \( 2R_o \)

- Cluster diameter \( d_c = 2R_o / [1-(\eta/\eta_c)]^{(j+1)/D} \)

<table>
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<th>Dimensional Invariants</th>
<th>2d</th>
<th>3d</th>
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<td>( \eta_c )</td>
<td>0.45</td>
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<tr>
<td>( j )</td>
<td>11/18</td>
<td>11/16</td>
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<tr>
<td>( D )</td>
<td>1.9</td>
<td>2.5</td>
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**Fractional He release** is given by a material’s volume fraction with clusters intersecting the surface

- Integration over linked-volume fraction within \( d_c \)-thick layer gives the quantity of He released.

- From dimensional invariants in classical percolation theory,

  \[
  d_c = \frac{2R_o}{(0.45 - \eta)^{0.848}},
  \]

  \( 2R_o = \) minimum bubble spacing

  \( \eta = \) projected area fraction

**For small particles and thin films, this layer is a significant He fraction at younger age, lowering the Effective Critical He/M.**
Early He release behavior and the onset of rapid release are inter-related.

- He atoms generated within the escape depth of surfaces and surface-connected porosity produces the early release fraction (ERF).
- In materials where bubbles are nucleated by He self-trapping, measurement of the ERF can provide information on the long-term He retention behavior: $\text{ERF} \rightarrow \text{Crit He/M.}$

He escape depth, $\lambda_{\text{esc}} \approx d_z/2$

- Bubble nucleation conditions
- Near-surface bubble denuded zone
- Bulk bubble spacing distribution
- Critical He/M for Rapid Release

Early Release Fraction (ERF)
Summary: Bubbles have 4 stages of evolution

- **Nucleation** occurs quickly by He self-trapping or trapping at intrinsic defects
  - sets bubble spacing distribution throughout life
  - self-trapping produces a lognormal spacing distribution
  - tested by He diffusivity, $^3$He NMR data

- **Isolated growth** occurs by accumulation of He atoms generated within source volumes
  - high bubble pressures produce long-range hydrostatic tension and short-range shear
  - pressures are determined by bubble growth mechanism
    (platelets are preferred shapes when surface energy $\ll$ strain energy)
  - He born within escape depth of surfaces produces an early release fraction (ERF)
  - tested by swelling, PCT, NMR, lattice dilation, ERF, bubble & platelet dimensions

- **Short-range bubble interactions** create high inter-bubble ligament tension
  - ligament fracture conditions first occur for smaller, closely-spaced bubbles
    but, support from the surrounding lattice prevents fracture
  - NMR data fits short-range, enhanced shear $p_s \propto 1/[r(1+\varepsilon)]$ behavior

- **Inter-bubble ligament fracture** results from planar percolation of the fracture condition
  - integral of fracture condition (over spacing distribution) increases with He/M
  - fracture occurs when projected “fracture area” = critical threshold for fracture percolation
  - rapid He release “appears earlier” when fracture cluster diameters become significant
  - tested by rapid He release data
We are continuing to test the model using available data on other metal systems.

Knowledge of the mean bubble/platelet density is needed to make use of any data.

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Suggested future work:

• Calculate void volumes created by lattice defects and impurities (DFT)
  - Alloys and impurities have potential to vary bubble spacing distribution
• Measure He self-trapping energies (HeIRE)
• Formulate physical parameters in lognormal spacing distribution function
  \[ F(R) = C \exp \left\{ - \frac{[\ln(R-R_o)/m]^2}{2\sigma_R^2} \right\} \]
• Change distribution with nucleation conditions (ERX at LLNL)
• Determine bubble pressures and shapes in young tritides (NMR, TEM)
• Examine the potential for stress-directed bubble growth (MD)
• Follow bubble linkage development near the Critical He/M (NMR)
• Measure changes in the onset of rapid release with powder size (HeRel)

To be useful for model testing, new measurements on tritides must include characterization of the bubble spacing distribution (or at least the mean bubble spacing).
A new Early Release Experiment (ERX) will test the bubble nucleation model

- **Goal**: Measure the Early Release Fraction for Pd tritide with various nucleation conditions.

- Tritium overpressure is maintained on samples at all times, even when alloquats of gas are removed.

- Tritium is extracted from each alloquat by a small SAES getter, leaving the $^3$He.

- The apparatus is currently installed in a tritium glove box in the LLNL tritium facility.

- After several months, the material will be removed and examined by TEM to determine the bulk bubble density.