Continuum-scale modeling of hydrogen and helium bubble growth in metals

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Motivation: Analysis of bubble growth in ITER-grade W samples exposed in TPE

- Precipitation affects migration through material
- Bubble growth depends on microstructure
- Growth mechanisms critical to developing realistic models

<table>
<thead>
<tr>
<th>exposure type</th>
<th>ion energy [eV]</th>
<th>duration [min]</th>
<th>flux ($\Gamma_i$) [$m^2 s^{-1}$]</th>
<th>fluence ($\Phi$) [$m^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LF</td>
<td>100</td>
<td>60</td>
<td>$4.9 \times 10^{21}$</td>
<td>$1.8 \times 10^{25}$</td>
</tr>
<tr>
<td>HF</td>
<td>100</td>
<td>120</td>
<td>$1.5 \times 10^{22}$</td>
<td>$1.1 \times 10^{26}$</td>
</tr>
</tbody>
</table>

- TPE plasma exposures at INL
- Microscopy at Shizuoka
Retention measurements correspond closely with those obtained in other laboratories.

Previous work by Alimov et al:
- ITER-grade W
- \( E = 38 \text{ eV} \)
- \( \Phi = 10^{22} \text{ D m}^{-2} \text{ s}^{-1} \)

Comparable exposure conditions

Retention measurements correspond closely with those obtained in other laboratories.

Previous work by Alimov et al:
- ITER-grade W
- $E = 38 \text{ eV}$
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Comparable exposure conditions:

TPE retention measurements:
- Correspond closely with Toyama/IPP meas.
- Confirm accepted retention temp. dependence.

Surface morphology variation with temperature

Key features:
- Non-uniform coverage
- Bubbles are small (<10 μm dia.) compared with warm-rolled W material.
- Absent at temperature extrema.
EBSD measurements reveal dependence on grain orientation

- Grain orientation indicated by inverse pole plot.
- Bubbles visible on grains with <111> and <110> directions aligned normal to surface
- Considerable distortion within individual grains
- Un-annealed sample showed increased distortion

SEM image of the same area
Atomic force microscopy reveals details of surface structure

- Atomic force microscopy provides information on the shape of the deformed surface.
- Individual bubbles identified and analyzed automatically.

**corresponding bubble size distributions**

![Graph showing bubble size distributions at 131 °C and 231 °C.](image)
What bubble growth mechanisms are active in W during plasma exposure?

- Near-surface plastic deformation
- Dislocation loop punching
- Vacancy clustering


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Far from the free surface, dislocation loop punching is favored

Three bulk precipitate growth mechanisms considered:

- Dislocation loop punching
  \[ p_{LP} \geq \frac{2\gamma}{r} + \frac{\mu b}{r} \sim \frac{1}{r} \]

- Griffith nano-crack extension
  \[ p_{NC} \geq \sqrt{\frac{\pi \mu \gamma}{(1 - \vartheta)r}} \sim \frac{1}{\sqrt{r}} \]

- Dislocation dipole expansion
  \[ p_{DE} \geq \frac{2\gamma}{s} + \frac{\mu d}{2r} \sim \frac{1}{r} + c \]

Based on methods developed in:
Near the free surface, bubbles may grow by crack extension.

Crack extension competitive with loop punching near surface:

\[
p_B \geq \frac{1}{r} \left( \frac{4\gamma(Eh)^{1/3}}{5C_1C_2} \right)^{3/4} \sim \frac{1}{r}
\]

Limitations:
- Correction for thick blisters
- Effect of plasticity (blunting of crack tip)
- Hydrogen effects

Bubble volumes measured with AFM correlate well with blister model

Volume modeled using blister test for thin film adhesion:

\[ V = \int y(r)2\pi rdr = C_1\pi a^2 y_c \]

Bubble volumes measured with AFM correlate well with deflection model

\[ V = \int y(r)2\pi rdr = C_1\pi a^2 y_c \]

Diffusion and trapping modeled with a continuum-scale approach

**Diffusion**: 1-D, uniform temperature:

\[
\frac{\partial u(x, t)}{\partial t} = D(t) \frac{\partial^2 u(x, t)}{\partial x^2} - q_T(x, t) - q_B(x, t)
\]

**Point defects**:
- 1.4 eV saturable traps, no nucleation.

**Bubbles**:
Modeled using a approach of Mills [J. Appl. Phys. (1959)].

\[
q_B(x, t) = \frac{\partial u_B(x, t)}{\partial t} = 4\pi D(t)r_B(x, t)N_B(x)[u(x, t) - u_{eq}(x, t)]
\]

Enthalpies for H migrating through W.

Dissolution of H in W is highly endothermic.
H equation of state takes into account non-ideal gas effects

**H₂ equation of state (EOS):**

- P > 1 GPa expected within small bubbles.
- At 300 K, H₂ solidifies at p=5.7 GPa.
- Tkacz’s [J. Alloys & Compounds (2002)] EOS to provide the best fit:
  \[ v = Ap^{-1/3} + Bp^{-2/3} + Cp^{-4/3} + (D + ET)p^{-1} \]
- San Marchi’s simplified EOS better at low pressure:
  \[ v = \frac{RT}{p} + b \]
When is bubble growth favorable?

**Calculation of equilibrium press.**

When is precipitate in equilibrium with mobile conc.?

- Equate chemical potentials of gas and solution phase.
- Calculate fugacity to account for non-ideal behavior:
  \[
  \ln(f/p) = \int_0^p \left( \frac{v(p,T)}{RT} - \frac{1}{p} \right) dp
  \]
- Equilibrium conc. given by:
  \[
  u_{eq} = \sqrt{f} S_0 \exp(-H_s/RT)
  \]

S₀ and Hₘ from Frauenfelder [JVST, 1969].
Summary of surface morphology findings

• ITER-grade W sample exposed in TPE show similar retention to Toyama/IPP studies.

• Analysis of surface morphology:
  – XPS shows implanted C reduced considerably
  – SEM/EBSD illustrate non-uniform bubble growth over surface
  – Bubble grow on (110) and (111) crystal planes
  – AFM analysis provide bubble volumes

• Modeling of bubbles:
  – Thin film adhesion model adapted to model blister grown on tungsten.
  – Model reproduces bubble sizes observed with AFM
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