Molecular Dynamics Simulations of Radiation-Enhanced Permeation of Hydrogen Isotopes In Ni

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Incorporating Grain Boundaries

Incorporating Statistics

(a) defect effects on xz diffusion in $\Sigma3\{111\}$ systems

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**Motivation**

- The TMIST-2 irradiation experiment at the Advanced Test Reactor at Idaho National Laboratory measured a tritium permeation enhancement in 316 stainless steel by a factor of ~2 to 5 relative to ex-reactor results.
- Grain boundaries and irradiation-induced defects may be both responsible.
- Statistics of diffusion cannot be captured by DFT calculations. Molecular dynamics (MD) simulations are required to understand this.
- The only literature stainless steel potential (Bonny et al, MSMSE, 21, 85004, 2013) incorrectly predicts phase separation.
- We therefore use Ni as an exemplar to perform extensive MD simulations on hydrogen diffusion in Ni to elucidate the tritium permeation enhancement in 316 stainless steels.
Grain boundaries parallel to xz plane are simulated with bi-crystals under periodic boundary conditions.

Single crystal and $\Sigma3\{111\}$, $\Sigma5\{100\}$, $\Sigma11\{311\}$ grain boundaries are studied.

Systems with and without point defects are both considered. Three different point defects (interstitials, vacancies, and Frenkel pairs) are independently simulated. Defect concentration is fixed at contain $C_{\text{def}} = 0.5\%$.

Systems contain a hydrogen concentration of $C_H = 2\%$.


MD simulations are performed at 13 temperatures 300 K, 325 K, ..., 575 K, 600 K for a period of $t_{\text{MD}} = 440$ ns (after 1 ns pre-equilibration).
Diffusion Analysis

• The coordinates \( \alpha_i(t) \) of \( N \) hydrogen atoms (\( i = 1, 2, \ldots, N \)), are recorded on a time interval of \( \Delta t \), i.e., at times of \( t = j\Delta t \), \( j = 1, 2, \ldots, m \) (\( m = t_{\text{MD}}/\Delta t \)), where \( \Delta t \) can be any multiple of the time step size \( dt \) used in the MD simulations.

• \( m+1-k \) measurements can be made for the displacement of a hydrogen atom \( i \) over a \( k\Delta t \) period: \( \Delta \alpha_{i,j}(k\Delta t) = \alpha_i(j\Delta t-k\Delta t) - \alpha_i(j\Delta t) \) where \( j = 1, 2, \ldots, m+1-k \).

• This allows us to calculate mean square displacement (MSD):

\[
\langle [\Delta \alpha(k\Delta t)]^2 \rangle = \frac{\sum_{i=1}^{N} \sum_{j=1}^{m+1-k} [\Delta \alpha_{i,j}(k\Delta t)]^2}{N(m+1-k)}
\]

• MSD can be fitted to diffusivities \( D \):

\[
\langle [\Delta \alpha(k\Delta t)]^2 \rangle = 2D_\alpha t
\]

\[
\langle [\Delta x(k\Delta t)]^2 \rangle + \langle [\Delta z(k\Delta t)]^2 \rangle = 4D_{xz} t
\]

\[
\langle [\Delta x(k\Delta t)]^2 \rangle + \langle [\Delta y(k\Delta t)]^2 \rangle + \langle [\Delta z(k\Delta t)]^2 \rangle = 6D_{xyz} t
\]

MSD convergence figure

\[ dt = 0.0005 \text{ ps}, \Delta t = 11.0 \text{ ps}, t_{\text{MD}} = 440 \text{ ns} \]
Defect Effects on H Diffusion in Ni Single Crystals

- Diffusivities are close with and without vacancies
- At the simulated interstitial concentration of 0.5%, interstitial increases diffusivities by 16.3 times at 300 K and 1.4 times at 600 K as compared with perfect crystals
- Activation energy of diffusion for perfect crystals is predicted to be 0.51 eV, as compared to the experimental value of 0.40 eV*

Defect Effects on H Diffusion in Ni with the Σ3{111} GB

- The coherent twin boundary almost has no effects on diffusivities with different defects except in the interstitial case.
- Interstitial increases on-plane diffusivities by 15.3 times at 300 K and 2.3 times at 600 K as compared with perfect crystals.
- Out-plane diffusivities are close to single crystals, indicating insignificant grain boundary trapping.
Visualization of \( \Sigma3\{111\} \) Grain Boundary

- Hydrogen does not segregate, but Ni interstitials and vacancies segregate at grain boundary
- Ni diffusion only occurs at the presence of interstitials and vacancies
- Interstitials cause reconstructions of atomic rows

\( C_H = 2\% \)
\( C_{\text{def}} = 0.5\% \)
Observation of Two $\Sigma 3\{111\}$ Grain Boundary Reconstructions due to Interstitials

- The 300 K reconstruction is similar to the one shown above, but the atomic rows in the 500 K reconstruction are different.
Statistical Effects of Initial $\Sigma3\{111\}$ GB Reconstructions

(a) interstitial effects on $xz$ diffusion in $\Sigma3\{111\}$ systems  
(b) interstitial effects on $y$ diffusion in $\Sigma3\{111\}$ systems

- Depending on reconstruction, the combination of interstitials and the $\Sigma3\{111\}$ grain boundary may significantly increase the on-plane diffusivities.
- Interstitial increases on-plane diffusivities by 146.7 times at 300 K and 2.4 times at 600 K as compared with the boundary alone case.
- Out-plane diffusivity is not significantly affected.
Defect Effects on H Diffusion in Ni with Σ5\{100\} GB

(a) defect effects on xz diffusion in Σ5\{100\} systems

(b) defect effects on y diffusion in Σ5\{100\} systems

- The Σ5\{100\} GB itself significantly increases the on-plane diffusion (relative to single crystal)
- All defects increase the on-plane diffusivities, especially vacancies (in single crystals, interstitials have the biggest effects and vacancies have negligible effects)
- Vacancy increases on-plane diffusivities by 9.2 times at 300 K and 2.2 times at 600 K as compared with the boundary alone case
- The out-plane diffusivities are significantly reduced as compared to bulk diffusion, indicating boundary trapping that is confirmed by the two segments
Hydrogen atoms strongly segregates at the GB
Ni interstitials and vacancies strongly segregate at the GB
No change in the orientation of atomic rows
Ni diffusion only occurs when ether interstitials or vacancies are present
No statistical effects of initial configurations on diffusivities were found

\[ C_H = 2\% \]
\[ C_{\text{def}} = 0.5\% \]
Defect Effects on H Diffusion in Ni with \( \Sigma 11\{311\} \) GB

- Diffusivities in the two on-plane directions slightly differ
- Defects increase on-plane diffusivities especially at low temperatures
- Interstitials most significantly increase on-plane diffusivities
- In the x- direction, interstitials increase diffusivities by 5.9 times at 300 K and 1.9 times at 600 K as compared with the boundary alone case
- In the z- direction, interstitials increase diffusivities by 4.1 times at 300 K and 1.9 times at 600 K as compared with the boundary alone case
- The out-plane diffusivities are significantly reduced as compared to bulk diffusion, indicating boundary trapping that is confirmed by the two segments
Visualization of $\Sigma 11\{311\}$ Grain Boundary

- Hydrogen atoms strongly segregates at the GB
- Ni interstitials and vacancies strongly segregate at the GB
- No change in the orientation of atomic rows
- Ni diffusion only occurs when ether interstitials or vacancies are present
- No statistical effects of initial configurations on diffusivities were found

$C_H = 2\%, \ C_{\text{def}} = 0.5\%$
Activation Energy and Pre-exponential Factors

Table I. Activation energies $Q$ and pre-exponential factors $D_0$ for different cases. Note that subscript “xyz” indicates isotropic bulk diffusion, “y” indicates out-of-plane diffusion, “xz” indicate isotropic in-plane diffusion, “x” and “z” indicate that the anisotropic in-plane diffusion is further split into two directions.

<table>
<thead>
<tr>
<th></th>
<th>No defects</th>
<th>Vacancies</th>
<th>Interstitials</th>
<th>Frenkel pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{xyz}$ (eV)</td>
<td>0.508</td>
<td>0.455</td>
<td>0.407</td>
<td>0.435</td>
</tr>
<tr>
<td>$D_{0,xyz}$ (Å²/ps)</td>
<td>3.835×10²</td>
<td>8.925×10¹</td>
<td>5.959×10¹</td>
<td>9.075×10¹</td>
</tr>
<tr>
<td></td>
<td>$\Sigma^3{111}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{xz}$ (eV)</td>
<td>0.483</td>
<td>0.465</td>
<td>0.441</td>
<td>0.302</td>
</tr>
<tr>
<td>$D_{0,xz}$ (Å²/ps)</td>
<td>2.283×10²</td>
<td>1.190×10²</td>
<td>2.336×10²</td>
<td>1.553×10¹</td>
</tr>
<tr>
<td>$Q_y$ (eV)</td>
<td>0.475</td>
<td>0.448</td>
<td>0.459</td>
<td>0.453</td>
</tr>
<tr>
<td>$D_{0,y}$ (Å²/ps)</td>
<td>1.666×10²</td>
<td>8.089×10¹</td>
<td>1.941×10²</td>
<td>1.503×10²</td>
</tr>
<tr>
<td></td>
<td>$\Sigma^5{100}$</td>
<td></td>
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</tr>
<tr>
<td>$Q_{xz}$ (eV)</td>
<td>0.395</td>
<td>0.301</td>
<td>0.291</td>
<td>0.300</td>
</tr>
<tr>
<td>$D_{0,xz}$ (Å²/ps)</td>
<td>8.623×10¹</td>
<td>3.376×10¹</td>
<td>1.413×10¹</td>
<td>2.073×10¹</td>
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<tr>
<td>$Q_y$ (eV)</td>
<td>0.716</td>
<td>0.672</td>
<td>0.864</td>
<td>0.747</td>
</tr>
<tr>
<td>$D_{0,y}$ (Å²/ps)</td>
<td>2.289×10³</td>
<td>1.116×10³</td>
<td>1.767×10⁵</td>
<td>5.497×10³</td>
</tr>
<tr>
<td></td>
<td>$\Sigma^{11}{111}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_x$ (eV)</td>
<td>0.476</td>
<td>0.395</td>
<td>0.393</td>
<td>0.391</td>
</tr>
<tr>
<td>$D_{0,x}$ (Å²/ps)</td>
<td>1.271×10²</td>
<td>2.907×10¹</td>
<td>4.808×10¹</td>
<td>2.888×10¹</td>
</tr>
<tr>
<td>$Q_z$ (eV)</td>
<td>0.493</td>
<td>0.447</td>
<td>0.432</td>
<td>0.465</td>
</tr>
<tr>
<td>$D_{0,z}$ (Å²/ps)</td>
<td>3.474×10²</td>
<td>1.262×10²</td>
<td>1.983×10²</td>
<td>2.420×10²</td>
</tr>
<tr>
<td>$Q_y$ (eV)</td>
<td>0.655</td>
<td>0.703</td>
<td>0.627</td>
<td>0.620</td>
</tr>
<tr>
<td>$D_{0,y}$ (Å²/ps)</td>
<td>1.388×10²</td>
<td>3.342×10²</td>
<td>1.528×10²</td>
<td>8.077×10²</td>
</tr>
</tbody>
</table>

$C_H = 2\%$
$C_{\text{def}} = 0.5\%$

Point defects + grain boundaries can reduce on-plane diffusion energy barrier, in agreement with experiments*

1. Robust MD diffusion simulation methods have been developed to account for statistical interactions between diffusion species, grain boundaries, and irradiated defects. Highly converged results with almost no statistical errors are demonstrated.

2. The predicted activation energy of H diffusion in defect-free single crystal Ni, 0.51 eV, compares well with the experimental value, 0.40 eV.

3. For single crystals, 0.5% interstitial increases H diffusivities by 16.3 times at 300 K and 1.4 times at 600 K as compared with perfect crystals. Vacancy does not sensitively change diffusivities.

4. Interstitials cause different reconstructions of $\Sigma 3\{111\}$ grain boundaries. Some reconstructions may have significantly increased on-plane H diffusivities: by 146.7 times at 300 K and 2.4 times at 600 K as compared with the boundary alone case.

5. Defects significantly increase on-plane H diffusivities on $\Sigma 5\{100\}$ grain boundary.

6. $\Sigma 5\{100\}$ and $\Sigma 11\{311\}$ grain boundaries have significant H trapping effects, leading to significantly reduced out-plane H diffusivities.

**Major Conclusions**