First-Principles Studies of Tritium Species Dissociability and Diffusivity Across the Interface of Nickel-Plated Zircaloy-4

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Research Scientist, NETL Support Contractor
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Scope of Work

Four Subtasks

- **Task 1:** Exploring $^3H_2$ and $^3H_2O$ binding sites and their dissociation on the (111) surface of Ni. Based on available literature data, we will obtain the dissociation energy according to the possible dissociation step of $^3H_2O\rightarrow O^3H^+H\rightarrow O^+H^+H$, $^3H_2O\rightarrow O^+H^+H^3H$, and $^3H_2\rightarrow^3H^+H$. **Completed**

- **Task 2:** Determining the $^3H$ species dissolve from surface into Ni bulk. For those dissociated species from Task 1, we will calculate their diffusion barriers from surface to the bulk to identify the most possible $^3H$ species that can be dissolved into Ni metal, and verify if NiO$_x$ or Ni(O$^3H$)$_x$ phase can be formed. **Completed**

- **Task 3:** Identifying the energy barrier of $^3H$ species diffusion in the Ni bulk. Based on the $^3H$ species dissolved into Ni metal and the formation of NiO$_x$ or Ni(O$^3H$)$_x$ phase from Task 2, we will calculate the energy barriers of $^3H$ species diffusion in Ni bulk (with NiO$_x$ or Ni(O$^3H$)$_x$) to determine which $^3H$ species can get through the Ni coating to reach the Ni-Zircaloy-4 interface. **Completed**

- **Task 4:** Build the interface of Ni and Zr metal. We will create possible Ni-Zr interface and clarify the most stable configuration for further study (FY24) of $^3H$ species diffusion across the interface and then dissolution into Zircaloy-4 getter to form metal hydrides. **Completed**
### Milestones/Deliverables

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Tangible and Measurable Achievement (Verification)</th>
<th>Due Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>Obtain configurations of $^3$H species ($^3$H, $O^3$H, O) on Ni (111) surface and calculate their diffusion barriers in Ni coating layer</td>
<td>Mar. 31, 2023</td>
</tr>
<tr>
<td>M2</td>
<td>For $O^3$H and O species diffusions, determine if NiO/Ni(OH)$_2$ phase can be formed</td>
<td>Jul. 31, 2023</td>
</tr>
<tr>
<td>M3</td>
<td>Create few most feasible Ni-Zr interface models for further FY24 work</td>
<td>Aug. 31, 2023</td>
</tr>
<tr>
<td>M4</td>
<td>Wrap up the calculations into manuscript and final report</td>
<td>Sep. 30, 2023</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Deliverable</th>
<th>Description of Data and Information/Knowledge</th>
<th>Due Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>Monthly informal status reports (e.g., email)</td>
<td>NLT Last Business Day of Each Month</td>
</tr>
<tr>
<td>D2</td>
<td>Mid-year review presentation</td>
<td>NLT Apr. 30, 2023</td>
</tr>
<tr>
<td>D3</td>
<td>End-of-year presentation at the Tritium Science Technical Exchange</td>
<td>NLT Sep. 30, 2023</td>
</tr>
<tr>
<td>D4</td>
<td>Final formal report (e.g., NETL technical report)</td>
<td>Sep. 30, 2023</td>
</tr>
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</table>
Deliverables

Publications


Presentations

Mechanism of Dissociation of $^3$H$_2$O and $^3$H$_2$ on Ni(111)

**Literature Review**

- $H_2O ightarrow H + H$

- $H_2 (g) ightarrow H + H$

<table>
<thead>
<tr>
<th>Size</th>
<th>Method</th>
<th>$E_a$(eV)</th>
<th>$E_r$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 x 4</td>
<td>PBE+vdW</td>
<td>0.09* (0.25 ML)</td>
<td>-0.60</td>
</tr>
<tr>
<td>4 x 4</td>
<td>PBE+vdW</td>
<td>0.03** (0.125 ML)</td>
<td>-0.75</td>
</tr>
<tr>
<td>4 x 4</td>
<td>PBE+vdW</td>
<td>0.13** (0.25 ML)</td>
<td>-0.74</td>
</tr>
</tbody>
</table>


*Both H-atoms located at the fcc and hcp sites adjacent to each other. **fcc and hcp sites opposite to each other. ML = monolayer – defines H coverage.
Possible Stable Compounds of Nickel

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space Group</th>
<th>Formula Unit</th>
<th>Total Energy HSE06</th>
<th>Total Energy PBE</th>
<th>Total Energy PBE+U</th>
<th>HSE06 ΔH</th>
<th>PBE ΔH</th>
<th>PBE ΔH Corrected</th>
<th>PBE+U ΔH Corrected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Fm-3m</td>
<td>1</td>
<td>-6.448</td>
<td>-5.459</td>
<td>-1.842</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>H₂</td>
<td>1</td>
<td>-7.713</td>
<td>-6.772</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>1</td>
<td>-17.036</td>
<td>-9.862</td>
<td>-9.862</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NiO</td>
<td>Fm-3m</td>
<td>2</td>
<td>-17.970</td>
<td>-11.655</td>
<td>-10.278</td>
<td>-3.004</td>
<td>-1.265</td>
<td>-1.945</td>
<td>-4.184</td>
</tr>
<tr>
<td>NiO₂</td>
<td>P-3m1</td>
<td>1</td>
<td>-25.491</td>
<td>-17.350</td>
<td>-14.277</td>
<td>-2.007</td>
<td>-2.029</td>
<td>-3.389</td>
<td>-3.933</td>
</tr>
<tr>
<td>Ni₃O₄</td>
<td>Fd-3m</td>
<td>8</td>
<td>-61.366</td>
<td>-41.783</td>
<td>-34.696</td>
<td>-7.950</td>
<td>-5.681</td>
<td>-8.401</td>
<td>-12.165</td>
</tr>
</tbody>
</table>

Formation energy of NiₓOᵧHₓ is defined as: \[ \Delta H(NiₓOᵧHₓ) = E_{DFT}(NiₓOᵧHₓ) - x\mu_{\text{solid}}^{\text{Ni}} - y\mu_{\text{gas}}^{\text{O}} - z\mu_{\text{gas}}^{\text{H}} \]

ΔH corrected obtained using DFT O₂ corrected value

PBE - Perdew-Burke-Ernzerhof
Ni(OH)$_2$ Formation and Stability

**Thermodynamic Basis**

- Stability requires smaller atomic chemical potential than corresponding elemental solid, i.e., $\mu_i \leq \mu_i^{\text{solid/gas}}$
  
  and
  
  $$\Delta \mu_{Ni} + 2\Delta \mu_O + 2\Delta \mu_H = \Delta H(Ni(OH)_2)$$
  $$\Delta \mu_i = \mu_i - \mu_i^{\text{solid/gas}}$$
  $$\Delta \mu_i \leq 0, \quad i = Ni, O, H$$

- Constraints on $\Delta \mu_i$ to avoid the formation of other competing phases, by considering the existing solids NiO, Ni$_2$O$_3$, Ni$_3$O$_4$, NiO$_2$, NiOOH
  
  $$\Delta \mu_{Ni} + \Delta \mu_O \leq \Delta H(NiO)$$
  $$\Delta \mu_{Ni} + 2\Delta \mu_O \leq \Delta H(NiO_2)$$
  $$2\Delta \mu_{Ni} + 3\Delta \mu_O \leq \Delta H(Ni_2O_3)$$
  $$3\Delta \mu_{Ni} + 4\Delta \mu_O \leq \Delta H(Ni_3O_4)$$
  $$\Delta \mu_{Ni} + 2\Delta \mu_O + \Delta \mu_H \leq \Delta H(NiOOH)$$
Stable chemical potential region of the bulk Ni(OH)$_2$ in terms of the chemical potentials $\Delta \mu_O$, $\Delta \mu_{Ni}$, and $\Delta \mu_H$ using PBE functional. Points A, B, C, D, and E define the limiting stable conditions, the allowed chemical potential range for Ni(OH)$_2$, to be a stable phase.
Stable chemical potential region of the bulk Ni(OH)$_2$ in terms of the chemical potentials $\Delta \mu_O$, $\Delta \mu_{Ni}$, and $\Delta \mu_H$ using HSE06 functional. Points A, B, C, and D define the limiting stable conditions, the allowed chemical potential range for Ni(OH)$_2$, to be a stable phase.
HSE06 correctly predict NiO as the most stable among all Ni oxides in agreement with experiments.

PBE incorrectly assigns the lowest formation energy to Ni$_3$O$_4$.

PBE+U follows the same trend as HSE06.

The ΔH per atom of Ni(OH)$_2$ is lower than that of NiOOH in HSE06 (-1.25 eV/at vs. -1.03 eV/at), but it is the reverse in PBE (-0.82 eV/at vs. -0.85 eV/at).
$^3$H and O Diffusion thru Ni(111) Surface

Diffusion of H from Ni(111) Surface to Bulk

![Diagram showing energy profiles for different states of hydrogen and oxygen diffusion through Ni(111) surface.]

- $E_{\text{migr}} = E_{\text{TS}} - E_{\text{IS}}$
- $E_r = E_{\text{FS}} - E_{\text{IS}}$

H: fcc
- White: H
- Green: Ni

H: octahedral
- White: H
- Red: O

H: tetrahedral
- Green: Ni

Legend:
- White: H
- Green: Ni
- Red: O
H and O Diffusion thru Ni(111) Surface (cont.)

H Migration from Surface to Subsurface

![Energy vs Reaction Coordinate Diagram](image)

- $E_{\text{mig}} = 0.572 \text{ eV}$
- $E_{\text{f}} = 0.460 \text{ eV}$
- $E_{\text{mig}} = 0.618 \text{ eV}$
- $E_{\text{f}} = 0.500 \text{ eV}$
H and O Diffusion thru Ni(111) Surface (cont.)

O Migration from Surface to Subsurface

\[ 0 = \text{Niv}, \text{Ni vacancy} \]
H and O Diffusion thru Ni(111) Surface (cont.)

\[ \text{O}_{\text{subsurf-octa}} + 2\text{H}_{\text{fcc}} \rightarrow \text{O}_{\text{subsurf-octa}} + \text{H}_{\text{fcc}} + \text{H}_{\text{subsurf-octa}} \]
H and O Diffusion thru Ni(111) Surface (cont.)

\[ \text{O}_{\text{surf-fcc}} + 2\text{H}_{\text{surf-fcc}} \rightarrow \text{O}_{\text{surf-fcc}} + \text{H}_{\text{surf-fcc}} + \text{H}_{\text{subsurf-oct}} \rightarrow \text{O}_{\text{surf-fcc}} + 2\text{H}_{\text{subsurf-oct}} \]
H and O Diffusion thru Ni(111) Surface (cont.)

\[ 2O_{\text{surf-fcc}} + 2H_{\text{surf-fcc}} \rightarrow 2O_{\text{surf-fcc}} + H_{\text{surf-fcc}} + H_{\text{subsurf-oct}} \rightarrow 2O_{\text{surf-fcc}} + 2H_{\text{subsurf-oct}} \]
H and O Diffusion thru Ni(111) Surface (cont.)

\[ \text{O}_{\text{surf-fcc}} + \text{OH}_{\text{surf-fcc}} + \text{H}_{\text{surf-fcc}} \rightarrow \text{O}_{\text{surf-fcc}} + \text{OH}_{\text{surf-fcc}} + \text{H}_{\text{subsurf-oct}} \]
Subsurface Ni(OH)$_x$ Formation - Case 1

$O_{\text{subsurf-octa}} + H_{\text{subsurf-octa}} + H_{\text{fcc-octa}} \rightarrow OH_{\text{subsurf}} + H_{\text{fcc-octa}}$

$O_{\text{subsurf}} + H_{\text{subsurf}} + H_{\text{fcc}}$
Subsurface Ni(OH)$_x$ Formation - Case 2

$O_{\text{subsurf-octa}} + 2H_{\text{fcc-octa}} \rightarrow O_{\text{subsurf-octa}} + H_{\text{hcp-octa}} + H_{\text{fcc-octa}} \rightarrow OH_{\text{subsurf}} + H_{\text{fcc-octa}}$

OH formation

H$_{\text{fcc}}$ + O$_{\text{subsurf}}$

H$_{\text{hcp}}$ + O$_{\text{subsurf}}$

H subsurf octah
Subsurface Ni(OH)$_x$ Formation - Case 3

Migration of OH Species from Surface to Subsurface

Activation barrier could not converge

$E_r = 1.944$ eV

Migration of OH species from the surface to the subsurface is less probable
O Diffusion from Subsurface to Subsubsurface

$O_{\text{subsurf-octah}} \rightarrow O_{\text{subsubsurf-tetrah}} \rightarrow O_{\text{subsubsurf-octah}}$

Diagram showing the transition from $O_{\text{subsurf-octah}}$ to $O_{\text{subsubsurf-octah}}$ through $O_{\text{subsubsurf-tetrah}}$. The energy profile is indicated with a graph, showing the reaction coordinate in Å and energy in eV.
Zr/Ni Interface Models

Zr(0001)/Ni(111) Interfaces and Optimization

Ni(111) : 9 x 9
Zr(0001) : 7 x 7

Different lattice mismatch

Ni(111) : 5 x 5
Zr(0001) : 4 x 4

Energy (eV)

Ni(111)/Zr(0001) interface distance (Å)

\( d_z \)
Zr Surface Calculations – M. Redington

Zr(0001) and Zr(10-10) Surfaces

\[ \gamma = \frac{E_{slab} - N E_{bulk}}{2A} \]

3H adsorption on surfaces

<table>
<thead>
<tr>
<th>Site</th>
<th>FCC</th>
<th>Bridge</th>
<th>HCP</th>
<th>Top</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{bind} ) (eV)</td>
<td>-0.987</td>
<td>-0.737</td>
<td>-1.006</td>
<td>0.264</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>Bridge (upper layer)</th>
<th>Bridge (lower layer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{bind} ) (eV)</td>
<td>-0.797</td>
<td>-0.767</td>
</tr>
</tbody>
</table>
Summary and Conclusions

- We explored $^3\text{H}_2$ and $^3\text{H}_2\text{O}$ binding sites and their dissociation on the (111) surface of Ni and concluded that the possible dissociation steps are $^3\text{H}_2\text{O} \rightarrow \text{O}^3\text{H} + ^3\text{H} \rightarrow \text{O} + ^3\text{H} + ^3\text{H}$, and $^3\text{H}_2 \rightarrow ^3\text{H} + ^3\text{H}$.

- Our thermodynamical calculations and analysis show that there exits a stable chemical potential region where $\text{NiO}_x$ or $\text{Ni(O}^3\text{H)}_x$ phase forms.

- $^3\text{H}_2$ and $^3\text{H}_2\text{O}$ will dissociate on the surface of Ni and diffuse into the subsurface. Our diffusion barrier results predict:
  - O will most likely stay in the Ni layer to form $\text{NiO}_x$ or $\text{Ni(O}^3\text{H)}_x$ due to its high diffusion energy barrier compared to that of $^3\text{H}$.
  - Formation of $\text{NiO}_x$ or $\text{Ni(O}^3\text{H)}_x$ phase in Ni subsurface layer is limited by O diffusion energy barrier and Ni vacancy defects.
  - Only $^3\text{H}$ will pass through Ni layer to across Ni-Zircalony-4 interface to form metal hydrides.

- Interface models Ni(111)/Zr(0001) were created and optimized for further study (FY24) of $^3\text{H}$ species diffusion across the interface and then dissolution into Zircaloy-4 getter to form metal hydrides.
Thank You!

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