Atomistic modeling of unit processes for oxidation and hydrogen-pickup, and connections to higher length scale models

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Collaborators to whom we provide input:
Mike Short (MIT); Jaime Marian (UCLA); Dane Morgan, Izabela Szlufarska (UW-Madison)

Update for CASL Leadership Review at MIT, 04.30.2015
A new framework is to be developed with newly added colleagues (Jaime Marian, UCLA; Donghua Xu, UTK), and without Morgan, Szlufarska and Thornton, in Phase II.
Objective: Develop and provide atomistic and quantitative models for ZrO$_2$ as input to continuum level corrosion and hydrogen pickup models.

[Zr Alloy]

Coherent ZrO$_2$ (Barrier Layer)

Porous ZrO$_2$

Predominantly Tetragonal

Predominantly Monoclinic

Suboxide ZrO$_{2-x}$

Planar Compression

Oxygen diffusion

H$_2$O

H$^+$

SPP

Contributions in phase I

Corrosion of zirconium alloys

H-pickup of Zirconium alloys

Oxygen Self-diffusion in ZrO$_2$

Tetragonal-Monoclinic transition

Density Functional Theory

Statistical Thermodynamics

Dilute Charged Defect Equilibria in a Metal Oxide

Kröger-Vink Diagram for tetragonal ZrO$_2$

Hydrogen solubility

Interplay between stress and H

M. Youssef and B. Yildiz


+ one in review, and one in preparation
Equilibria of point defects

Oxygen Self-diffusion in ZrO$_2$

$D_O(T,P_{O_2}) =$  
Defect Concentration  
$\times$ Mobility

Kröger-Vink Diagram for tetragonal ZrO$_2$

Density Functional Theory

Statistical Thermodynamics

Dilute Charged Defect Equilibria in a Metal Oxide
Connecting our work to others

1- Combine Density Functional Theory (DFT) calculations with statistical mechanics modeling to compute temperature and composition dependent oxygen diffusivity: \( D(T,x) \)

2- Feed MAMBA/BDM and Peregrine with the calculated diffusivities.
Oxygen diffusion \((T, \text{PO}_2) = \text{concentration} \times \text{migration}\)

Provides input for the oxidation model, HOGNOSE (Short)

Migration barriers (eV) calculated using CI-NEB method

<table>
<thead>
<tr>
<th></th>
<th>&lt;100&gt;</th>
<th>&lt;001&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_{O}^{**})</td>
<td>0.37</td>
<td>0.58</td>
</tr>
<tr>
<td>(V_{O}^{x})</td>
<td>1.48</td>
<td>1.24</td>
</tr>
</tbody>
</table>

M. Youssef and B. Yildiz
Validating the overall oxygen self-diffusivity

Experiments:
Park and Olander,

Impurities explain the small difference from the experimental data.

M. Youssef and B. Yildiz
Equilibria of point defects

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Hydrogen solubility

H-pickup of Zirconium alloys
Zirconium alloy degradation in nuclear reactors

H ingress - Detrimental

Coherent \( \text{ZrO}_2 \) (Barrier Layer)

Porous \( \text{ZrO}_2 \)

~20 \( \mu \text{m} \)

Hydrogen pickup through barrier \( \text{Zr-oxide} \)

Fe, Cr, Ni, Sn, Nb ...

Sub-oxide \( \text{ZrO}_{2-x} \)


Zirconium alloy degradation in nuclear reactors

Hydrogen pickup through barrier Zr-oxide
The key point we build in this topic: The ‘valley’ of hydrogen absorption on the electron chemical potential space of the Zr-oxide

M. Youssef and B. Yildiz (in review, 2015)

- We uncovered the electron chemical potential (or, equivalently the Fermi level, $E_F$) as the descriptor of the absorption of hydrogen into ZrO$_2$.

- Higher $E_F$ accelerates H-reduction and H$_2$ gas evolution at the surface. **Good!**

- Provides a physics-based guide for Zr-alloy design to minimize H-pick-up.

- Provides H-solubility values for the hydrogen-pick-up models.
The volcano of H-pickup into Zr alloys

- No physical explanation for this intriguing behavior, since 1960s.
- It takes 40 years to design and qualify alloys for nuclear reactors.

Explaining this volcano may facilitate faster design of Zr alloys

Simplified picture for H-pickup

H solubility in the oxide

H⁺ Reduction / H₂ Evolution

Transition Metal

ZrO₂

Zr

Explanation

Design

M. Youssef and B. Yildiz, in review (2014)
The volcano of hydrogen solubility in ZrO$_2$

\[ \log_{10}(\text{H sol, doped / H sol, undoped}) \]

3d transition metals in Zr

Formation free energy (eV)

Electron chemical potential, \( \mu_e \) (eV)

Valence band

3d transition metals in ZrO$_2$
Valley of hydrogen solubility on the $\mu_e$ space

Kinetic acceleration of $H^+$ reduction and $H_2$ evolution

Thermodynamic minimization of $H$ solubility

M. Youssef and B. Yildiz, in review (2015)
3d transition metals on the valley to design alloys

Kinetic acceleration of H⁺ reduction and H₂ evolution

Thermodynamic minimization of H solubility

M. Youssef and B. Yildiz, in review (2015)
Niobium on the valley to design Zr alloys

Kinetic acceleration of $\text{H}^+$ reduction and $\text{H}_2$ evolution

$\text{Nb}$ defects in $\text{ZrO}_2$

U. Ootganbatar, M. Youssef, W. Ma and B. Yildiz,

\[ \mu_e \uparrow \implies \text{e- conductivity} \uparrow \implies \text{H}^+ \text{ reduction} \uparrow \]

\[ \sigma \propto n_c \propto \exp\left(\frac{\mu_e - E_{CBM}}{k_B T}\right) \]

* Nb increases \( \mu_e \rightarrow 10^4 \) times faster e conduction
\( \rightarrow \) improved H resistance (*)
Unexplored elements on the valley to design alloys

- Kinetic acceleration of $H^+$ reduction and $H_2$ evolution
Comparison of cost and availability

Cost

<table>
<thead>
<tr>
<th>Element</th>
<th>Cost of Corresponding Commodities ($/100g)</th>
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<tr>
<td>Nb</td>
<td>4.05</td>
</tr>
<tr>
<td>P</td>
<td>0.011</td>
</tr>
<tr>
<td>Ta</td>
<td>20.72</td>
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<tr>
<td>Mo</td>
<td>2.05</td>
</tr>
<tr>
<td>W</td>
<td>4.04</td>
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</table>

Availability

<table>
<thead>
<tr>
<th>Element</th>
<th>Abundance on earth crust (ppm by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>17</td>
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<tr>
<td>P</td>
<td>1050</td>
</tr>
<tr>
<td>Ta</td>
<td>1.7</td>
</tr>
<tr>
<td>Mo</td>
<td>1.2</td>
</tr>
<tr>
<td>W</td>
<td>1.25</td>
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</table>
Conclusion 1

The volcano of H solubility in ZrO$_2$ provides an explanation for the volcano of H-pickup in Zr.
n-type doping is a viable design strategy for H-resistant Zr alloys.

- Gain at least a decade from the design timeline

M. Youssef and B. Yildiz, in review (2015)
Plans for Phase II: Corrosion and H-pickup processes in ZrO$_2$, investigated at the atomistic level, as input to mesoscale models:

- Effect of stress and extended defects (including precipitate phase boundaries; grain boundaries) on O-diffusion and H-pickup and diffusion.
- Fracture criteria for ZrO$_2$ based on stress, phases, and Li content.
- Surface reactions at water/ZrO$_2$ interface (source term for corrosion and H-pickup).
- Guided by experiments of Was (UM).
- Provide quantitative input to the continuum level H-pick up models (used to be of Morgan & Szlufarska at UW-Madison) and mesoscale oxidation / corrosion model of M. Short at MIT, and Jaime Marian at UCLA.
Dominant Hydrogen Diffusion Path and Barriers
(this is leveraged by a student (Ming Yang) on fellowship, and not by CASL funds)

CRYSTAL STRUCTURE-MONOCLINIC ZRO2
Hopping 1 in O3

Inner sub plane
$E_{\text{forward}} = 0.47 \text{ eV}$
$E_{\text{backward}} = 0.42 \text{ eV}$

Hopping 2 in O3

Inner sub plane
$E_{\text{forward}} = 0.27 \text{ eV}$
$E_{\text{backward}} = 0.22 \text{ eV}$

Rotating in O3

Inter sub plane
$E_{\text{forward}} = 0.47 \text{ eV}$
$E_{\text{backward}} = 0.42 \text{ eV}$

- Hopping 1 and Rotating are the two rate-limiting-step (0.47 eV), while hopping 2 is relatively easier (0.27 eV).
- Hydrogen attached with O4 plane is 0.5 eV higher than hydrogen attached with O3 plane. Hydrogen will diffuse in the O3 plane for the most of time.
- Any diffusion path can be constructed from the three elementary step.
Modeling the interfaces between ZrO2 and oxidized Intermetallic Precipitates as a path for oxygen and hydrogen ingress

Zr(Cr,Fe)$_2$ precipitates incorporated into the oxide layer on Zircaloy-4

Schematic diagram of oxide film of Zr(Cr,Fe)$_2$ precipitate with Cr$_2$O$_3$ layer at the top surface

- Corrosion rate depends on the nature of the protective oxide formed
- Secondary phase particles formed in zirconium oxide layer
- Study oxide interfaces to understand the defect distribution in protection layer

Defect Equilibria at Oxide Interfaces: DFT + Continuum Model

- Defect formation energy in bulk/across interface is calculated from DFT
- Bulk defect concentration profile is used as boundary condition for continuum model
Defect Equilibria at Oxide Interfaces: DFT + Continuum Model

Continuous model:

Poisson’s Equation

\[ \varepsilon \nabla^2 \Phi = -\sum \rho \]

Drift-diffusion Equation

\[ \frac{d^2 c_D}{dx^2} + \frac{q_D e}{k_B T} \left[ c_D (1 - c_D) \frac{d^2 \Phi}{dx^2} + (1 - 2c_D) \frac{dc_D}{dx} \frac{d\Phi}{dx} \right] = 0 \]

\[ \frac{d^2 c_{e,h}}{dx^2} + \frac{q_{e,h} e}{k_B T} \left[ c_{e,h} \frac{d\Phi}{dx} + c_{e,h} \frac{d^2 \Phi}{dx^2} \right] = 0 \]

Equilibrium Condition

\[ \int \rho dx = 0 \]

Flow chart for solving defect concentrations across the interface under different temperature and oxygen partial pressure
Dislocation Interactions in Zr for Clad Creep, Growth and Plasticity

Yue Fan, Sidney Yip and Bilge Yildiz
Department of Nuclear Science and Engineering, Massachusetts Institute of Technology

Collaborators: Yuri Osetskiy, Stas Goulubov, Roger Stoller (ORNL) & Blas Uberuaga, Art Voter, Carlos Tome (LANL)

Update for CASL Leadership Review at MIT, 04.30.2015
The team, topics and methods in PCI-CLAD (vision until 2013)

- **LANL**
  - TAD method
  - Cluster mobility vs size
  - Point defect absorption by dislocations

- **ORNL**
  - Dimer+KMC method
  - Cluster mobility vs size
  - Dislocation bias on different types of defects

- **MIT**
  - ABC method
  - Interaction between mobile dislocation and obstacles (voids, loops, SIA clusters)

- Growth RDT
- Climb vs. glide

Benchmark different methods on a unit process.
Contributions till 2013

- Yield strength of structural materials
  - flow stress upturn at high strain rate
  - strain-rate sensitivity → important input to VPSC creep model

- Moving dislocation interaction sessile cluster
  - important unit process for creep/growth
  - strain rate effects on mechanisms
    - low rate: SIA absorption
    - high rate: defects recovered

- Constitutive relations as interface to VPSC of LANL

- Point defects anisotropic diffusion in Zr
  - benchmark with new methods in MPO
    - Vacancy and SIA migration
### Publications: creep; corrosion/hydrogen


5. “First-Principles Assessment of the Reactions of Boric Acid on NiO (001) and ZrO2 (-111) Surfaces” (a CRUD material), in *Journal of Physical Chemistry-C*, 2012.


Back-up slides next....
Framework to predict the equilibria in ZrO$_2$ co-doped with a metal and hydrogen

Charge Neutrality Condition

\[
\sum_d \sum_q q[d^q] + p_v - n_c = 0
\]

0 K formation energies using Density Functional Theory (PBE functional)

Finite-T excitation using Density Functional Theory (phonons using harmonic approximation)

Apply charge neutrality and construct Kröger-Vink diagram

[1] Vienna Ab initio Simulation Package (VASP)
Defect equilibria in co-doped monoclinic ZrO$_2$

Zinc + Hydrogen in ZrO$_2$ at 600 K

**Extract $\mu_e$ for H$^+$ reduction/evolution**

**Extract the solubility of H**

**BAD!**

**GOOD!**