Materials and Hydrogen Isotope Science at Sandia’s California Laboratory

Presented by
Jonathan Zimmerman

Featuring work by
Dorian Balch, Norm Bartelt, Dean Buchenauer, Noelle Catarineu, Donald Cowgill, Farid El Gabaly Marquez, Richard Karnesky, Robert Kolasinski, Douglas Medlin, David Robinson, Joseph Ronevich, Julian Sabisch, Christopher San Marchi, Ryan Sills, Thale Smith, Joshua Sugar, Xiaowang Zhou

40th Tritium Focus Group Meeting, Albuquerque, NM, October 23-25, 2018
Outline

- Timeline of Hydrogen Science at Sandia-CA
- Facilities and Capabilities
  - Hydrogen Effects on Materials Laboratory (HEML)
  - Hydrogen Transport and Trapping Laboratory (HTTL)
  - Hydrogen Surface-Interactions Laboratory (HSIL)
  - Computational Material Science Tools and Techniques
- Research Highlights
  - Hydrogen Embrittlement of Structural Materials
  - Helium Bubble Nucleation and Growth in Tritium Storage Materials
Timeline of Hydrogen Science at Sandia-California

Sandia’s core mission to support the nuclear deterrent has enabled science and engineering for energy programs


- EXPERIMENTAL HYDROGEN PIPELINE FACILITY
- FUSION ENERGY SCIENCES
- METALLURGY
- EMBEDDED ATOM METHOD
- TRITIUM RESEARCH
- MINING LOCOMOTIVE
- AUTOMOTIVE STORAGE
- H2 FUELING INFRASTRUCTURE PARTNERSHIPS
- LIFETRUCK LIFECYCLE REQUIREMENTS
- CONFERENCE ORGANIZATION
- MOBILE LIGHTING
- H2FIRST
- MULTI-LAB RESEARCH CONSORTIA
Sandia’s Work in Hydrogen Isotope Science

• Understanding and prediction of hydrogen and helium embrittlement of structural materials

• Characterizing the interaction of tritium with materials used for fusion energy technologies for optimum design and selection

• Developing materials and technologies for hydrogen fuel cells to provide power for vehicle transportation, maritime vessels & infrastructure, industrial uses, etc.
  • Reliable, low-cost equipment for hydrogen delivery and large-scale storage
  • Solid materials for on-board storage of hydrogen
  • Production of hydrogen from renewable energy sources
  • Behavior of hydrogen releases to understand risks and assure safety
Hydrogen Effects on Materials Laboratory

The Hydrogen Effects on Materials Laboratory (HEML) is the cornerstone of Sandia’s research expertise in hydrogen compatibility of materials and a core capability for the U.S. DOE. The laboratory houses specialized assets for evaluating materials performance in high-pressure gaseous hydrogen.

- **Fracture and fatigue testing in high-pressure gaseous hydrogen** – Standard tensile, fracture and fatigue test configurations are executed with concurrent gaseous hydrogen exposure at pressure up to 140 MPa.

- **High-pressure fracture and fatigue testing at temperature** – Loading of a variety of test specimen configurations (standard tensile, fracture and fatigue tests) at controlled (constant) temperature in the range of 220K to 450K concurrent with gaseous hydrogen exposure at pressure up to 140 MPa.

Hydrogen Effects on Materials Laboratory

- **Constant-displacement, environmentally-assisted crack growth testing** – Instrumented fracture mechanics specimens are loaded to constant displacement and exposed to gaseous hydrogen at pressure up to 200 MPa. The temperature can be independently controlled (usually constant) in the range of 200K to 440K. Subcritical cracking threshold and crack velocity can be measured.

- **Thermal precharging** – Materials and test specimens are exposed to high-pressure gaseous hydrogen or deuterium (up to 140 MPa) at elevated temperature (up to 573K) to produce controlled hydrogen content within the specimens prior to evaluation.

- **Pressure cycling in controlled temperature** – Exposure of metals and non-metals (polymers) to pressure cycles up to 100 MPa at controlled (constant) temperature within the range 220K and 400K.
Hydrogen Transport and Trapping Laboratory

Hydrogen transport and trapping determines features of the interactions between hydrogen and materials. The effects of hydrogen on mechanical properties can be strongly influenced by transport (or diffusion) of hydrogen in materials on the time scale of testing.

- **Gas-phase permeation** – Permeation and diffusion of hydrogen are measured by exposing one side of a thin foil of material to deuterium at ~0.5 bar and measuring the deuterium molecules that evolve on the down-stream side of the foil, which is at ultra-high vacuum. These tests may be conducted at up to 1000°C.

- **Thermal desorption spectroscopy (TDS)** – Gas-charged specimen is heated at a controlled heating rate to release the hydrogen, which is measured as a function of temperature. The resulting spectrum is analyzed to characterize the “strength” of the interactions between microstructural features and the hydrogen.

- **Local-electrode atom probe (LEAP)** – Atom-probe tomography enables atomic resolution reconstruction of microstructures, including identification of atomic sites of hydrogen bonding within bulk materials.
Hydrogen Surface-Interactions Laboratory

Just as critical as hydrogen-induced embrittlement and trapping of hydrogen is the understanding of factors that influence the adsorption and desorption of hydrogen at a material’s surface. Sandia has developed an array of specialized capabilities that can be brought to bear on the problem.

• **Angle-resolved ion energy spectrometry (ARIES)** – Detects light adsorbates such as hydrogen, and uses low energy ion beams (<3 keV) to probe a material’s surface. Scattered and recoiled particles then provide information on surface structure and composition; detection of hydrogen concentrations as low as 0.03 ML is possible.

• **Ambient pressure x-ray photoelectron spectroscopy (AP-XPS)** – Measures the elemental composition, chemical state and electronic state of the elements that exist within a material at its surface and within a sub-surface region (<10nm).

• **Low energy electron microscopy (LEEM)** – Uses high-energy electrons (15-20 keV) to image atomically clean surfaces, atom-surface interactions, and thin (crystalline) films.

• **Scanning transmission x-ray microscopy (STXM)** – Measures the distribution of chemical species within small particles.
Hydrogen Surface-Interactions Laboratory

XPS study of role of surface oxides during dehydrogenation of complex metal hydrides.

LEIS results produced with ARIES informs and validates Mg(BH₄)₂ surface model development

LEEM has enabled real time imaging of O₂ chemisorption on X52 steel surfaces.
Computational methods are used to identify the mechanisms that govern hydrogen-assisted fatigue and fracture, diffusion and transport of hydrogen isotopes within materials, and the evolution of microstructural features that can trap hydrogen (e.g. dislocations, grain boundaries).

Sandia researchers model hydrogen interactions across multiple length scales, working closely with experimentalists to inform the macroscopic response of materials in hydrogen environments. Results are used to develop component-scale predictive models.

- **Density functional theory (DFT)** – Equations governing the behavior of electron orbitals are solved to compute the energetics and dynamics of atomic systems with very high fidelity.

- **Molecular dynamics (MD) using semi-empirical potentials** – The interactions of millions of atoms can be studied over nanosecond time scales. MD provides a valuable tool for studying fundamental hydrogen-defect interactions (dislocations, grain boundaries, crack tips).

DFT predicted binding energy of tritium to 32 different Pd alloys (3%) vs. volume expansion due to alloying.

Growth of He bubbles (yellow), stacking faults (red) and dislocations (blue) during tritium decay of PdT$_{0.85}$
Dislocation dynamics (DD) – Motion and extension of large ensembles of dislocation lines is used to simulate the effects of plastic deformation. The time and length scale of these simulations allows for a stronger comparison with experiments than for MD and DFT.

Crystal Plasticity (CP) – Enables the study of polycrystalline materials. Direct comparisons with high resolution strain mapping experiments is possible. Non-intuitive CP models are possible with machine learning approaches to infer stress and plastic flow rules.

Continuum Finite Element Methods (FEM) – Multiphysics tools have been developed for studying coupled deformation and hydrogen diffusion. Multiscale methods enable concurrent coupling between continuum models and high resolution models (e.g. CP) in key regions of interest, such as a crack tip.

Hydrogen Embrittlement in Structural Materials

Over the long-term, hydrogen isotopes dissolve into metals and degrade their mechanical properties. In tritium containing components, tritium decays to helium bubbles resulting in additional embrittlement.

Understanding the effects of hydrogen and helium on deformation and fracture of structural alloys (such as stainless steel and aluminum) and their welds is critical to predict the long-term performance and reliability of engineered components.

Sandia, in collaboration with other national labs, seeks to gain this understanding and discriminate between hydrogen and helium effects.

Comparisons suggest different geometries produce similar values of fracture toughness, with cross-geometry variability not exceeding multi-specimen variability.
Temperture and Rate Effects on Hydrogen Embrittlement

- Welds exhibited fracture toughness dependence on testing rate.
  - Fracture toughness ($J_{IH}$) was measured in hydrogen precharged condition at 293K and 223K for 304L, 316L, and 21-6-9 steels welded with 308L filler metal.
  - Slower test rate resulted in lower fracture toughness
  - In general, temperature had less significant effect on fracture toughness values.
    - Negligible for 304L and 21-6-9 welds
    - Some temperature dependence for 316L

Previously, rate effects were thought to be negligible due to very low mobility of hydrogen in austenitic stainless steels; however, recent findings suggest:
  - Conservative fracture toughness measurements can only be obtained by slow testing rates
  - Short range mobility of hydrogen may be enhanced in presence of stress resulting in apparent testing rate effects
Microstructure Evolution in Hydrogen Precharged Materials

- Electron microscopy (TEM, EBSD) is used to quantify baseline deformation microstructures in terms of dislocation density at select deformation amounts in hydrogen precharged tensile samples of forged 304L.

  Example: ε- and α'-martensite at shear bands in tensile-strained hydrogen-charged 304L stainless steel used in high-pressure reservoirs

TEM image reflects Olsen & Cohen model for α'-martensite nucleation at shearbands

Observations test hypothesized mechanisms for strain-induced martensite formation and discover how these mechanisms change in the presence of hydrogen.
Hydrogen-Assisted Fracture of AM Austenitic Stainless Steels

- Additive manufactured austenitic stainless steels show interesting strength characteristics
  - Questions remain about reproducibility of materials and microstructures, but defects appear to be an intrinsic characteristic

- AM is particularly attractive for demanding applications in extreme environments, such as hydrogen compatibility

- Many additive processes are intrinsically solidification based
  - Therefore, knowledge of the performance of weld microstructures may be transferrable

- Our experiments have focused on 304L stainless steel made using Directed-Energy Deposition (DED) and Power Bed Fusion (PBF) capabilities
AM Microstructure is Similar to Weld Microstructures

Microstructure of AM steels (both DED and PBF) features elongated grains, similar to GTA welds but at a finer length scale. This elongation appears aligned to build direction in DED materials.
Effects of Hydrogen Precharging on Tensile Properties

- Thermal H-precharging
  - Exposure to gaseous hydrogen until saturated with hydrogen (~60 days)
  - Pressure: 138 MPa, Temperature: 300°C
  - Hydrogen content ~140 ppm (wt)

- Mechanical testing in air in H-precharged condition is similar to \textit{in situ} testing in high-pressure gaseous hydrogen for tension, fatigue and fracture
  - Must consider the H-solute hardening: strength increase of 10-20%

- Ductility of PBF 304L is significantly lower than forged 304L
  - No H: RA = 40-50% (AM) vs. RA = 80% (forged)
  - With H: RA = 13-20% (AM) vs. RA = 50+% (forged)

<table>
<thead>
<tr>
<th>Build geometry</th>
<th>Designation</th>
<th>condition</th>
<th>YS (MPa)</th>
<th>TS (MPa)</th>
<th>El (%)</th>
<th>RA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLM Ring</td>
<td>L1</td>
<td>AR</td>
<td>414</td>
<td>641</td>
<td>57</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>483</td>
<td>654</td>
<td>19 (17 min)</td>
<td>20</td>
</tr>
<tr>
<td>SLM Ring</td>
<td>N1</td>
<td>AR</td>
<td>413</td>
<td>621</td>
<td>45</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>481</td>
<td>621</td>
<td>12 (7.4 min)</td>
<td>13</td>
</tr>
<tr>
<td>Forging</td>
<td>55C</td>
<td>AR</td>
<td>452</td>
<td>674</td>
<td>68</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>484</td>
<td>758</td>
<td>58</td>
<td>49</td>
</tr>
<tr>
<td>Forging</td>
<td>60C</td>
<td>AR</td>
<td>506</td>
<td>694</td>
<td>66</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>569</td>
<td>784</td>
<td>60</td>
<td>68</td>
</tr>
</tbody>
</table>

- AM also exhibits lower YS and TS, albeit less dramatic differences than for ductility
Effects of Hydrogen Precharging on Fracture Properties

- Fracture toughness of AM stainless steels can be very high in air (>300 Mpa-m$^{1/2}$)
- When H-precharged, fracture resistance of AM materials is less than forged material

Fine fracture features consistent with H-assisted fracture and microstructure

- Flat facets may represent solidification features
- Lack of fusion defects do not play an obvious role

As in welds, hydrogen-assisted fracture in AM austenitic stainless may be related to ferrite and compositional microsegregation

Helium Bubble Nucleation and Growth in Tritium Storage Materials

- Sandia has a long history of studying the physical mechanisms associated with storage of hydrogen isotopes in a solid material.
- Decay of tritium produces helium (He) atoms that cluster and form bubbles.
- For He in palladium (Pd), He gas is released from the metal at an accelerated rate at some critical concentration of He/Pd.
- Experiments reveal dislocation loops and other defects in these aged samples.

We seek to identify the physical mechanisms governing nucleation and growth of He bubbles, and that lead to the accelerated release of He gas.
Atomic-Scale Modeling is Used to Characterize H/T Diffusion

\[ D = D_{0.1} \cdot \exp\left(\frac{Q_{0.1}}{kT}\right) + D_{0.2} \cdot \exp\left(\frac{Q_{0.2}}{kT}\right) \]

- MD simulations predict linear Arrhenius plots at low hydrogen concentrations, non-linear Arrhenius plots at high concentrations, in good agreement with experiments.
- A two-barrier model can account well for the non-linear Arrhenius behavior at high hydrogen concentrations.
- The two-barrier model can be interpreted physically in terms of different local hydrogen compositions and environments that are active at high hydrogen content.
  - In hydrogen-poor environments, diffusion occurs through hops between compositionally homogeneous sites, which gives rise to a single effective diffusion energy barrier.
  - In hydrogen-rich environments, diffusion occurs through hops of hydrogen atoms between sites with varying compositions, which tend to exhibit a higher effective diffusion barrier.
Helium Bubble Nucleation, Growth and Release

- MD simulation is also being used to study the diffusion of helium atoms through a metal-tritide lattice and the atomic displacements that characterize bubble nucleation.

- Bubble growth is accompanied by extensive plastic deformation, i.e. formation of dislocations and stacking faults.

- At low amounts of $^3$He, dislocation loops are isolated to single bubbles.

- At moderate amounts of $^3$He, loops form a network between bubbles.

- Also evident is anisotropic swelling resulting in aspherical bubbles.

Initial work with semi-empirical potential did not show inter-bubble rupture, just formation of a thin membrane.
Predicting Accelerated Release of He Due to Inter-Bubble Rupture

- Earlier theory by Wolfer’s predicts that inter-bubble fracture occurs at a He content that depends on the ratio of ideal tensile strength to shear strength for the metal hydride.
- We used DFT to assess the fidelity of our Pd-T potential and to predict when inter-bubble rupture should occur.

For T/Pd = 0.65,
(He/M)\(_{cr}\) = 0.3125 for DFT
(He/M)\(_{cr}\) = 3.45 for MD

Further progress made recently in microscopy and microanalysis of tritiated Pd alloy to characterize helium bubble characteristics, including locations and pressures.

The total number, volumes, and 3D positions of the helium bubbles in a Pd alloy aged under tritium for 4 years were determined by electron tomography.

Electron energy loss spectroscopy (EELS) identifies the locations of bubbles in the Pd matrix and can be used to determine the He pressure within each individual bubble.

More details coming up in talks by Catarineu and Robinson.
Lack of correlation between a bubble’s size and its capture volume indicates current model of bubble nucleation and growth is incomplete.

Analysis of distributions of bubble sizes and capture volumes suggests He bubble nucleation is random, homogenous, and ongoing throughout the aging process.

More details coming up in talks by Catarineu and Robinson.
Summary

• Sandia has a long history of hydrogen isotope scientific research that has been impactful to its national security missions.

• Sandia-California maintains a broad suite of experimental and computational capabilities and expertise to maintain its momentum in this field.

• Notable among the many research topics staff address are…
  • Hydrogen embrittlement of structural materials (metals), where we continue to build the scientific base that connects processing to (micro-)structure to properties.
  • Hydrogen storage materials, where we advance characterization techniques and computational models to predict the long-term result of containment of hydrogen isotopes.

• Much of our expertise has come through productive collaborations with SNL-NM and other DOE national laboratories.