

Reversible Hydrogen Storage Materials – Structure, Chemistry and Electronic Structure

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***A Participant in the DOE Metal Hydride Center
of Excellence***

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Project ID # STP 23

This presentation does not contain any proprietary or confidential information

Timeline

- Project start date: FY 05
- Project end date: FY 09
- Percent Complete: New Project

Budget

- Total project funding
 - \$1,253, 389
 - \$313,350
- Funding for FY05: \$150,000

Barriers addressed

- Optimization of absorption/desorption kinetics of solid-state storage systems
- Theoretical modeling to guide material development
- Improve understanding of fundamental processes impacting alloy development that surpass targets.

Targets

Gravimetric capacity:	>6%
Volumetric capacity:	> 0.045 kg H ₂ /L
Min/Max delivery temp:	-30/85°C

Participant in DOE Metal-Hydride Center of Excellence, providing characterization and modeling of fundamental structural and chemical processes occurring during absorption/desorption cycle.

Specific collaborations.

Sandia National Laboratories – understand the fundamental processes controlling hydrogen absorption/desorption from NaAlH_4 .

Hughes Research Laboratory – understand structural and chemical changes associated with hydrogen absorption/desorption from Mg/Li-based hydride systems.

Univ. of Pittsburgh and Carnegie Mellon University - develop a "thermodynamic toolkit" based on the cluster-expansion method to determine phase formation mechanisms and stabilities from Density Functional formation energetics.

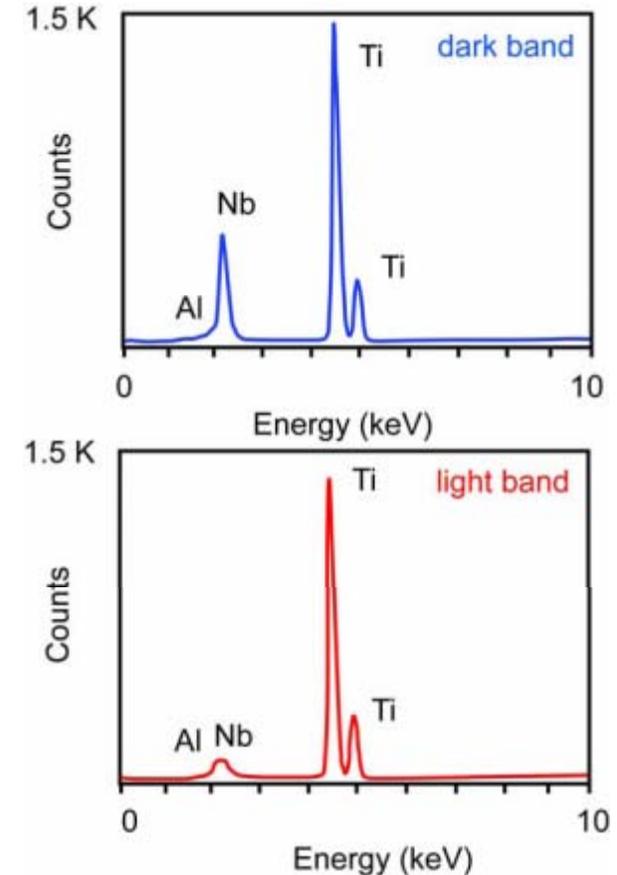
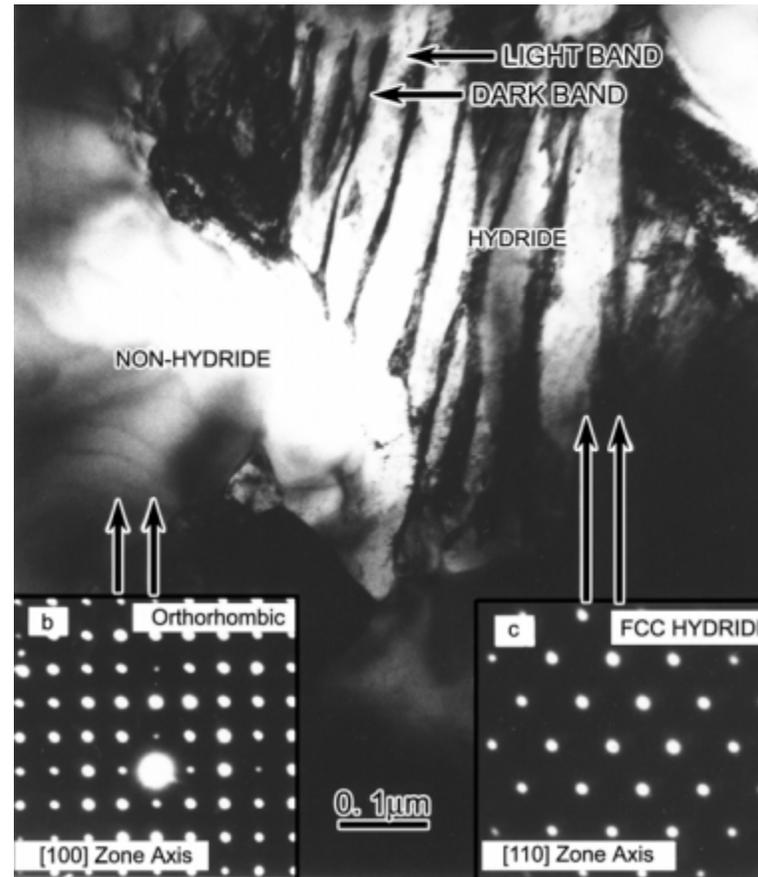
To provide the Sandia MHCoE with insight to the fundamental mechanisms and processes controlling the kinetics of hydrogen absorption/desorption from candidate complex metal hydride systems designed to meet the storage system targets.

- To characterize the structural, chemical, and bonding changes occurring during the absorption/desorption cycles.
 - identify absorption/desorption mechanisms for candidate systems to guide alloy development
 - Determine sensitivity to contaminants
- To provide theoretical modeling to guide materials development.
 - Provide a toolkit for partners to use to evaluate the potential impact of

- Use state-of-the-art characterization capabilities to determine the structure, chemistry and bonding of candidate systems.
- Determine the fundamental processes controlling the absorption/desorption from alanate and light-metal solid-state storage systems.
- Use electronic structure calculations to evaluate strategies for manipulating the hydrogen – metal bond to improve absorption/desorption kinetics.
- Develop models to aid identification and development of new solid-state storage materials.

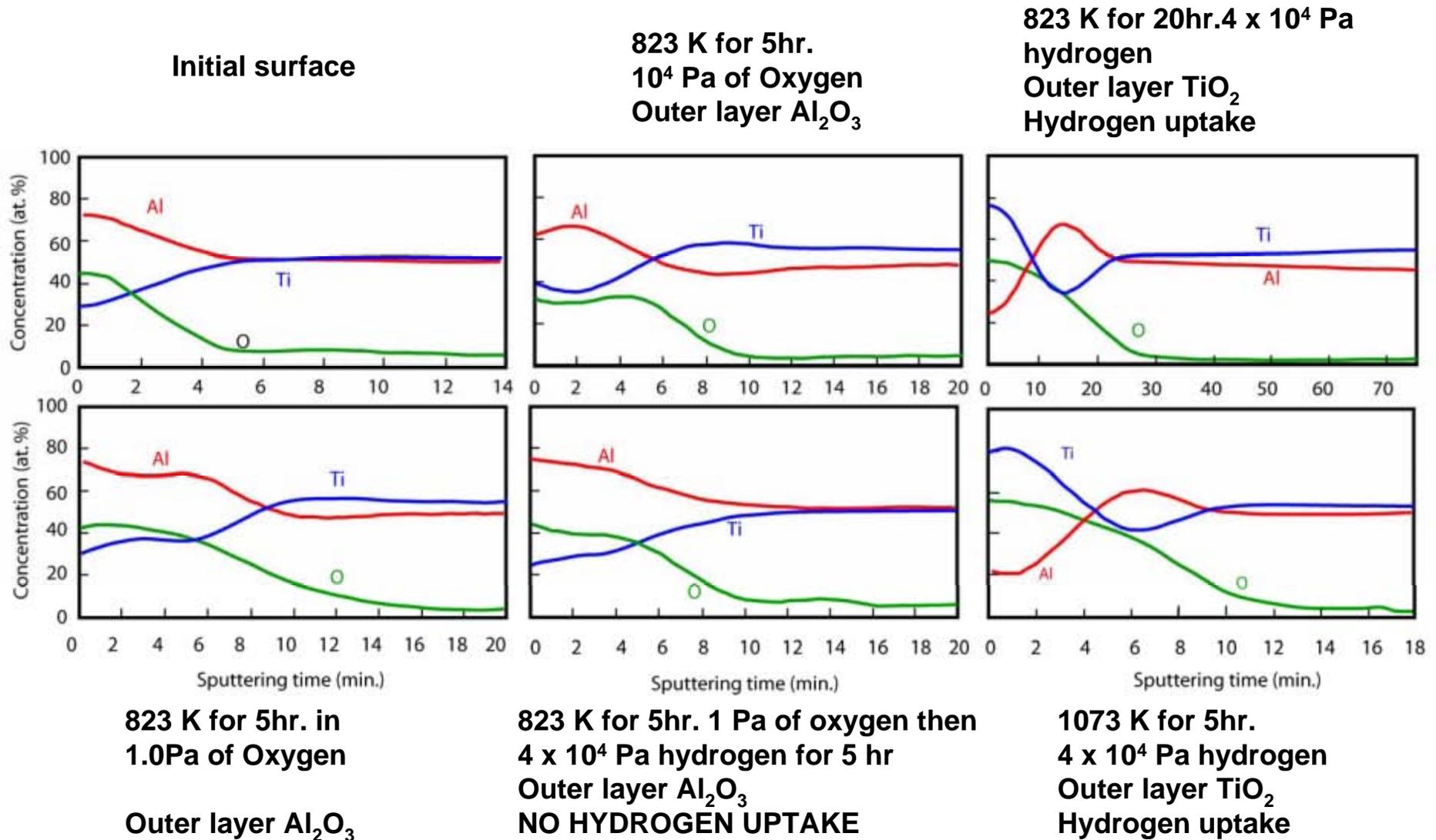
Element redistribution following high temperature and high pressure gas phase charging of a Ti-25Al-10Nb-3V-1Mo alloy

Al and to some extent Nb is being rejected from the hydride as it drives toward the formation of the binary TiH_2 .



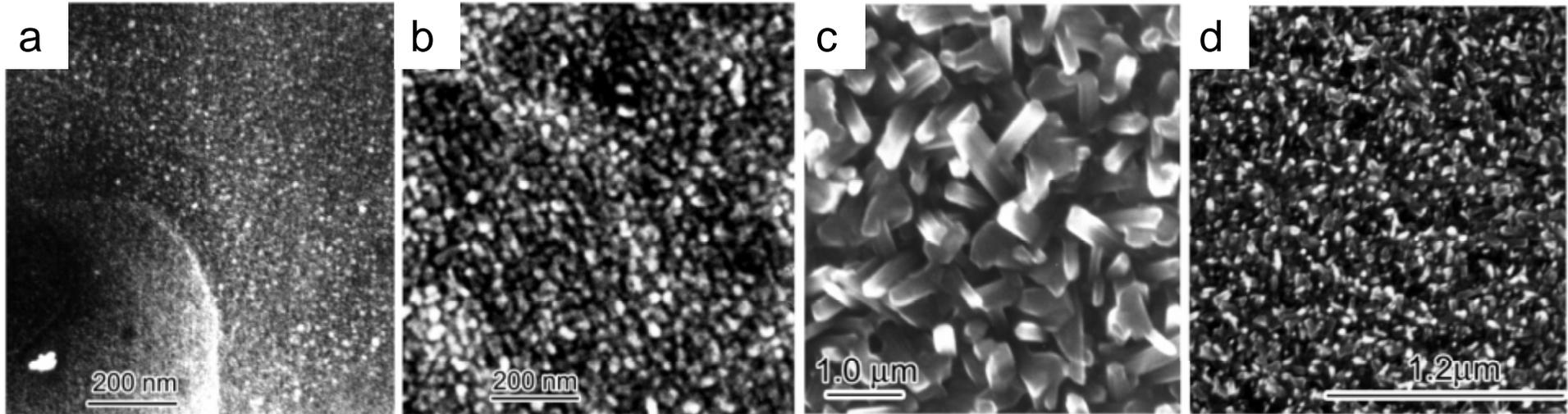
Composition not restored on hydrogen desorption impacts subsequent absorption cycle. Enhanced elemental diffusion in presence of hydrogen.

Change in surface chemistry impacts hydrogen absorption in TiAl



Hydrogen uptake conditions require surface is predominantly TiO₂.
Formation of this layer is kinetically not thermodynamically limited.

Change in surface morphology of TiAl



823 K for 5hr. 1 Pa of oxygen then 4×10^4 Pa hydrogen

1073 K for 5hr in 1 Pa oxygen

1073 K for 5hr in 1 Pa oxygen + 4×10^4 Pa hydrogen for 5hr

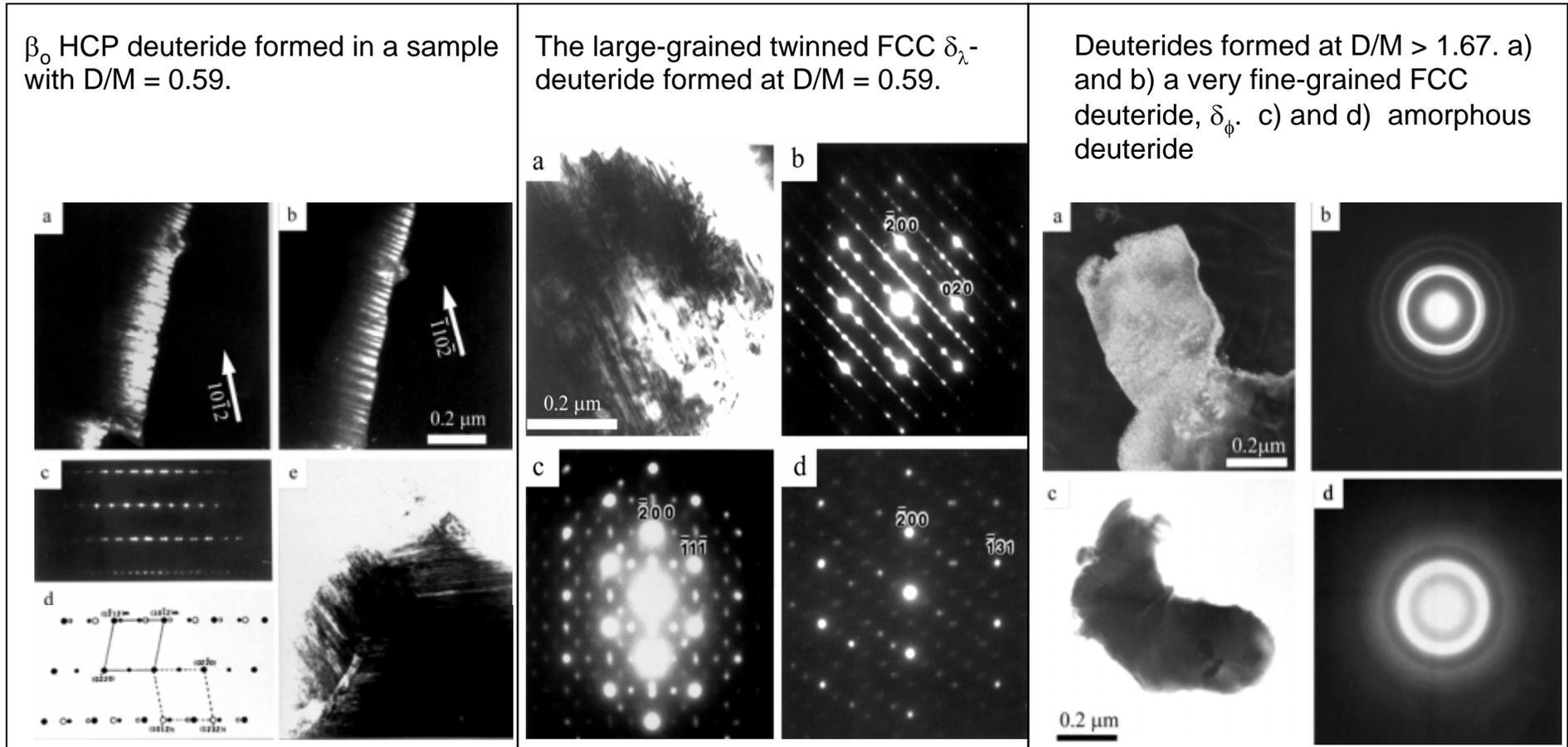
823 K in 4×10^4 Pa hydrogen for 20 days

Outer layer TiO_2
Hydrogen uptake

Outer layer TiO_2
Hydrogen uptake

Change in surface chemistry and structure impacts hydrogen uptake in TiAl. Absorption occurs only when the surface is predominantly TiO_2 .

Increasing hydrogen concentration →

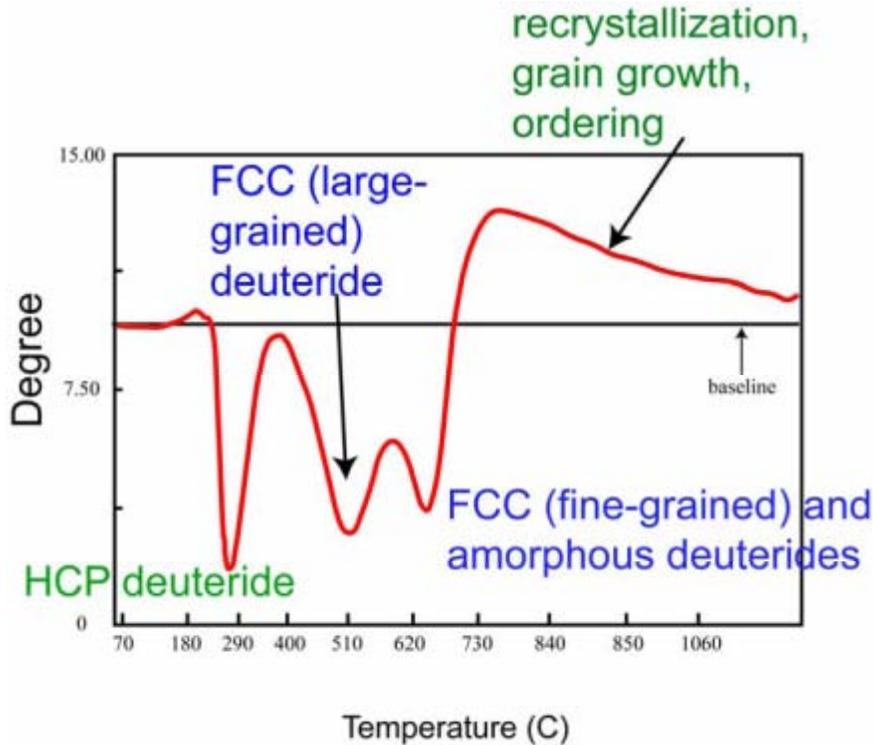


D/ M = 0.18; Solid solution of deuterium in α_2 and twinned deuteride with ordered DO_{19} structure, β_0
D/ M = 0.59; β_0 + Large grained FCC twinned deuteride, δ_1
D/ M = 1.67; β_0 + δ_1 + fine grained FCC twinned deuteride, δ_f + amorphous.

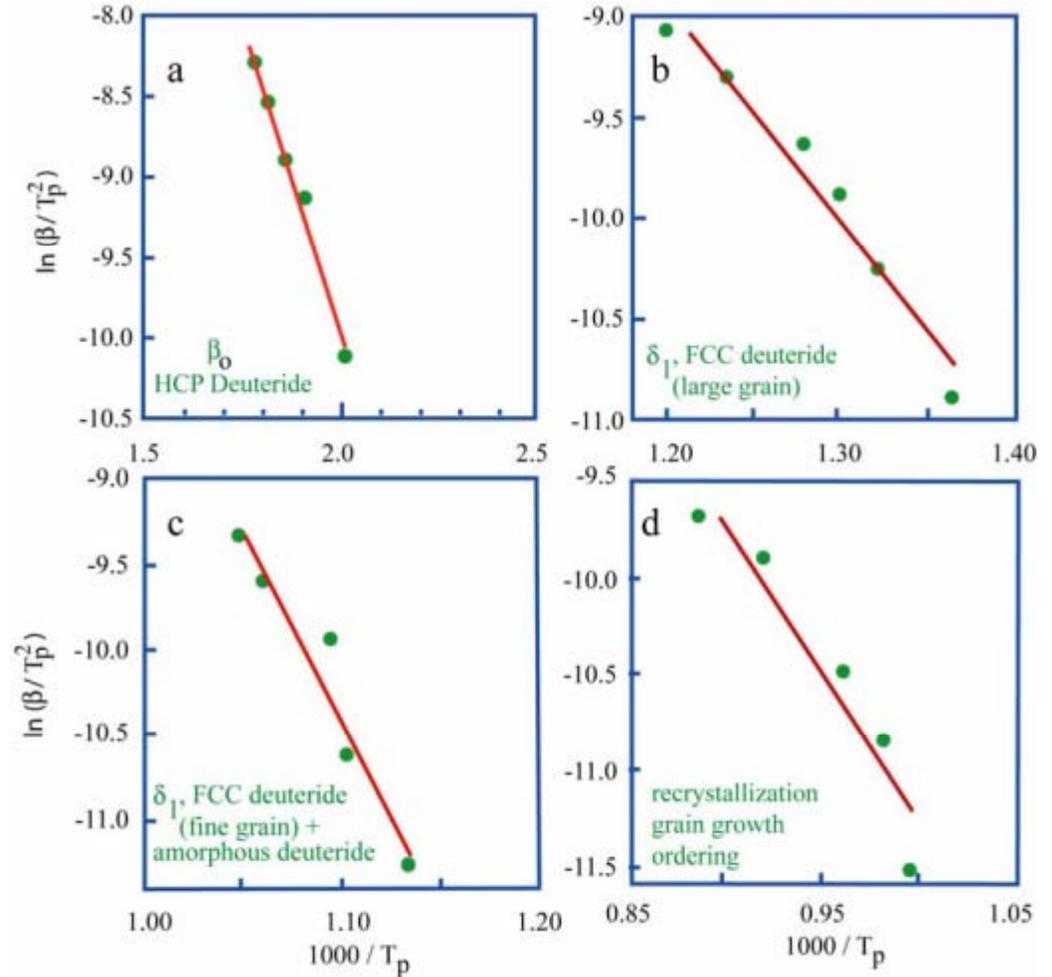
Driving force for the refinement of FCC structure and formation of amorphous phase is the difference in site energies for deuterium in the lattice and in grain boundaries.

Kissinger plots for the different peaks in the DTA spectrum

Differential thermal analysis

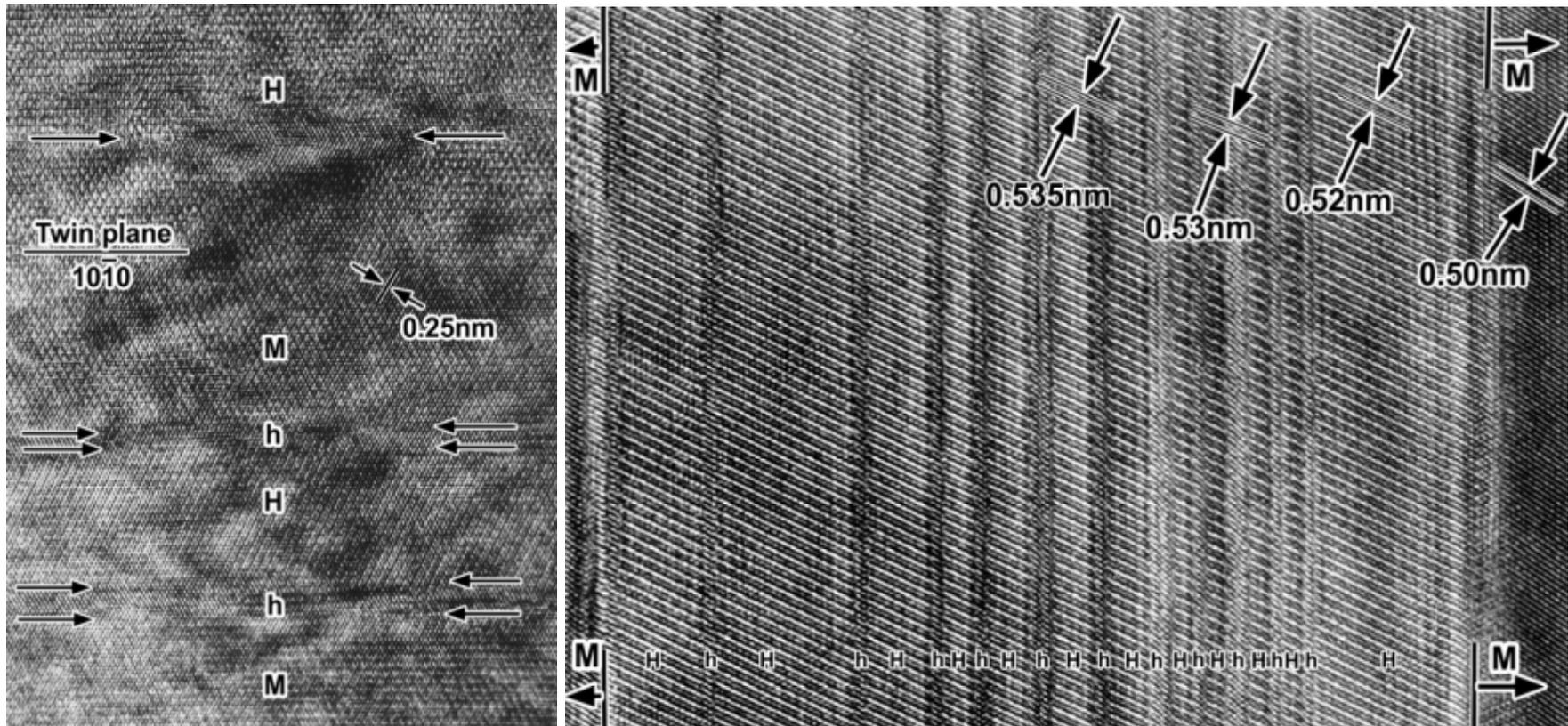


Kissinger Plots



Determination of the enthalpies of formation.

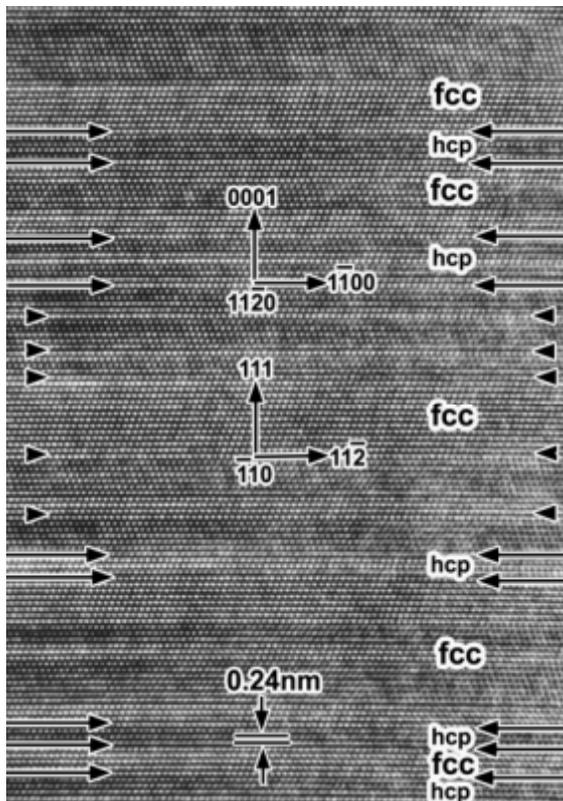
Increasing hydrogen concentration



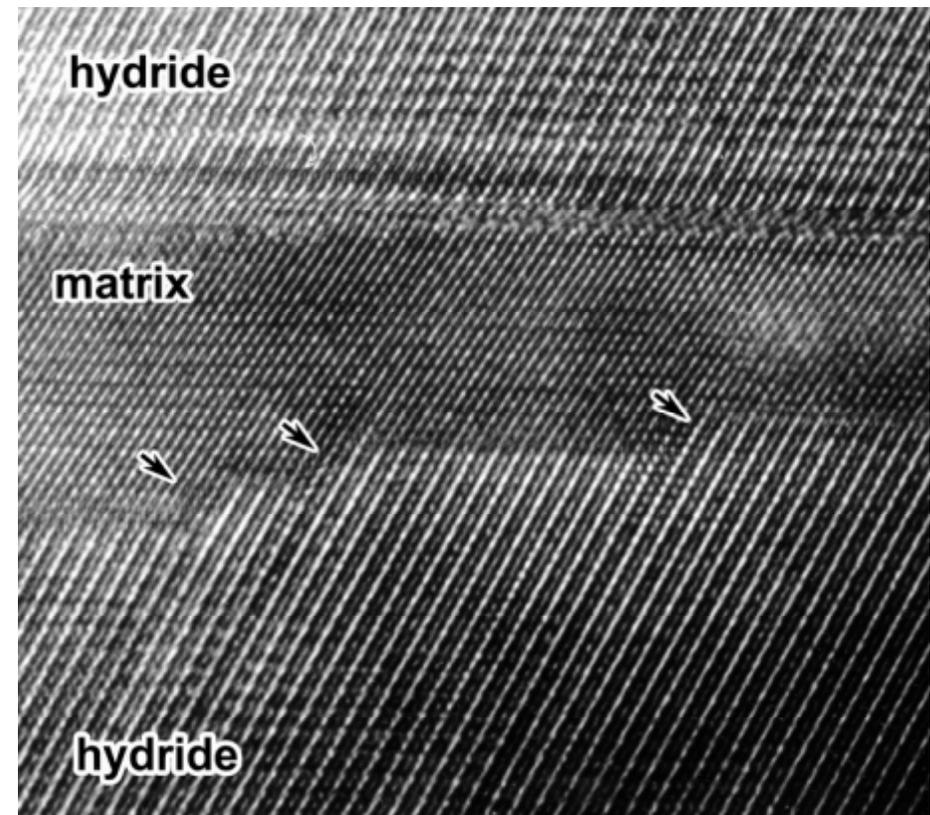
Matrix DO_{19} $a = 0.575 \text{ nm}$, $c = 0.463 \text{ nm}$; Hydride DO_{19} $a = 0.610 \text{ nm}$, $c = 0.490 \text{ nm}$

Volume expansion accommodated by internal twinning of hydride with variants of different thickness, variation in hydrogen concentration through thickness minimizes lattice mismatch.

Transition from the DO_{19} hydride to the FCC hydride with increasing hydrogen concentration. Note twin structure in the FCC hydride.



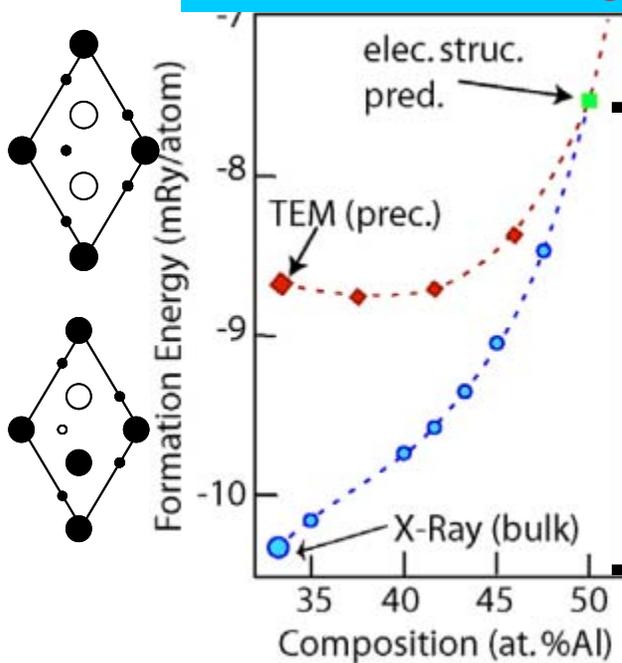
Comparison of hydride/matrix interface structures



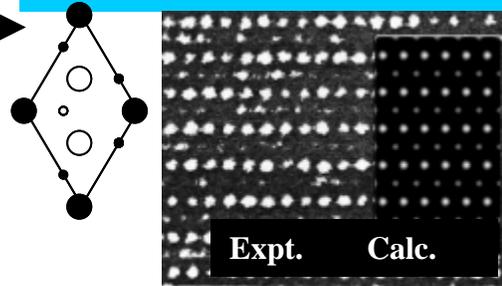
Ledge structure indicates hydride growth mechanisms.

Alloy Thermodynamic Toolkit to predict thermodynamic stability of phases via small sets of calculated structural energies based upon reliable cluster-expansion method.

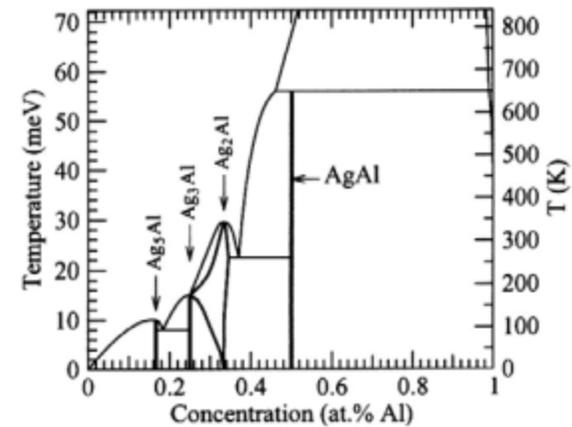
Predicted formation energies



Predicted metastable phase reinterpreted TEM
Acta Mater. 50, 2443 (2002)



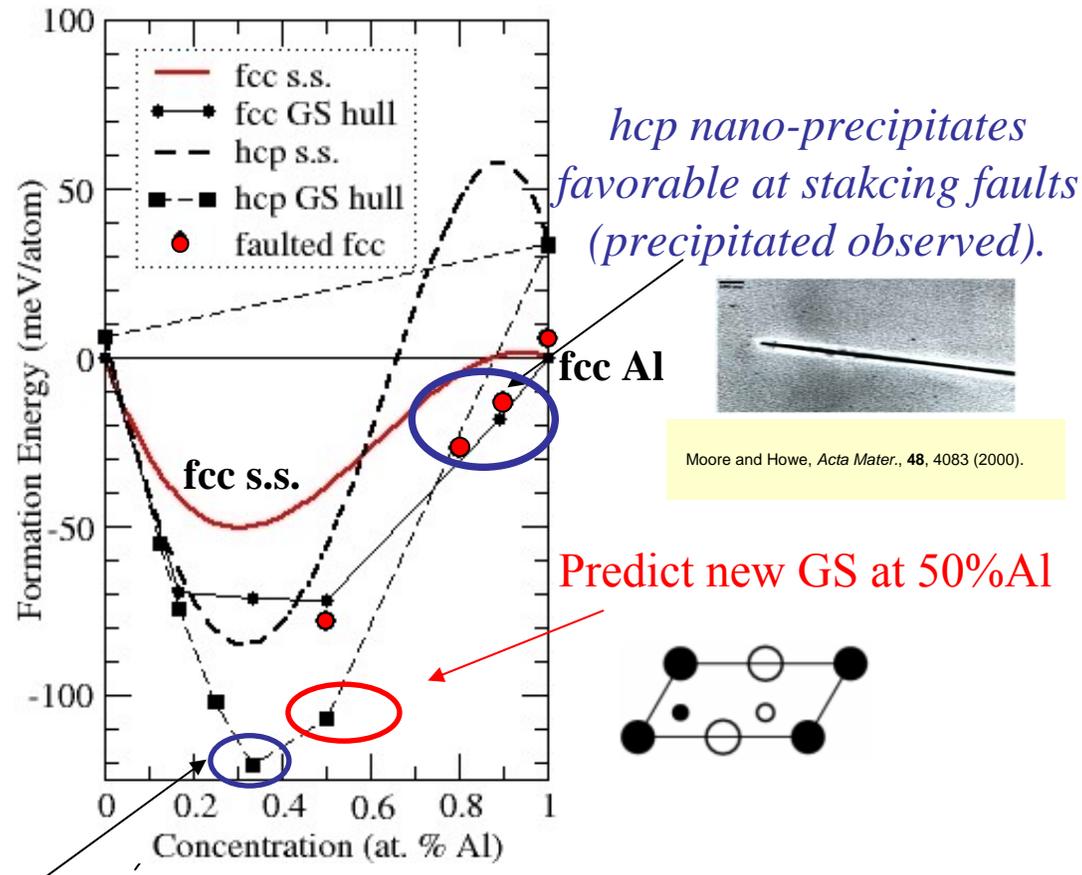
Predict New Stable Phases
Phys. Rev. B 67, 064104-8 (2003)



Toolkit does phase diagram

Components of Toolkit have been constructed and used independently. Modules are being integrated in C++.

Example Application: fcc and hcp Al-Ag solid-solution energies via toolkit components



Neumann GS at Ag₂Al

Use of toolkit successfully predicts new structures and precipitates – verified experimentally.

Identified electronic means to maximize H and stabilize ternary

Calculation find 60% increase in H uptake!

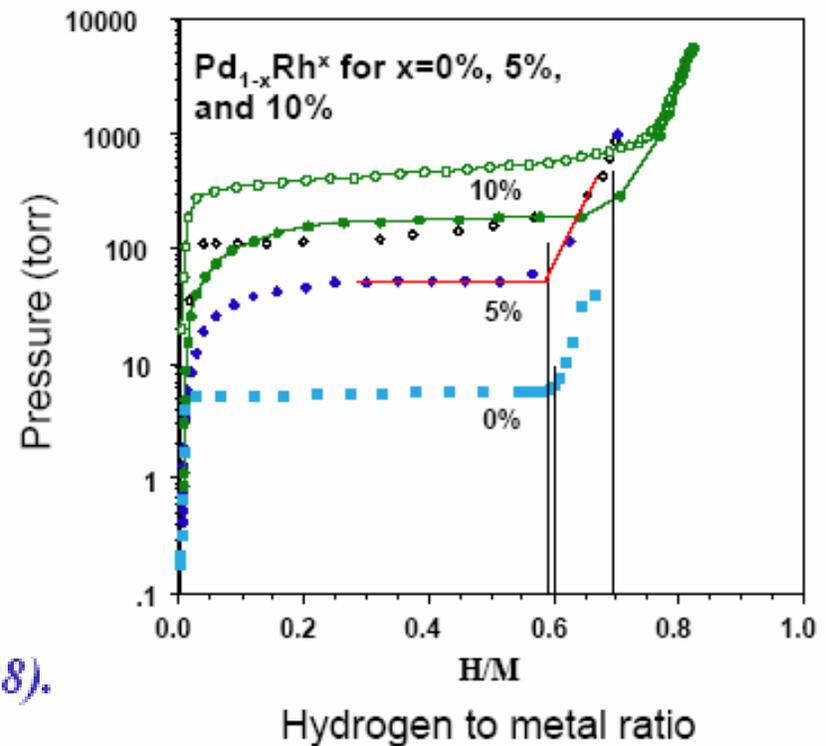
alloys	Calculated hydride d-holes	H/M observed
Pd(100)	0.62	0.60
Pd(95)Rh(5)	0.60	0.58
Pd(90)Rh(10)	0.73	0.70
Pd(93)Rh(5)V(2)	0.89	
Pd(90)Rh(8)V(2)	0.98	

Designed Ternary H-Storage Alloy

Pd₉₀Rh₈V₂ has optimal H/M max. and needed thermodynamically stable s.s. phase.

Confirmed experimentally at Sandia, CA (1998).

Predicted maximum Hydrogen-to-metal ratio *H/M* (vertical lines) during dehydriding in **Pd-Rh** agrees with measured desorption max. (S. Guthrie, Sandia).



Calculated desorption H/M ratio corresponds to measured values. Theoretical modeling used to provide guide to alloy development – H storage of ternary predicted and then confirmed experimentally!

- Determine safe and best practices for preparing samples of air sensitive materials for structural and chemical characterization in the electron microscope.
- Characterize initial chemistry and structure of alanates and Mg-based alloys.
- Validation and testing *of toolkit*.
- Establish ORACLE™ type searchable database for toolkit operation.

- Determine the differences in chemistry and structure following an absorption/desorption cycle for alanate and Mg-based structures
- Deliverable of toolkit and database to MHCoE partners 2005-6 to allow rapid additions of alloy structural energies from MHvCE partners.
- Investigate initial systems with electronic-structure methods to guide experiment in improvements or explain observations.
- Determine *alloying effects on Mg- and Li-based systems to understand effects of bonding and structure, impacting potential H capacity.*
- *Investigate interfacial solute and surface effects, where, potential, most reactivity takes place.*

