Theory Focus Session on Hydrogen Storage
DOE Hydrogen Program Review
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Kinetics, Mechanics and Microstructure Changes in Storage Media

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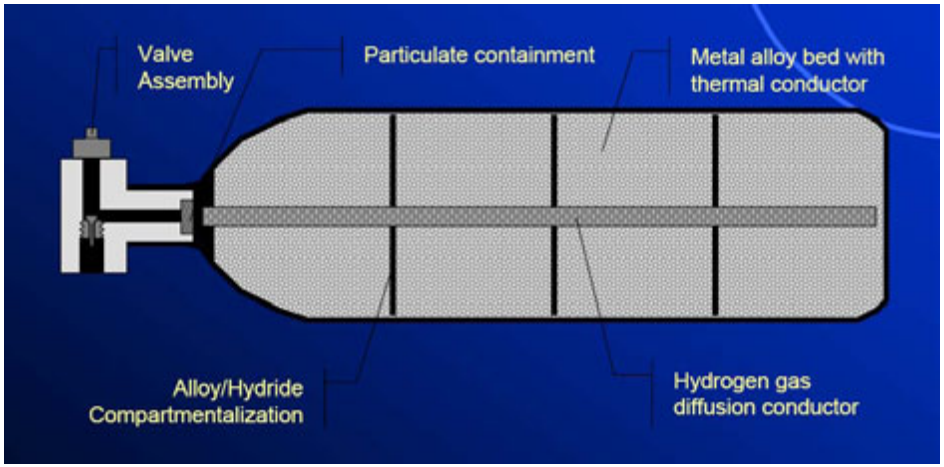
Objective

- The objective of this talk is to expose a number of materials science modeling needs for solid hydrogen storage media.
- Specifically, this talk emphasizes the connection between kinetics, thermodynamics, mechanics and microstructure changes
- This is an important gap between molecular models and experiments.

Outline

- Kinetics of hydrogen uptake/release
- Effects on storage medium microstructure
- Critical modeling areas and approaches

Hydride storage concepts



Ovonic Hydrogen Systems, LLC

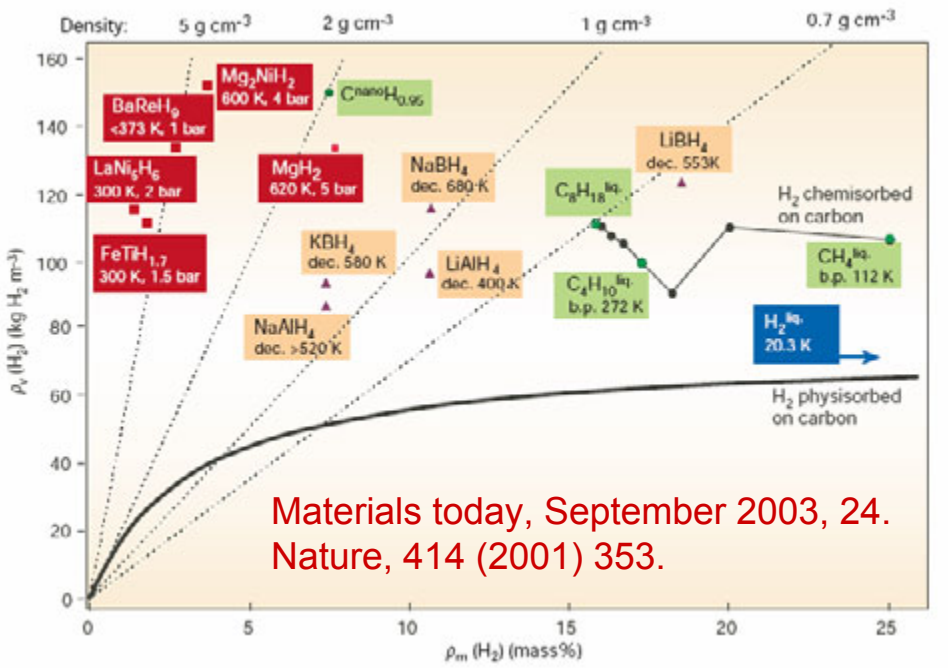
Figures on this page are adopted from a presentation by N.T. Stetson, 2005

Prototype

Current onboard concepts of solid media storage utilize some sort of packed beds or pellets of hyrdogen-carrying solid phase, deigned to allow uptake and release of hydrogen.

Material systems

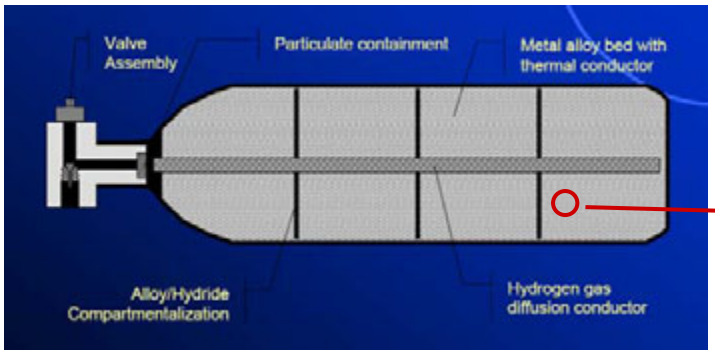
- Hydrogen absorbing **alloy**
- **Metal hydrides** (metallic bonded materials, transition metals, reversible)
- **Complex hydrides** (ionic/covalently bonded materials, may require catalysts, multi-step reactions)
- **Chemical hydrides**



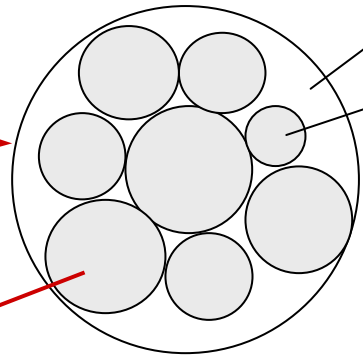
Key properties

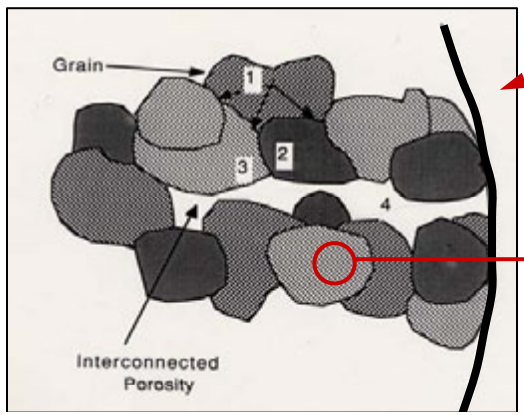
- p-C-T relationship for reversible hydride formation
- Storage capacity
- Kinetics of storage and delivery
- Lifetime of storage media
- Stability of storage material in the presence of contaminant gas

Inside the tank



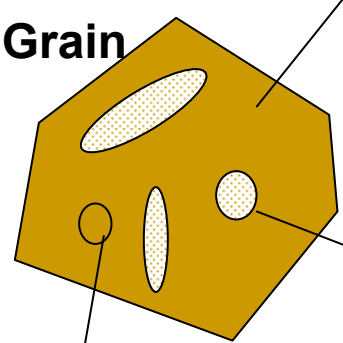
Representative pebble packed bed volume





One **particle** contains grains, grain boundaries, pores, etc.

Grain



Matrix:
- Metal (charging)
- Hydride (discharging)

Second phase:
- Hydride (charging)
- Metal (discharging)

Other phase

Hydrogenation/dehydrogenation

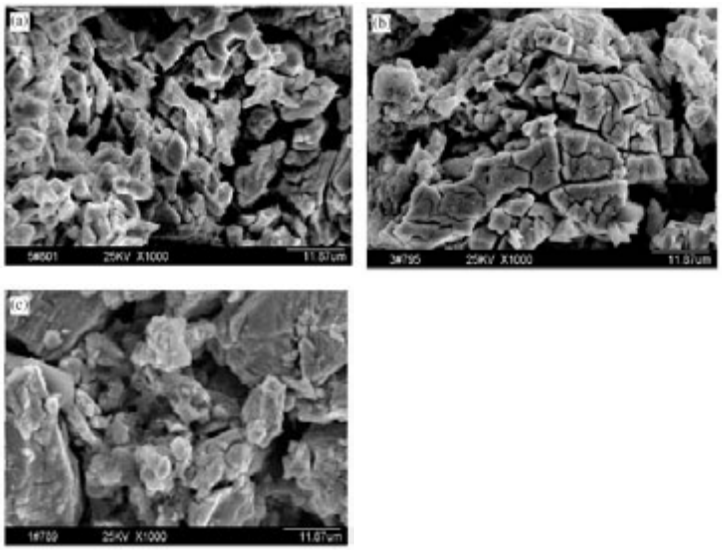
Hydrgenation process

- H_2 molecules land on surface, dissociate and get adsorbed (surfaces can be messy)
- H atoms dissolve and diffuse into matrix → lattice expansion at H/M ratio < 0.1 (bulk diffusion, trapping).
- As H/M ratio increases, strong H-H interaction take place and the hydride phase (b) forms in the parent (a) phase.
- **Free volume change**:
  - can be up to 30% for some system
  - Results in large stresses → material refinement by fracture and re crystallization
  - Deteriorates the materials at large # of cycles.

Microstructure changes during cycling

Some examples

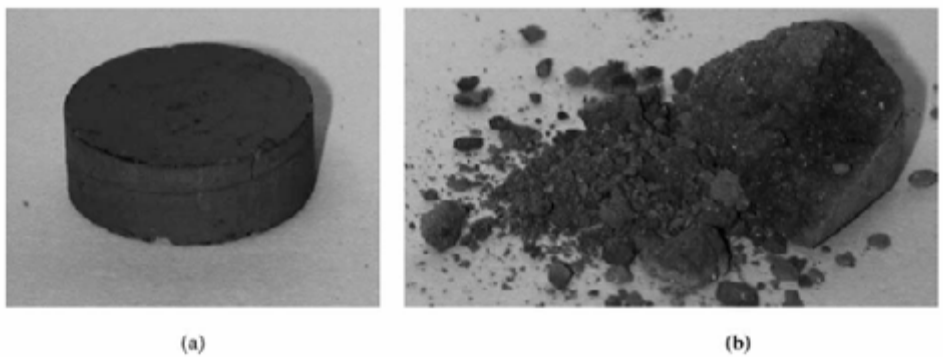
Cycling and microstructure changes



Particle shapes in $La_{1-x}Li_xNi_{3.2}Co_{0.3}Al_{0.3}$ complex hydride electrode after 100 charge/discharge cycles:

(a) x = 0.0, (b) x = 0.1, and (c) x = 0.2

(X. Wei et al, Int. J. Hydrogen Energy, to appear)



Mg-20% wt Mm alloy pellet after 20 hydriding/dehydriding cycles.

(N.E. Tran et al., J. Alloys and Compounds 407 (2006) 240.)

J.-M. Joubert et al. / Journal of Alloys and Compounds 330–332 (2002) 208–214

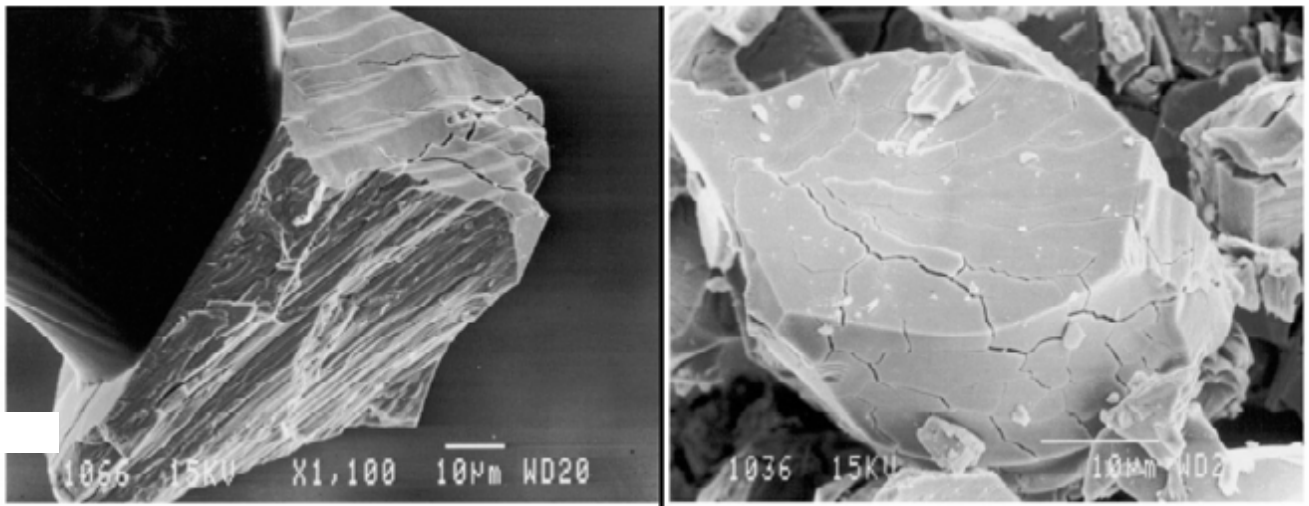


Fig. 4. S.E.M. observation of $LaNi_{4.75}Co_{0.75}$ (a) and of $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ (b) after hydrogen cycling. $LaNi_{4.75}Co_{0.75}$ sample is a single crystal glued on the top of a glass needle. The direction of the fibers is [00*l*], and the indexation of the plane is 00*l*, as obtained after orientation of the crystal with a single crystal diffractometer.

La-Ni-Co, and La-Mn-Ni-Co-Al systems

Nucleation and growth of hydride on Gd surfae

M. Brill et al. / Journal of Alloys and Compounds 330–332 (2002) 492–497

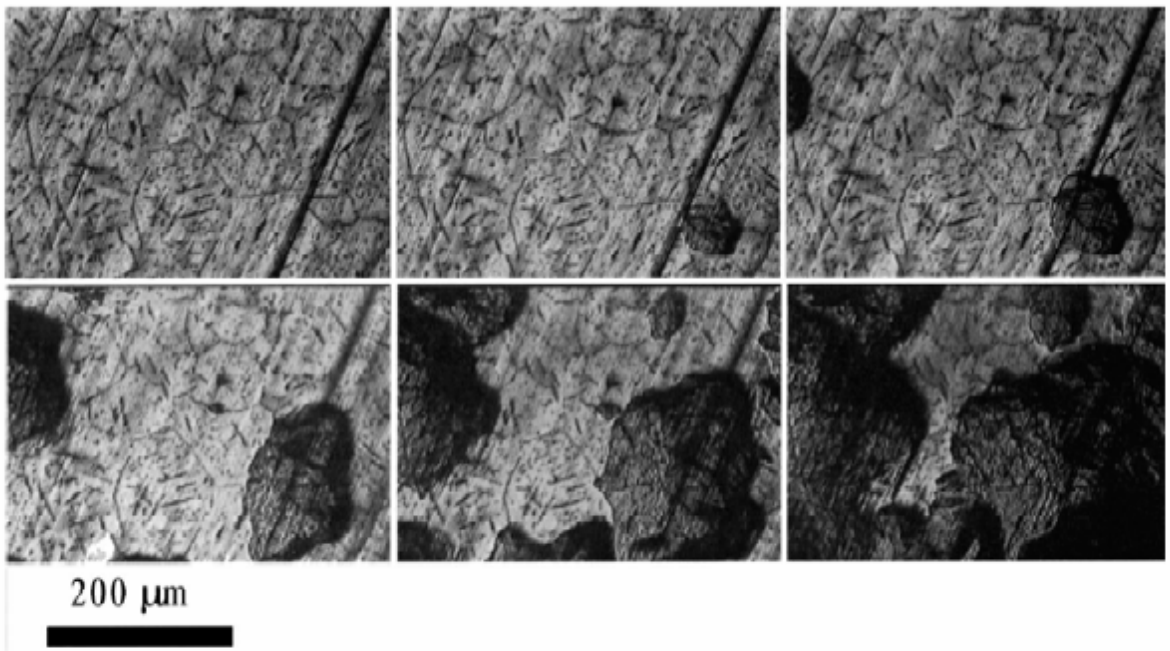


Fig. 2. Time evolution of the hydride phase on a polycrystalline gadolinium surface pre-exposed to low-pressure (10 mbar) hydrogen at 200°C for 1 h. The hydriding conditions were the same as in Fig. 1. The series of pictures correspond to $t = 0$, 20, 30, 40, 50 and 60 s after the introduction of 1000 mbar H_2 pressure.

Alanates

G.J. Thomas et al. / Journal of Alloys and Compounds 330–332 (2002) 702–707

First cycle

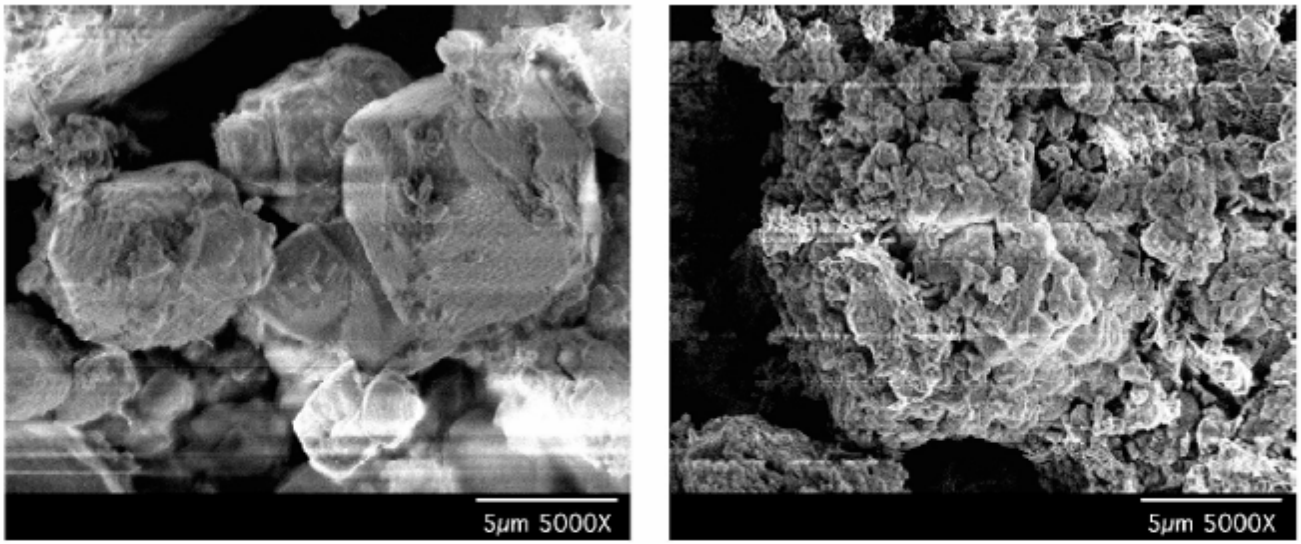


Fig. 4. Scanning electron micrographs of material during the first desorption cycle. (a) Na_3AlH_6 and Al remaining after hydrogen desorption from $NaAlH_4$. (b) Material after complete desorption to NaI and Al phase.

Five cycles

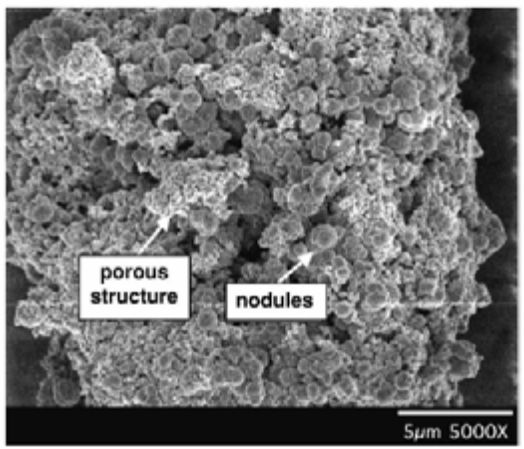
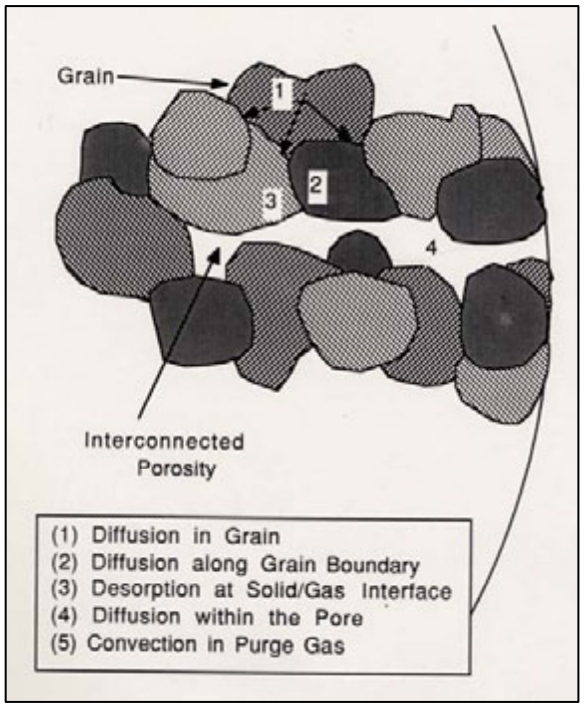
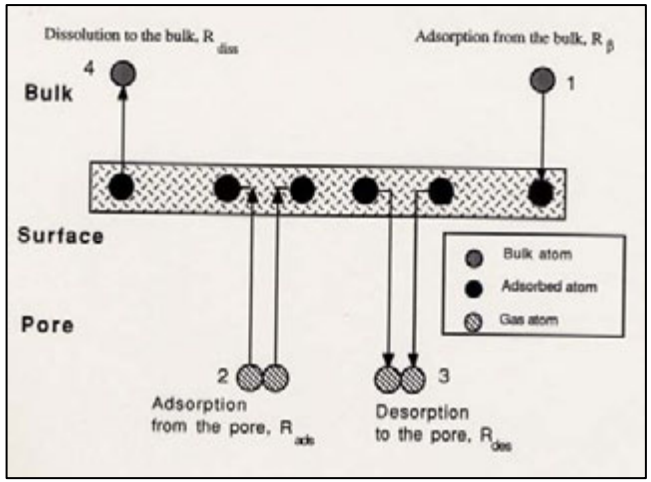
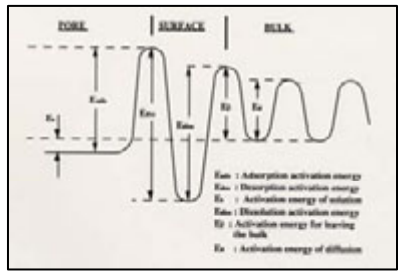


Fig. 5. Scanning electron micrograph of fully desorbed material after five absorption/desorption cycles.

Cycling: microstructure-kinetics-thermodynamic connection



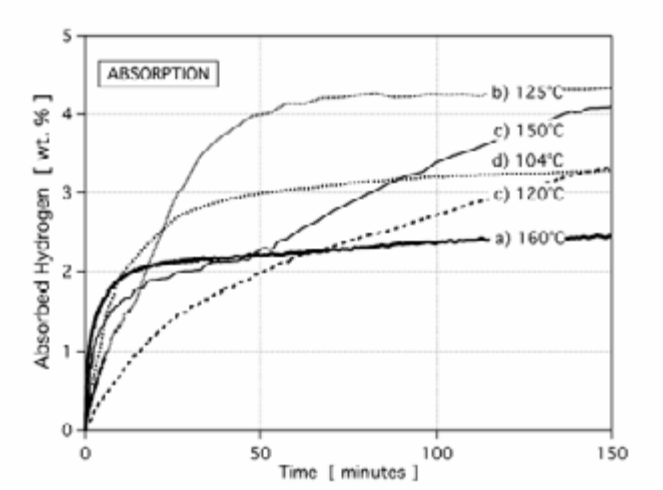




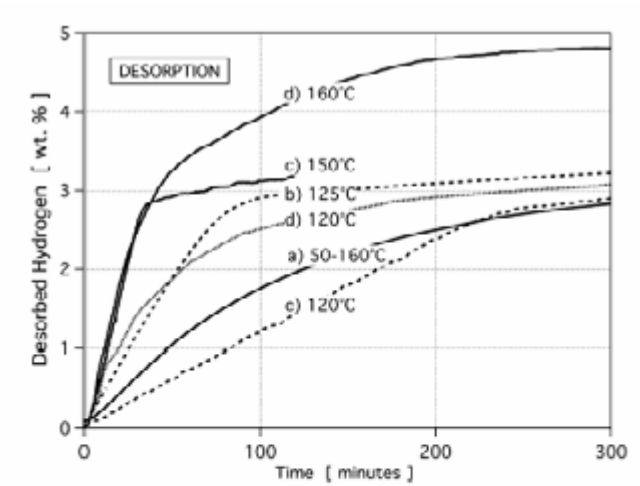
The material morphology is critical in all thermodynamic and kinetic processes that take place during the hydrogen uptake and release. The interaction between the microstructure and these processes is two-way.

Transient response of storage media

Alanates (G. Thomas and co-workers, SNL)



Charging



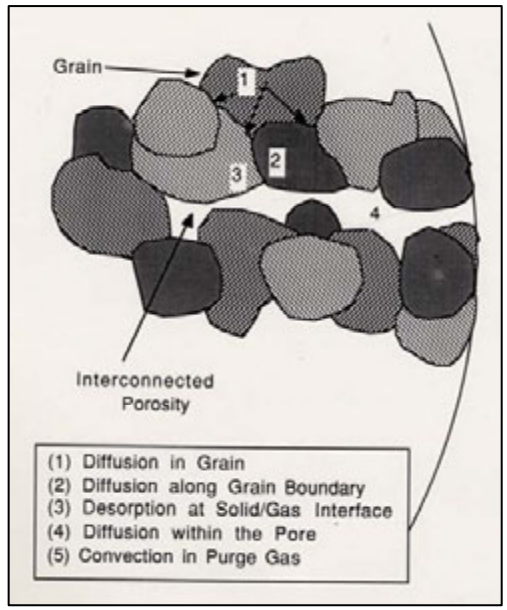
Discharging

Time kinetics curves depend on the microstructure …

Modeling needs

(molecular scale models – QM, MD, MC)

- Surface kinetics (hydrogen)
  - Individual surface reactions, as function of coverage
  - Variability of surface atomic structure and composition
  - Surface diffusion
  - Dissolution into the bulk
- Grain boundary/interface kinetics (hydrogen)
  - Do these provide alternative diffusion paths?
- Bulk Kinetics (hydrogen & metal)
  - H diffusion and trapping at defects in various phases (chemical diffusion)
  - Metal diffusion (during phase transitions)



Modeling needs (cont.)

(molecular, meso-scale models)

- Effect of lattice strain on kinetics
  - Adsorption, desorption, and dissolution kinetics
  - Bulk diffusion
  - GB diffusion

(Mesoscale)

- Microstructure evolution
  - Nucleation, growth, coarsening processes
  - Spinodal-like decomposition and composition flucutations
  - Grain boundary mobility
  - Interface mobility
  - Coupling with mechanical fields

Modeling needs (cont.)

- Mechanics (meso-continuum scale modeling)
  - Free volume changes is a big issue – large strains
  - Constitutive response of both parent and forming phases (elastic and yielding characteristics)
  - Fracture mechanisms, void nucleation
- Thermodynamics
  - Free energy of various phases as function of composition
  - Energy of grain boundaries and interfaces

Literature on microstructure evolution (not much)

- Two papers on phase field models to study phase changes in Zr-H system (Chen, Penn State) in the context of mechanical response of Zr alloys
- One paper on hysteresis in Pd-H system (Krenn, LLNL) directly related to metal hydrides
- Scattered attempts by Japanese authors at modeling diffusion using simple homogenization methods

Initial microstructure modeling effort at FSU

- Develop models to understand the coupling between kinetics, thermodynamics, mechanics, and microstructure during hydrogenation and dehydrogenation of solid storage media.

- Establish high performance computational capability to simulate the kinetic processes and microstructure changes in these media.

  - Large free volume change → Lagrangian Phase Field (LPF) approach.
  - Implicit integration schemes, front tracking schemes
  - Galerkin-LS FEM, high-order discretization methods.
  - Full coupling with finite deformation mechanics.
  - MD modeling of kinetic processes.

- Collaborate with molecular modelers and experimentalists.

Summary

- Hydrogen storage brings about challenging **microstructure science** problems that are intimately connected with the kinetic and thermodynamic response of the storage media.
- There is a lack of theoretical/computational modeling capability in this area.
- The development of these microstructure evolution modeling capabilities will fill the gap between the molecular level models and the experiments. It will also allow the comparison between materials using criteria beyond the crystal structure and free energy of compound formation.
- These capabilities are also vital to the development of engineering design and performance evaluation codes.