Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials

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Overview

• **Timeline**
  – Project Start Date: January 2005
  – Project End Date: 2/28/2010
  – Percent Completion: ~25%

• **Budget**
  – Total Project Funding: $997,921
    • DOE Share: $778,828
    • Contractor Share: $199,093
  – Funding Received FY05: $150,000/$37,500
  – Funding Received FY06: $150,000/$37,500

• **Barriers Addressed**
  – **B**: Weight and Volume
  – **M**: Hydrogen Capacity and Reversibility
  – **N**: Lack of Understanding of Hydrogen Physisorption and Chemisorption.

• **Partners**
  – HRL Laboratories: collaborations about new material systems and complex/destabilized hydride system development
  – University of Pittsburgh: collaborated to obtain interfacial energies for Mg/MgH₂ interface
Objectives

• **Perform In-Situ Structural Studies of Hydrogen Storage Materials**
  – Utilize high brightness x-ray source at Stanford Synchrotron Radiation Laboratory
  – Construct Sieverts apparatus for in-situ control of hydrogen content
  – Demonstrate feasibility of in-situ synchrotron studies

• **Investigate Light Metal Hydride Model Material Systems**
  – Use designed thin film model systems to investigate phase change and catalytic processes associated with hydrogen cycling

• **Develop Kinetic Model of Nanoparticle Phase Transformations**
  – Build continuum models of nanoparticle kinetics to illuminate mechanisms of hydride formation in nanoscale materials
Approach

• **In-Situ Structural Studies**
  – Real time structural analysis using high brightness synchrotron radiation
  – in-situ hydrogen charging of candidate materials
  – Correlate structural changes with hydrogen charging characteristics

• **Model Material System Design and Synthesis**
  – Design and grow model material systems using physical vapor deposition techniques such as sputtering

• **Kinetic Modeling of Nanoparticle Transformations**
  – Model kinetic processes of phase transformations in nanoparticles to guide future material selection and design
Kinetic Studies Using XRD

- Hot stage attachment on diffractometer allows hydride content to be monitored during sample discharge
  - Comparison of integrated intensities for Mg and MgH₂ yields fraction of film reacted

- Initial studies at Stanford Synchrotron Radiation Laboratory (SSRL) showed promise of XRD technique
  - Mg peaks intensify while MgH₂ peaks disappear as sample is discharged

- Further applications using in-house XRD equipment brought more quantitative kinetic data

- Utilizing hotstage on in-house XRD we obtained detailed kinetic information for several thin film samples
  - Plot integrated intensity for Mg(002) and MgH₂(110) peaks vs. time
Mg$_2$Si System

- **Initial attempts at hydriding monolithic Mg$_2$Si films were unsuccessful**
  - Even at high (~200 bar) pressures and long (~48 hr) times using HRL’s facilities
  - No MgH$_2$ phase seen in XRD data

- **Questions:**
  - Is the hydrogen diffusing through the Mg$_2$Si?
  - Is there a problem with nucleation of the hydride phase in the Mg$_2$Si?
  - Are the distances for the Si or Mg to diffuse in the structure to form the MgH$_2$ phase to large?
  - Is the Mg$_2$Si compound too stable for the reaction to proceed at an appreciable rate?

- **Designed and deposited wide variety of multilayered structures to examine problems being encountered**
  - Structures contained layers of Mg, Mg$_2$Si, and Pd in various configurations
Mg$_2$Si System: Samples

- **Monolithic Mg$_2$Si films with Pd capping layer**
  - Demonstrate ability to deposit alloy samples and attempt to hydride from dehydrided state
  - Unable to hydride samples (200 bar H$_2$ for 48 hr)

- **Non-stoichiometric monolithic Mg$_2$Si film with Pd capping layer**
  - Deposited with excess Mg at ~Mg$_{2.8}$Si
  - Attempt to nucleate hydride formation with excess Mg

- **Attempted same geometry with Ge additions**
  - No silicide decomposition

- **After hydriding at 200 bar H$_2$ for 48 hr**
  - Complete transformation of Mg$_2$Si into MgH$_2$ and Si not observed
Mg$_2$Si System: Samples

- **Catalyst layer sample**
  - Attempt to catalyze formation of MgH$_2$ with layer of Mg on top of Mg$_2$Si layer
  - Mg completely hydrided
  - Mg$_2$Si did not decompose into MgH$_2$ + Si

- **Sensor layer sample**
  - See if H$_2$ is diffusing through the Mg$_2$Si layer
  - Mg layer beneath Mg$_2$Si completely hydrided - H$_2$ diffused through Mg$_2$Si layer
  - Mg$_2$Si did not decompose into MgH$_2$ + Si

- **Other multilayer samples**
  - Thin Mg$_2$Si/Mg and Mg$_2$Si/Pd multilayers deposited to investigate effect of reducing diffusion length for Si in samples
  - Mg$_2$Si did not decompose into MgH$_2$ + Si
Mg\textsubscript{2}Ge/Si Structures

- With little success of Mg\textsubscript{2}Si system, we looked at alloying with Ge
  - Samples with Ge additions have shown increased kinetics over pure MgH\textsubscript{2}.*

- Using co-deposition, we deposited alloy samples of Mg\textsubscript{2}Si/Ge
  - 400 nm Mg\textsubscript{2}Si.75Ge.25 + 25 nm Pd
  - Mg\textsubscript{2}Si.5Ge.5 + 25 nm Pd

- After hydriding at 200 bar H\textsubscript{2} for 48 hr, Mg\textsubscript{2}Si/Ge remained
  - Small amount of MgH\textsubscript{2} seen
  - System still kinetically limited
Epitaxial Mg Films

- We grew Mg epitaxially on Al₂O₃ (001) and MgO (111) for the first time; done at RT and up to 100°C.
  - High-angle x-ray diffraction of as deposited samples indicates Mg grows singly oriented in the (001) orientation, with the c-axis out of plane.
  - High-angle x-ray diffraction after charging indicates MgH₂ forms singly oriented in the (110) orientation.

- From this information we are able to determine the crystallographic orientation between Mg and MgH₂ in the films.
Epitaxial Mg Films

- Phi scans indicate how MgH2 (110) plane lies on the Mg (001) plane

- With the high angle scans, they show MgH2 (110) [001] // Mg (001)[100]

- Observed solid phase epitaxial (SPE) regrowth of Mg during dehydriding process
  - Mg grew back in original orientation
  - Evidenced by comparing scans (a)-before hydriding vs. (c)-after dehydriding
Epitaxial Mg Films

- **Solid Phase Epitaxial (SPE) regrowth**
  - Growth of solid phase occurs at interface between original material and transformed material, not in transformed material or at another interface.
  - Crystal quality of regrown material will match that of original material, not that of transformed material.
    - XRD rocking curves will match.

**SPE Regrowth**
On discharge, Mg regrows epitaxially on the remaining Mg at Mg/MgH$_2$ interface, not at MgH$_2$/Pd interface.

**Non-SPE Regrowth**
Non-epitaxial (less highly oriented) Mg regrows from MgH$_2$/Pd interface.

Mg growth direction
Epitaxial Mg Films

• Films regrew in original Mg orientation upon discharging
  – Verified with XRD Phi scans

• XRD rocking curves show that Mg regrew on existing (untransformed) Mg
  – Strong evidence for SPE regrowth
  – Mg rocking curves returns to original shape after discharging
  – Did not nucleate at MgH$_2$/Pd interface due to broad rocking curves for MgH$_2$
    • Much wider than Mg rocking curves
Catalyst Placement

• **Investigate effect of bulk vs. surface catalyst placement**
  - Ti catalyst has shown good results with NaAlH4, try with Mg as initial system
  - Compare kinetics to Mg films without Ti catalyst

• **Reference sample**
  - 400 nm Mg film with 25 nm Pd capping layer on Si wafer substrate
  - Discharged over ~12 hrs at 82°C on XRD hotstage
  - Kinetics similar to samples used to establish technique

• **Surface catalyst:**
  - Thin layer of Ti (corresponds to ~5 wt. % Ti in Mg) deposited between Mg and Pd

• **Bulk catalyst:**
  - Same mass of Ti from above co-deposited with Mg
  - Deposited as solid solution mostly
Hydrogenation of Mg nanoparticles

- Equilibrium pressure altered by interface terms:

\[ P_{H_2}^{eq} = \exp \left[ \frac{\Delta G^o}{RT} + \frac{2\Delta \gamma V_M^{Mg}}{r_{Mg}RT} \right] \]

- Bond counting estimate for surface energy difference:

\[ \Delta \gamma = 1.74 \text{ J/m}^2 \]

- First principles calculation gives 1.86 J/m2, Karl Johnson and Bing Dai, private communication, 2005.

- Particles with d~4 nm have attractive Peq
Thermodynamic Modeling

- Extended solid solubility of H in Mg Nanoparticles
  - Interface cost drives up the energy of two-phase configuration

Two phase nanoparticle

- Extended solid solubility of H in Mg Nanoparticles
  - Interface cost drives up the energy of two-phase configuration

Energy of two-phase system above that of supersaturated solution!

\[ g = \gamma(N/m)/r(nm) \]


- Size changes the phase diagram!
  - Predicted supersaturation is 3 orders of magnitude above bulk

\[ \gamma = 1.46 \text{ J/m}^2 \]

(Dai, Johnson)
Transformation occurs as interface sweeps through particle

- For \( r < 3r^* \) nucleation is easier than in bulk!

**Nanoparticle Nucleation**
- Nucleation of second phase has interface energy cost

**Easier nucleation means lower driving forces needed for phase transitions**

**Nanoparticles have:**
- Dramatically different thermodynamics and phase stability
- Faster reaction kinetics
- Easier nucleation
- No “growth” phase
Future Work

- **Construct pressure vessel for use with XRD facilities to enable in-situ sample charging**
  - Extract kinetic data for sample charging
  - Observe structural changes related to hydriding and correlate with kinetics of samples

- **Continue investigation of additional material systems**
  - MgB and MgAl systems
  - Li-based systems
  - Go/No-Go decision point on Mg$_2$Si system

- **Continue investigation into kinetics of thin film phase transitions and role of catalyst placement in those transitions**
  - Mg system and others

- **Investigate nanoparticle systems as well as thin films using established techniques**
Responses to Previous Year Reviewers’ Comments

• Not applicable as we did not have a “Review” last year since it was our first year on the project
Publications and Presentations

• Presentations:


Critical Assumptions and Issues

- **Unable to observe hydriding directly with XRD using current equipment**
  - Developing new *in-situ* hydrogen charging chamber for use on XRD equipment

- **Assuming thin film materials absorbing at optimal storage capacity**
  - May be absorbing more/less hydrogen than bulk systems
  - Verify hydrogen content using quantitative methods
    - Sieverts, TGA, etc.

- **Have not directly observed phase transformation kinetics inferred from XRD studies**
  - Working on directly observing hydride distribution in thin film samples using other methods (SEM, TEM, SIMS, etc.)
Summary

• Developed method to measure extent of hydride decomposition and structural changes during desorption using XRD
  – Allows measurement of system kinetics during desorption

• Attempted to hydride Mg$_2$Si directly using variety of thin film systems and configurations
  – Unable to obtain segregated hydride system after H$_2$ exposure

• Grew epitaxial Mg films on Al$_2$O$_3$(001) and MgO(111) for the first time
  – Determined crystal orientation relationship between Mg and MgH$_2$ to be MgH$_2$ (110) [001] // Mg (001)[100]
  – See strong evidence for solid phase epitaxial (SPE) regrowth of Mg during desorption of films not completely hydried

• Began study of effect of catalyst placement (surface vs. bulk) on hydride formation and decomposition kinetics

• Continued efforts modeling the thermodynamics of nanoscale metal hydride material systems
  – Predicted extended solubility of H in Mg and possibility of altered phase transformation kinetics