IV.A.1b Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials

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Contract Number: DE-FC36-05GO15061
Project Start Date: January 1, 2005
Project End Date: February 28, 2010

Objectives

Develop fundamental understanding of metal hydride reaction kinetics:

- Kinetics limit practicality and reversibility of many promising metal hydride material systems:
  - Mg, MgSi, Li4Si, NaAlH4, LiBH4+MgH2, etc.
  - Initial work on MgSi showed that kinetic issues prevent system from achieving reversibility.

- Catalyst additions have shown some success in improving kinetics for some systems (i.e. Ti in NaAlH4), but little is known about the nature of these effects.

- Little is known about the kinetic mechanisms present in these systems, and in order to improve the kinetics for any of these metal hydride systems a sound understanding must be developed.

Develop understanding of metal hydride nanostructure thermodynamics:

- Many systems suffer from inappropriate thermodynamics (equilibrium pressure):
  - Mg, Al

- Continuum modeling suggests that reaction thermodynamics should be modified by reducing particle size to the nanometer regime.

- Develop understanding of metal hydride structures during phase change:
  - Material structure can play important role in reaction kinetics, especially during solid state phase transformations such as those in metal hydride reactions.
  - Understanding the interplay between material structure and reaction kinetics may provide insight on how to successfully engineer new materials with improved kinetics and storage properties.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(D) Durability/Operability
(E) Charging/Discharging Rates
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

Our project conducts fundamental research of metal hydride storage material reaction kinetics and thermodynamics, examining the effects of material structure and particle size on each using thin films and vapor deposition techniques to probe the effects in a controlled and quantitative manner. The research addresses the following DOE 2010 hydrogen storage technical targets:

- Gravimetric Capacity: 0.045 kg H2/kg
- Min/Max Delivery Temperature: -40/85°C
- System Fill Time: 4.2 min
- Minimum Full Flow Rate: 0.02 (g/s)/kW

Accomplishments

- Reaction depth into MgSi <1 nm, making system impractical for reversible storage.
The mechanism and kinetics of the metal/metal hydride transformation in metal hydride hydrogen storage materials plays a crucial role in determining whether a material meets the DOE on-board storage targets for 2010 and 2015. A fundamental understanding of these issues provides valuable insight into the ways in which various material systems can be engineered in order to meet specific material targets. Additionally, as the ability to engineer materials on the nano-scale emerges, new routes to tailoring specific material properties become possible. Specifically, by reducing the dimensions of metal hydride storage materials you can alter properties such as the hydrogen vapor pressure and storage capacity.

We extensively investigated reduced dimension metal hydride material systems and their hydrogen charging and discharging properties. We determined kinetic behavior and transformation mechanisms for magnesium-based thin film material systems using in situ hydriding and dehydriding with detailed XRD to examine the effects of material cycling. We also investigated the effects of reduced dimensionality on destabilized material systems such as Mg-Si. Additionally, we modeled the effects of reducing dimensions of hydrogen storage materials to the nano-scale (i.e. nanoparticles), revealing the possibility of drastically altered hydrogen storage properties in metal hydride nanoparticles, and constructed an analysis chamber to probe the differences in hydrogen storage properties (both thermodynamic and kinetic) between bulk and nanoparticle systems. Furthermore, we investigated kinetic and thermodynamic behaviors in the Mg/Ti and Mg/Al material systems.

Approach

In order to determine ways to engineer material systems to meet the DOE on-board storage targets for 2010 and 2015 we use a combination of thermodynamic modeling efforts combined with nanoscale material synthesis and various characterization techniques to gain a better understanding of the underlying kinetic mechanisms present in the metal hydride phase transformations. We make extensive use of XRD techniques, using both in-house facilities and facilities at the Stanford Synchrotron Radiation Lightsource, to characterize the structural changes of material systems as they undergo phase changes during hydrogen absorption and desorption. We can then correlate this structural information with kinetic data about the absorption and desorption rates to relate the structure of materials to their kinetic behavior. Additionally, we employ the use of a QCM apparatus to quantify the hydrogen uptake in extremely small sample sizes, allowing us to determine reaction thermodynamics and kinetics for thin film and nanoparticle samples. Finally, the modeling efforts provide insight on where future experiments should focus and help to explain behaviors seen in experimentally synthesized samples prepared using physical vapor deposition techniques.

Results

Over the last year, we made progress in several areas of our research and we continued utilizing our thin film deposition and analysis capabilities to investigate the fundamental kinetic mechanisms present in metal/metal hydride phase change reactions as well as the effect of particle size on both reaction kinetics and thermodynamics.

In our previous work investigating the reversibility of the Mg-Si system, we saw very little evidence for the formation of the hydride phase when starting from Mg-Si and hydrogen. However, when we processed the data from that study we noticed a systematic trend in the XRD data relating the amount of Mg-Si material remaining to the thickness of the original Mg-Si layer in multilayer films containing alternating layers of Mg and Mg-Si. If we assume the hydriding reaction proceeds from the edge of the Mg-Si layer inwards from both sides, then we can relate the fraction of Mg-Si material remaining after hydrogenation, f, to the reaction depth, d, through the equation f = 1 - 2d/l, where l is the initial Mg-Si layer thickness. Then, through careful XRD measurements of the Mg-Si peak intensities before and after exposure to hydrogen, we can measure the fraction of Mg-Si remaining and plot it versus the inverse layer thickness. Then, by fitting a line to the data we can extract d, the reaction depth into the Mg-Si layer. Figure 1 shows the data from our experiment along with a linear fit constrained to go through 1 for...
Building on the success of the experiments on the Mg$_2$Si system, we applied our thin film platform approach to the Mg/Al system. This system exhibits similar kinetic problems to Mg$_2$Si where the hydride phase (Mg(AlH)$_x$) fails to form from the constituent phases MgH$_2$, Al and H$_2$. In order to investigate this, we deposited several multilayer samples containing alternating Mg and Al layers with Pd capping layers, varying the Al layer thickness in each film. The multilayer films deposited as superlattices due to similarities in the lattice parameters for Mg and Al. However, XRD analysis shows evidence for layer intermixing between the Mg and Al at room temperature over the course of a few days. After exposure to 1 bar H$_2$ gas at 110°C for 10-20 hours, some XRD spectra showed no change relative to immediately before the anneal while others showed evidence for intermetallic phase formation, such as Mg$_x$Al$_{2-x}$. This experiment reveals that the films do not readily react with hydrogen as none of the films showed evidence for MgH$_2$ formation. The films seem to form Mg/Al alloy phases and these intermetallic phases, or the Al itself seem to block the hydrogen from entering the structure or they simply do not form a hydride phase. In order to determine the origin of these finding, we plan to study additional film structures where an Al layer of varying thickness lies between a single Mg layer and the Pd capping layer. These films will help determine the ability of hydrogen to diffuse through the film structure. The preliminary experiments seem to indicate that, in this system, hydrogen diffuses slowly while the host atoms diffuse fairly easily within each other, leading to alloy formation without evidence for any hydride phase formation.

We also made significant progress in our ongoing effort to develop a detailed model of the kinetic processes present in metal hydride phase transitions by utilizing highly controlled epitaxial Mg thin films. Our previous results showed strong evidence for hydride phase formation by a moving planar interface growth mechanism similar to the growth of an oxide layer on silicon first outlined by Deal and Grove [1]. However, this model applies only to semi-infinite slabs of Mg where the hydride layer may continue to grow forever. To accommodate our thin film samples, we modified this model by implementing a cutoff where the derivative of the interface position decreases linearly to zero over a width in time that corresponds to when the leading and trailing edges of the interface (due to roughness) reach the substrate. The in situ XRD data in Figure 2 shows integrated intensity versus time for the Mg(002) peak of 2,000 Å, 4,000 Å and 8,000 Å thick epitaxial Mg films grown on (001) Al$_2$O$_3$ with 250 Å thick Pd capping layers. The solid lines in Figure 2 represent fits to the function obtained from the diffusional model containing the cutoff described above to accommodate the finite thickness of the films. The good agreement between the data and model functions provides strong evidence for hydride formation without evidence for any hydride phase formation.

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that, to retain the faster linear reaction rates, material structures should have critical dimensions less than 120 nm (twice 60 nm). It also provides motivation for future studies to provide more details about the kinetic mechanisms present in the metal/hydride phase transition in this technologically important material.

We made progress using our QCM hydrogen chamber to analyze several different metal hydride materials. Our previous work using continuum modeling to analyze the effect of reduced dimensionality on metal hydride thermodynamics indicated an increase in the equilibrium pressure for magnesium particles with critical dimensions below ~10 nm. To investigate this we examined a thin film sample consisting of alternating layers of Mg and Pd, looking for equilibrium pressure in the QCM chamber by watching for the pressure where mass uptake ceased as we stepped from above the equilibrium pressure to successively lower pressures. As shown in Figure 4, the equilibrium pressure for a 400 nm thick Mg film matches well with that reported in the literature for thicker Mg films. A multilayer film with alternating 5 nm thick Mg layers and 10 nm Pd layers shows a preliminary equilibrium pressure measurement consistent with the measurements from the thicker film, indicating that the size effect predicted is much smaller in reality, or is significantly modified by the presence of the Pd layers. However, the measurement demonstrates the sensitivity of the QCM chamber technique. In another sample consisting of 400 nm of Mg + 10 wt% Ti deposited as a metastable solid solution capped with 25 nm of Pd on a QCM crystal we observe an equilibrium pressure increase of ~10x compared to thicker Mg films, as shown in Figure 4. The extracted enthalpy of reaction according to our data (-55 kJ/mol) matches well with calculated values from literature (-52 kJ/mol) and our equilibrium pressure measurements match well with other literature reports for similar systems.

Finally, we continued our collaboration with the team at NIST to examine the microstructural development of epitaxial Mg films when exposed to hydrogen using neutron reflectivity. We are set to perform in situ reflectivity experiments on a monolithic 1000 Å Mg film grown on (001) oriented Al₂O₃ and capped with 250 Å Pd. By taking measurements at different stages of hydrogenation and dehydrogenation we can track the motion of the Mg/MgH₂ interface and...
Conclusions and Future Directions

Conclusions

- Reaction depth into Mg\(_2\)Si <1 nm, making system impractical for reversible storage.
- Hydride growth kinetic experiments support moving planar interface model, <60 nm of reaction controlled growth from data – anything thicker suffers from diffusion limited growth (slower).
- QCM chamber able to detect \(P_{\text{eq}}\) in very thin Mg layers, no size vs \(P_{\text{eq}}\) dependence seen yet.
- Addition of 5% Ti in Mg gives ~10x increase in \(P_{\text{eq}}\), verification needed with further study.
- Mg/Al kinetic study underway using multilayer film/XRD approach successfully used with Mg\(_2\)Si.
- Neutron reflectivity with NIST underway to measure reaction depth and microstructure in epitaxial Mg films.

Future Directions

- Continue data collection and analysis with QCM chamber:
  - Find and exploit the limits of hydrogen uptake sensitivity for the instrument.
  - Attempt to confirm theoretical predictions about the change in equilibrium pressure as particle size is reduced.
  - Examine kinetics and thermodynamics for thin film and nanoparticle samples.
- Finish Mg/Al study:
  - New film architectures.
  - Higher pressure \(H_2\) anneals.
  - Faster turnaround to prevent intermixing.
- Finalize nanoscale Mg study:
  - Thinner Mg layers on QCM.
  - Careful measurements on existing samples.
- Further develop MgH\(_2\) kinetic model:
  - Develop general model to describe reverse reaction and phase growth with cycling.
- Continue/finalize Mg/Ti study:
  - Examine different Ti concentrations to look for \(P_{\text{eq}}\) differences and trends.
  - Examine cycling behavior of Ti-doped Mg films compared to pure Mg.
- Continue with neutron reflectivity study on Mg/MgH\(_2\) thin films with NIST:
  - Determine more specifics of reaction kinetics.
  - Interface motion/roughness/sharpness/etc.
  - Utilize new in situ hydrogen loading chamber at NIST.
  - Develop new models to describe data and incorporate findings into MgH\(_2\) growth model.

FY 2009 Publications/Presentations


References