

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

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Objectives

Develop fundamental understanding of metal hydride reaction kinetics:

- Kinetics limit practicality and reversibility of many promising metal hydride material systems:
 - Mg, Mg₂Si, Li₄Si, NaAlH₄, LiBH₄+MgH₂, etc.
 - Initial work on Mg₂Si 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 Mg₂Si <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).
- Quartz crystal microbalance (QCM) chamber able to detect P_{eq} in very thin Mg layers, no size vs. P_{eq} dependence seen yet.
- Addition of 5% Ti in Mg gives ~10x increase in P_{eq} , verification needed with further study.
- Mg/Al kinetic study underway using multilayer film/X-ray diffraction (XRD) approach successfully used with Mg_2Si .
- Neutron reflectivity with the National Institute of Standards and Technology (NIST) underway to measure reaction depth and microstructure in epitaxial Mg films.



Introduction

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_2Si . 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 nanoscale 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_2Si system, we saw very little evidence for the formation of the hydride phase when starting from Mg_2Si 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_2Si material remaining to the thickness of the original Mg_2Si layer in multilayer films containing alternating layers of Mg and Mg_2Si . If we assume the hydriding reaction proceeds from the edge of the Mg_2Si layer inwards from both sides, then we can relate the fraction of Mg_2Si material remaining after hydrogenation, f , to the reaction depth, d , through the equation $f = 1 - 2d/l$, where l is the initial Mg_2Si layer thickness. Then, through careful XRD measurements of the Mg_2Si peak intensities before and after exposure to hydrogen, we can measure the fraction of Mg_2Si 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_2Si layer. Figure 1 shows the data from our experiment along with a linear fit constrained to go through 1 for

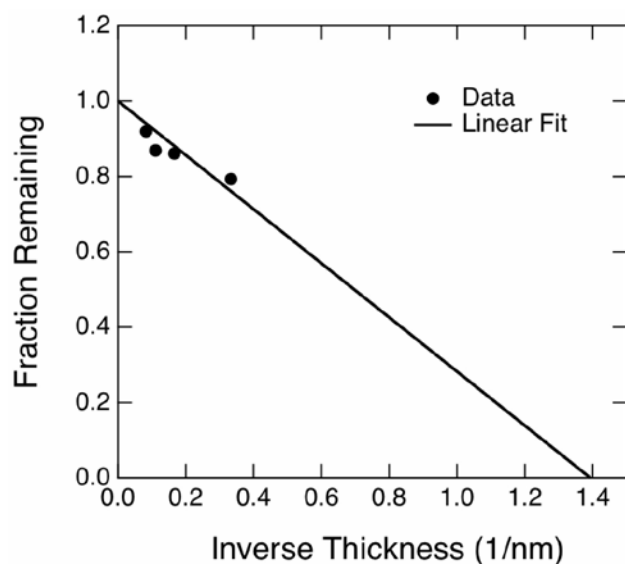


FIGURE 1. $\text{Mg}_2\text{Si}(111)$ XRD peak intensity ratios (after hydrogen annealing/before annealing) vs. reciprocal Mg_2Si layer thickness with a linear fit to the data constrained to go through 1 for infinite layer thickness.

infinitely thick ($1/l = 0$) Mg_2Si layers. The linear fit gives a reaction depth into the Mg_2Si layer of less than 0.5 nm. This means that, in order to achieve total hydrogenation, one would need stable Mg_2Si particle sizes below 1 nm. To put this in perspective, this represents a particle less than two Mg_2Si unit cells across. Particles of this size are extremely difficult to synthesize and rarely show properties concurrent with their bulk counterparts. These results indicate that the Mg_2Si system is not limited by hydrogen diffusion through Mg_2Si or nucleation of the MgH_2 phase, but rather by the transport of Mg and Si during phase segregation into separate MgH_2 and Si phases. In other words, the host atoms diffuse much slower than the hydrogen atoms in this system, leading to limited reversibility. Despite the promising thermodynamics of this system, kinetic limitations prevent it from performing as a practical material on even a modest scale.

Building on the success of the experiments on the Mg_2Si system, we applied our thin film platform approach to the Mg/Al system. This system exhibits similar kinetic problems to Mg_2Si where the hydride phase ($\text{Mg}(\text{AlH}_4)_2$) 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 $\text{Mg}_{17}\text{Al}_{12}$. 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 findings, 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_2O_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 growth through a moving planar interface from the top of the film downward. Figure 3 shows the data for the 4,000 Å and 2,000 Å thick films from Figure 2 plotted on a log-log scale with the data re-scaled to start at the graph origin in order to reveal the different regimes of the reaction. The faster linear regime (reaction limited) for both films is confined to Mg thicknesses below 60 nm. Beyond 60 nm the reaction transitions to the slower $t^{1/2}$ (diffusion limited) regime until the entire film transforms to the hydride phase. Extrapolating the $t^{1/2}$ trend to longer times shows that to transform a 1 μm thick film should take ~50 hours, consistent with literature reports. This analysis indicates

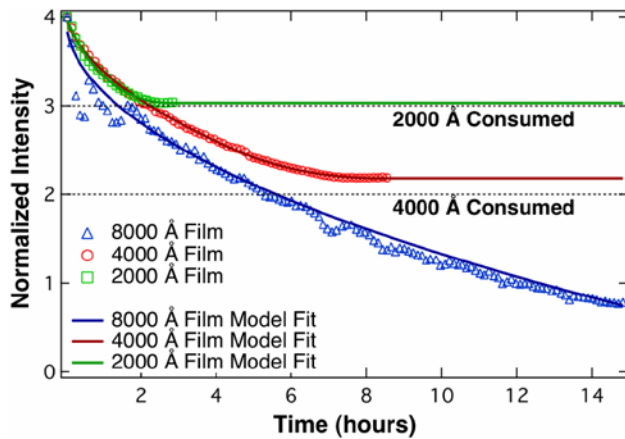


FIGURE 2. Mg(002) peak intensities vs. time for 2,000 Å, 4,000 Å and 8,000 Å thick films (symbols) showing good agreement to a fit of the function for moving interface hydride growth developed in this report.

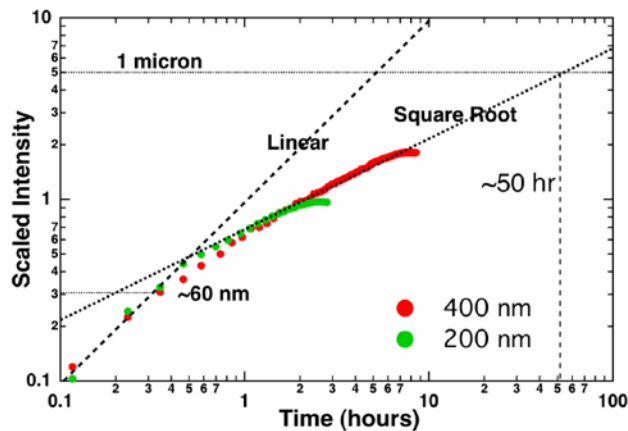


FIGURE 3. Log-log plot of the data for the 2,000 Å and 4,000 Å data shown in Figure 2 renormalized to zero intensity at zero time, showing a transition between the “linear” and “square root” growth regimes at a hydride thickness of ~ 600 Å. The data shows a time to hydride a $1 \mu\text{m}$ film of ~ 50 hours.

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

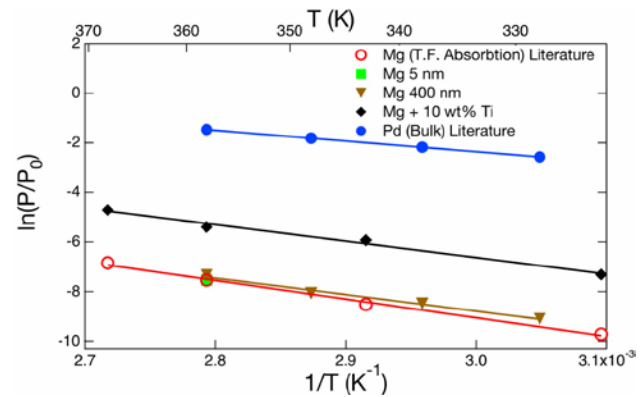


FIGURE 4. van't Hoff plot showing the natural log of the equilibrium pressure vs. reciprocal temperature for several samples measured with the QCM hydrogen pressure chamber. The 400 nm thick Mg film and the 5 nm thick Mg/Pd bilayer films both show equilibrium pressures consistent with bulk Mg. The Mg + 10 wt% Ti film shows equilibrium pressure $\sim 10\times$ that of bulk Mg and the Mg thin film samples.

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 literature² 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 $\sim 10\times$ 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) [3] and our equilibrium pressure measurements match well with other literature reports for similar systems [4,5]. Further work may shed light on the role of Ti concentration level on the equilibrium pressure in this system as well as the kinetic mechanisms present in the transformation.

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 Al_2O_3 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

determine the configuration of the film as the hydride phase forms. Preliminary modeling indicates that we should be able to resolve these features fairly reliably.

Conclusions and Future Directions

Conclusions

- Reaction depth into Mg_2Si <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_{eq} in very thin Mg layers, no size vs P_{eq} dependence seen yet.
- Addition of 5% Ti in Mg gives ~10x increase in P_{eq} , verification needed with further study.
- Mg/Al kinetic study underway using multilayer film/ XRD approach successfully used with Mg_2Si .
- 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_{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

1. “Nanostructured Materials for Hydrogen Storage,” Combined Materials Science and Engineering Physics Departmental Colloquium, Colorado School of Mines, March 2008.
2. “Quantitative quartz crystal microbalance studies of equilibrium pressures in thin film and nanoparticle metal hydrides,” Material Research Society Spring Meeting, San Francisco, CA, March 2008.
3. “Kinetic limitations of the Mg_2Si system for reversible hydrogen storage”, *Nanotechnology* vol. 20 p. 204017.

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5. Vermeulen, *et al.*, *J. Mat. Chem.*, **18** 3680 (2008).