
IV.A.5j Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials

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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 have 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 X-ray diffraction (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.

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 use of epitaxial thin film growth techniques to produce model systems with control over structure and composition. We make extensive use of XRD techniques, using both in-house facilities and facilities at the Stanford Synchrotron Radiation Laboratory (SSRL), 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. 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 (PVD) techniques.

Results

Our early results involving *in situ* XRD of samples while dehydriding made the case to pursue *in situ* hydriding capabilities. By monitoring peak intensities and analyzing peak shapes during the phase change, we can study the reaction kinetics while the films absorb hydrogen. Epitaxial thin films allow us to precisely control material parameters such as composition and microstructure, whereas previous kinetic studies were carried out on highly random bulk ingots, powders and ball-milled samples.

We can model the thin film hydride phase transition with a simple modified Deal-Grove type model where, instead of oxidizing Si, we hydrogenate Mg and obtain a functional form, as shown in Figure 1. Comparing the functional form obtained from analysis of the model to the data from the *in situ* hydriding and dehydriding experiments provides insight into the nature of the

hydride transformation kinetics. Upon comparison of the model form to the experimental data, as shown in Figure 2, we see that the close agreement between model and data indicates strong evidence for a planar interface motion growth mechanism in capped thin film systems instead of a nucleation and growth mechanism.

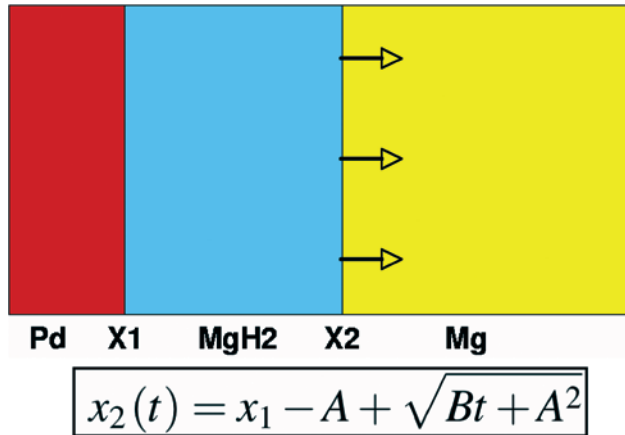


FIGURE 1. Schematic of Modified Deal-Grove Type Model Used to Describe Hydride Growth in Palladium Capped Magnesium Thin Films

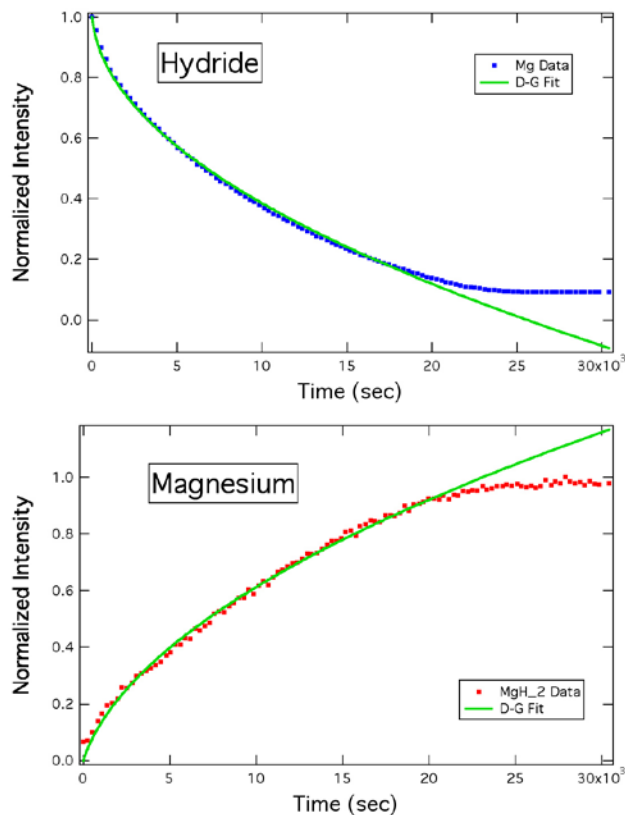


FIGURE 2. Comparison of Modified Deal-Grove Type Model Function (Line) with *In Situ* Hydriding Data for Magnesium and Magnesium Hydride (Squares) for a Palladium Capped Magnesium Thin Film

In addition to epitaxial pure Mg films, we deposited and analyzed epitaxial Mg films with small alloy additions. Analysis of a film deposited with 10 wt% Ti using our *in situ* hydriding capabilities shows substantially enhanced uptake kinetics compared to the pure Mg films, with the Ti-containing film achieving 50% hydrogenation 42% faster than the pure Mg films.

Our previous work also showed interesting results regarding epitaxial film dehydrogenation kinetics: evidence for a solid phase epitaxial (SPE) regrowth mechanism and an epitaxial relationship between Mg and MgH₂. Material stability is of great concern in the DOE long-term goals and we need to understand the kinetic mechanisms present during material cycling in order to successfully engineer a material to withstand repeated cycling under normal operating conditions. In our experiment, we exposed identical samples of 400 nm epitaxial Mg with a 25 nm Pd capping layer on (001) Al₂O₃ substrates to different charging conditions and two charge/discharge cycles to examine the effect of cycling on material texture and related kinetic mechanisms. The films were examined using XRD during each discharge cycle.

Film #1, charged at 90 psi H₂ and 100°C for 5 hrs to ~87% charged, showed almost complete regrowth of the Mg in the highly textured (002) epitaxial orientation. In contrast, Film #2, charged at 100 psi H₂ and 150°C for 5 hrs to ~98% charged, regrew with less texture than the original film with each successive charging and discharging cycle. The Mg (002) rocking curves of Film #1 and Film #2 are shown in Figure 3 after successive discharge cycles. The broadening of the Mg (002) rocking curve indicates degradation of the film texture and the presence of regrowth mechanisms other than the previously observed solid phase epitaxial regrowth mechanism. Film #2 also discharged significantly more slowly in the second cycle and other orientations of Mg (namely (101) began to show up in the film. Rocking curves for the second cycle of Film #2 are not shown because they became too broad to compare with those of the first cycle.

In addition to our work using XRD to study the kinetics of the Mg/MgH₂ phase transformation, we have begun collaboration with the National Institute for Standards and Technology (NIST) to exploit the sensitivity of neutrons to hydrogen in order to further characterize the kinetics of the Mg/MgH₂ phase change in thin film systems. Using reflectivity measurements, we can track the Mg/MgH₂ interface motion and measure hydrogen concentration depth profiles. We hope to learn:

- How the interface motion depends on charging and discharging conditions, such as temperature and pressure (using specular scans);
- How the nature of the interface (roughness, sharpness, etc.) changes with changing conditions and alloy additions (using off-specular scans); and

- How the nature and motion of the interface affects the phase change kinetics for thin film systems.

Initial measurements show promising results (Figure 4), with a significant change in reflectivity seen due to incorporation of hydrogen into the film.

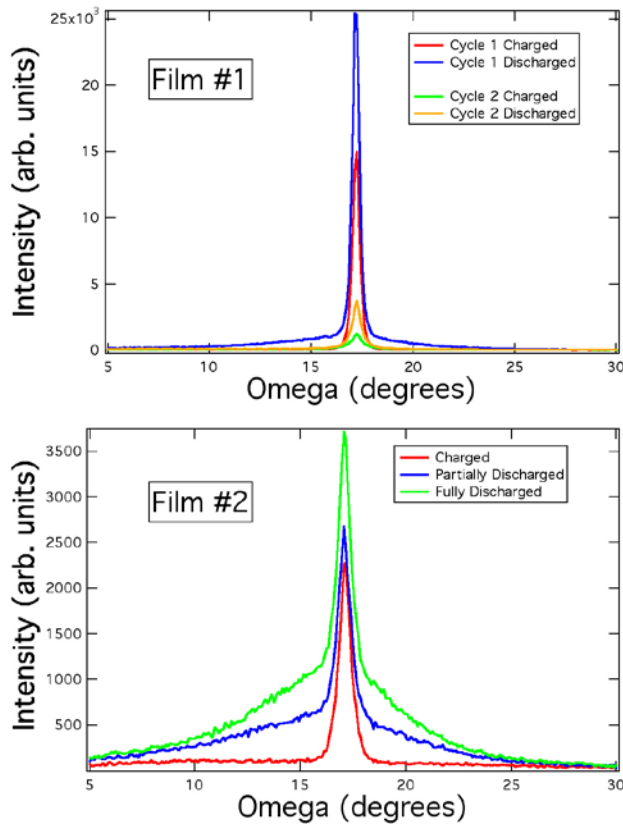


FIGURE 3. Mg (002) Rocking Curve Progressions for Film #1 and Film #2 Showing the Emergence of Less Well Oriented Mg Regrowing in Film #2 and Mostly Solid Phase Epitaxial Regrowth in Film #1

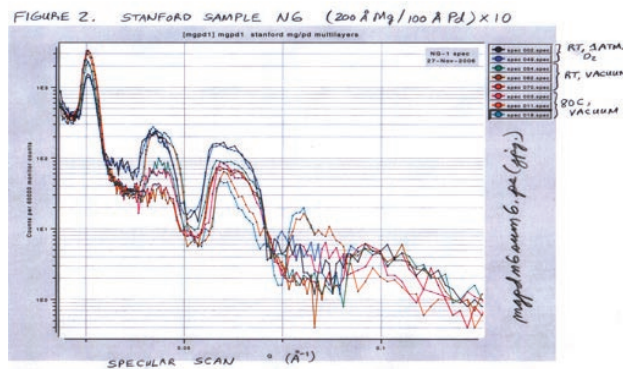


FIGURE 4. Preliminary Neutron Reflectivity Data Showing Changes in Peak Intensities as the Sample, a Multilayer Film Containing 10 Bilayers of 10 nm Palladium and 20 nm Magnesium, is Heated and Hydrogen is Removed

Future experiments will need to implement solutions to substrate and cleanliness issues.

Conclusions and Future Directions

In conclusion, over the last year we have made great progress in understanding the kinetic mechanisms present in the Mg/MgH₂ phase transition using *in situ* XRD of epitaxial thin films of Mg combined with kinetic modeling. Cycling epitaxial Mg films revealed information about the evolution of material texture and reaction kinetics as magnesium is cycled. Finally, we began collaboration with NIST to examine the Mg/MgH₂ interfacial region and hydrogen profile in epitaxial Mg films using neutron reflectivity. In the coming year, we will continue our investigation of the effects of alloy and catalyst additions to model metal hydride thin film systems as well as begin investigating new material systems that are of interest to the center partners. We also plan to intensify our efforts generating and analyzing nanoparticles of metal hydride materials to investigate the effects of particle size on thermodynamic properties such as equilibrium hydrogen vapor pressure.

Conclusions

- Strong evidence for moving planar interface growth and diffusion limited kinetics for epitaxial Mg films seen with use of newly completed *in situ* XRD hydrogen charging chamber.
 - Mg containing systems should be nanostructured to enhance kinetics as growth model indicates diffusion limited growth.
- 42% faster uptake kinetics seen for epitaxial Mg films containing 10 wt% Ti.
 - Theory groups should investigate how addition of catalyst elements such as Ti affect hydride formation transformation kinetics and structure.
- Slower discharge rates seen with loss of texture in epitaxial Mg films. More textural degradation seen in films charged more completely.
 - Attempts should be made to stabilize material texture during transformations (i.e., nanostructuring, alloy additions, etc.) as discharging rates decrease with loss of material texture.
 - Modeling efforts to explain increased textural degradation with faster charging rates and higher conversion fractions could provide insight into ways to avoid degradation effects.
- Collaboration begun with NIST to leverage neutron reflectivity to gain further insight into kinetic mechanisms in thin film systems, particularly information regarding the interfacial region separating the metal and hydride regions of the films.

Future Work

- Continue applying our successful thin film techniques used for Mg, Mg₂Si, and Mg/Ti systems to new material systems of interest to MHCoe partners such as Mg(BH₄)₂, Ca(BH₄)₂, and Mg-Ti-Al alloys.
- Intensify efforts at developing capabilities for *in situ* generation and analysis of metal nanoparticles using physical vapor deposition and a quartz crystal microbalance to measure the hydrogen sorption properties of metal nanoparticles gravimetrically without exposing the sample to oxygen.
- Further collaboration with NIST to explore the characteristics of the Mg/MgH₂ interface in epitaxial thin films.

FY 2007 Publications/Presentations

1. R. Kelekar, H. Giffard, S.T. Kelly and B.M. Clemens, "Formation and Dissociation of MgH₂ in Epitaxial Mg Thin Films," *J. Appl. Phys.*, Vol. 101, p. 114311.
2. Y.W. Lee, B.M. Clemens and K. Gross, "A Novel Seiverts' Type Volumetric Apparatus for Analyzing Hydrogen Storage Properties of Very Small Quantities of Samples," *J. Alloys and Compounds*, (accepted 2006).
3. "A Study of Magnesium Hydride Thin Film Phase Transition Kinetics Using In-Situ Hydriding/Dehydriding," American Physical Society, March meeting, Denver, CO, March 2007.
4. "Magnesium/Magnesium Hydride Thin Film Phase Transition Kinetics and Structure," Stanford Synchrotron Radiation Laboratory 33rd Annual Users Meeting, Menlo Park, CA, October 2006.
5. "Nanostructures for Hydrogen Storage," Technical University of Denmark, Chemistry Department Colloquium, June 2006.
6. "Nanostructures for Hydrogen Storage," Energy Nanotechnology Conference, MIT, June 26-28, 2006.
7. "Nanostructures for Hydrogen Storage," Telluride Workshop on Chemical Modification of Surfaces, August 2006.
8. "Nanostructures for Hydrogen Storage," University of Pennsylvania, Department of Materials Science and Engineering Colloquium, October 12, 2006.
9. "Nanostructured Materials for Hydrogen Storage," American Vacuum Society, Thin Film Users Group, March 7, 2007.
10. "Nanomaterials for Hydrogen Storage," Johns Hopkins University, March 9, 2007.
11. "The Effect of Size on the Thermodynamics and Kinetics of Hydrogen Storage," Lawrence Berkeley-Metal Hydride Center of Excellence Joint Workshop, March 13, 2007.