IV.A.4b Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

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Introduction

Traditional metal hydrides have been well studied over the last several decades but these systems fall short of the gravimetric density requirements of the transportation sector. The light metal hydrides that can meet appropriate densities will be required to work within a suitable thermodynamic range. Unfortunately, many simple hydrides have heats of reaction that are too high. Hydride destabilization, in which thermodynamically impractical hydrides can be made useable, defines appropriate candidate reactants that are capable of meeting the temperature/pressure requirements of engineering interest.

Even in simple model hydride destabilized systems however, kinetic limitations at engineering operating temperature ranges presents problems. Mg_2Si is an example of a system that should undergo both dehydrogenation and hydrogenation on the basis of thermodynamic properties. Because the system does not appear to hydrogenate, we have been investigating the role that reactant particle size plays in hydrogenation and in our efforts to overcome kinetic barriers in otherwise thermodynamically tractable systems.

Approach

We are using a variation of the gas condensation technique in order to synthesize hydride and hydride precursors at size scales that are at least an order of magnitude smaller than can be achieved by mechanical attrition or ball-milling, the latter which typically produces particles on the micron size scale and which is the typically employed method for attrition/mixing. We have also been using the techniques of transmission electron microscopy (TEM) to characterize size and elemental distributions of mechanically mixed samples.

Results

We have encountered some difficulties with disproportionation in the direct synthesis of the Mg_2Si alloy. We have, consequently been studying the synthesis of precursors. The upper left TEM of Figure 1 shows Si

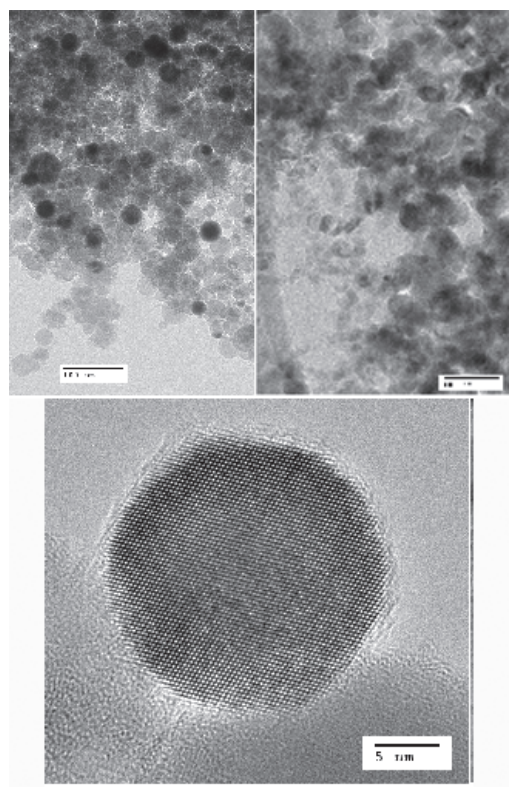

FIGURE 1. Upper left figure is from a gas-condensed run in Ar forming gas. Bottom high resolution TEM image is from the same run and shows a high degree of crystallinity in spite of the fact that a 10% hydrogen mixed is used, and which presumably minimizes the extent of oxide formation in the short run. Upper right image is from a commercial product that was sold as having a 5 nm sized distribution. Size bar is 100 nm in that image.

particle size distributions obtained using an Ar forming gas. Individual particles are resolved throughout the structure and no evidence of grain boundary necking is apparent. The central high-resolution image shows a typical nanoparticle that retains high crystallinity during synthesis in forming gas. The lower right image shows a commercial Si product that was obtained as a 5 nm size material. Size and size distributions are larger than 5 nm in the commercial material. We are still synthesizing and evaluating this material, but have at least overcome some of our earlier issues related to poor yields in our initial runs.

We have also been working with partner lab, HRL Laboratories, in trying to understand the basis for improved kinetics in "dilution" milled material. Figure 2 shows a 5 hr milled "stoichiometric" $2MgH_2$ + Si sample synthesized at HRL that shows that in spite of the long milling/mixing time employed, that the microstructure that is still very heterogeneous. The particles on the left hand side of this agglomerate show MgH_2 particles at the top and bottom with a Si particle in the middle. These particles are still separated by ~0.5 micron length scale, implying that solid state diffusion will have to occur over length scales that impose severe kinetic impediments.

In Figure 3 we show the same agglomerate (inverted 180° vertically) along a scanning transmission electron microscope (STEM) image with x-ray maps that show the heterogeneity of the Si distribution (center bottom image). So in spite of the long milling time that is meant to result in comminuted and mixed material in order to reduce diffusion path lengths, this has not occurred.

An agglomerate of the "dilution" milled sample, where the stoichiometry of the Si is 10x greater than the "stoichiometric," sample is shown in Figure 4 and the elemental maps of Si (lower left) and Mg (upper right) show a high degree of uniformity of elemental distribution. While this stoichiometry is inappropriate for applications, the results do indicate that by forcing

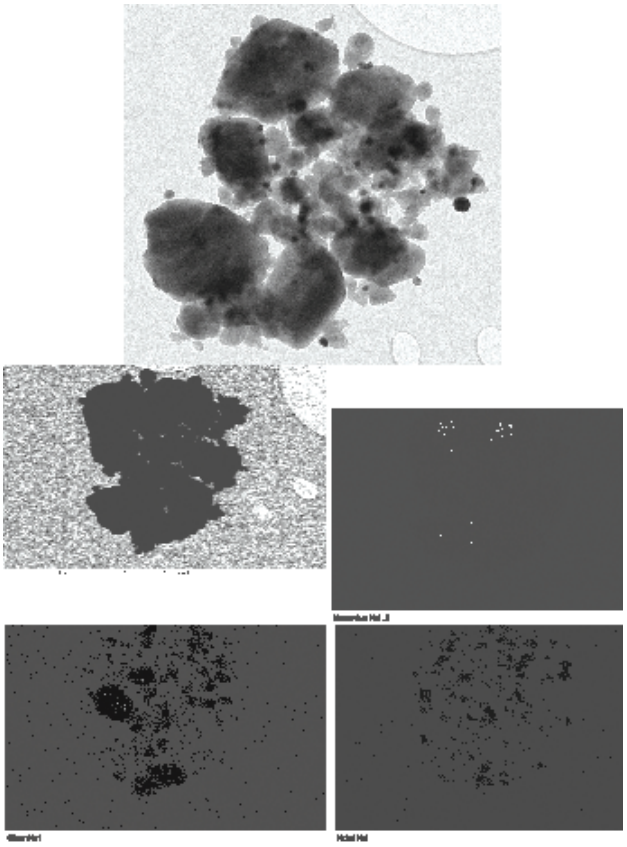

FIGURE 3. At the top is a vertically inverted image from Figure 2. A STEM image is shown in the middle left with a Mg map in the middle right. The lower left image shows the Si distribution and Ni catalyst map is shown in the lower right.

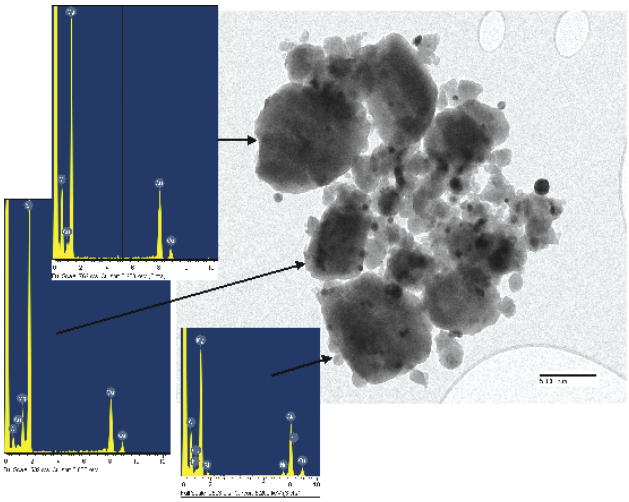

FIGURE 2. An agglomerate of MgH_2 mixed with Si after 5 hrs of milling time. The x-ray fluorescence plots on the left show regions that are dominated by either Mg or Si.

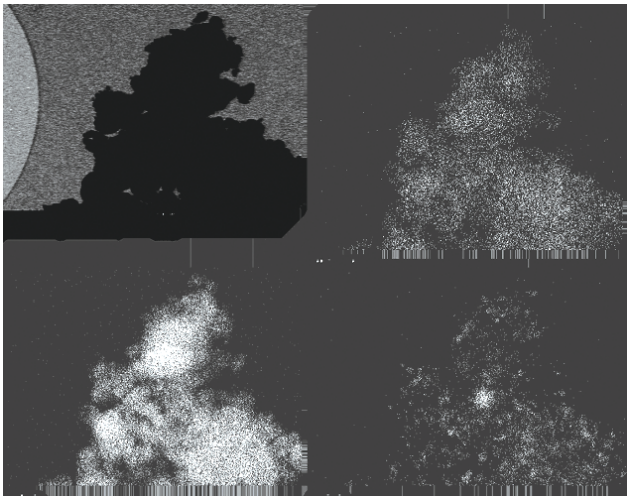

FIGURE 4. Data from a "dilution" milled agglomerate. Upper left image is a STEM image. Upper right shows the Mg distribution, Si distribution is shown in the lower left and Ni catalyst is shown in the lower right.

the MgH_2 reactant to be in closer spatial contact with the Si reactant, kinetics, at least for dehydrogenation, can be improved and made consistent with what we know from van't Hoff plot data.

Dark Field imaging shows that the Mg particles are on also reduced from a size scale that reaches 500 nm, to one where 10 nm particles that surround the Si is more typical, explaining the markedly improved kinetics of the dilution milled sample that was shown by Greg Olson of HRL Laboratories at the FY 2006 Program review.

Conclusions and Future Directions

Mg_2Si has been a difficult system to work with. Only one report from Michel Latroche in France suggests that this system can be rehydrogenated. Presumably, the Si-Mg covalent bonds make the reformation of MgH_2 difficult. We plan to continue working with this system over the next several months but have been looking at another system suggested by Karl Johnson of Pitt, based on $Ca(AlH_4)_2$, as a reactant with $LiBH_4$. This reaction has a low reaction heat and our initial nuclear magnetic resonance (NMR) results shown in Figure 5 show some success in the synthesis of this material via chemical routes, although we are also working with Jason Graetz of Brookhaven in attempting direct synthesis via mechanical mixing using his AlH_3 material as a precursor. On its own, $Ca(AlH_4)_2$ will be an inadequate system from an engineering standpoint but we anticipate that reactions with other hydrides to offer some promise for applications.

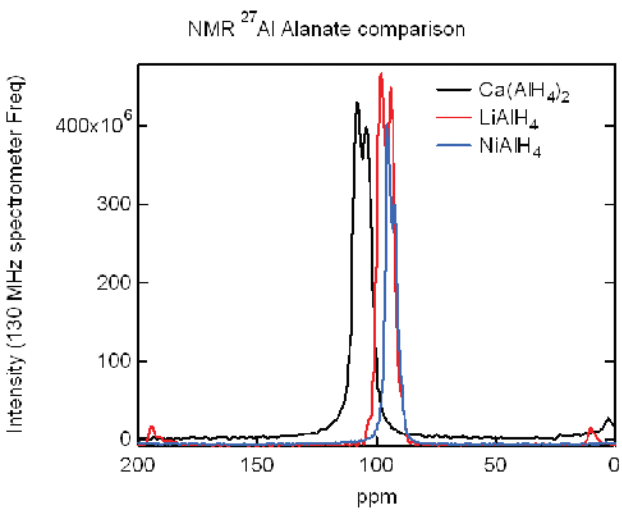

FIGURE 5. The plots above show an NMR data comparison from several alanates of interest. We have had initial success in the synthesis of $Ca(AlH_4)_2$ and will be reacting this material with other hydrides.

FY 2006 Publications/Presentations

1. "NMR and X-ray Diffraction Studies of Phases in the Destabilized LiH-Si System," R. C. Bowman, Jr.(JPL), S.-J. Hwang(Caltech), C. C. Ahn(Caltech), and J. J. Vajo(HRL), Mater. Res. Soc. Symp. Proc. **837** (2005) paper N3.6.1.

2. "Studies of Thermodynamics and Phases Produced in the Destabilized LiH-Si System," R.C. Bowman, Jr. (JPL), S.-J. Hwang(Caltech), C. C. Ahn(Caltech), A. Dailly, J. J. Vajo(HRL), T. J. Udovic(NIST), M. Hartman(NIST), and J. J. Rush(NIST), invited talk at the Nordic Energy Research Meeting, Krusenberg, Sweden, 17-18 June 2005.

3. "Neutron Scattering Investigations of a Destabilized LiH:Si System for Hydrogen Storage Applications," M. R. Hartman(NIST), T. J. Udovic(NIST), J. J. Rush(NIST), R. C. Bowman, Jr. (JPL), J. J. Vajo(HRL), and C. C. Ahn(Caltech), 2005 Fall MRS Meeting, Boston, MA, December, 2005.

4. "Reversibility and Phase Compositions of Destabilized Hydrides Formed from LiH," **R. C. Bowman, Jr. (JPL), S-J. Hwang(Caltech), C. C. Ahn(Caltech), A. Dailly, M. R.** Hartman(NIST), T. J. Udovic(NIST), J. J. Rush(NIST), and J. J. Vajo(HRL) (NIST), invited presentation at the Spring 2006 MRS Meeting, 17-20 April, 2006.

5. "Neutron Scattering Investigations of a Destabilized LiH:Si System for Hydrogen Storage Applications," M. R. Hartman(NIST), T. J. Udovic(NIST), J. J. Rush(NIST), R. C. Bowman, Jr. (JPL), J. J. Vajo(HRL), and C. C. Ahn(Caltech), presented at the Spring 2006 MRS Meeting, 17-20 April, 2006.