Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

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California Institute of Technology
with Metal Hydride Center of Excellence

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This presentation does not contain any proprietary or confidential information

Project ID # STP 8

Overview

Timeline

- Project start date: October 1, 2004
- Project end date: September 30, 2009

On board hydrogen storage Barriers and Targets

(B) Weight and volume of on board hydrogen storage systems

(M) Reversibility of high capacity solid state storage materials

(N) Kinetics (fueling/refueling times) associated with current solid state storage materials

Budget

- Total project funding
  - DOE share $1.15M (5 yrs)
  - Contractor share $287.5k (5 yrs)
- Funding for FY05
  - DOE share $150k
  - Contractor share $37.5
- Funding for FY06
  - DOE share $250k
  - Contractor share $62.5k

Partners

Interactions/ collaborations:

Jet Propulsion Laboratory (Robert C. Bowman, Jr.)

HRL Laboratories (John Vajo and Greg Olson)

University of Hawaii (Craig Jensen)

Stanford (Bruce Clemens)

Univ. Pittsburgh (J. Karl Johnson)

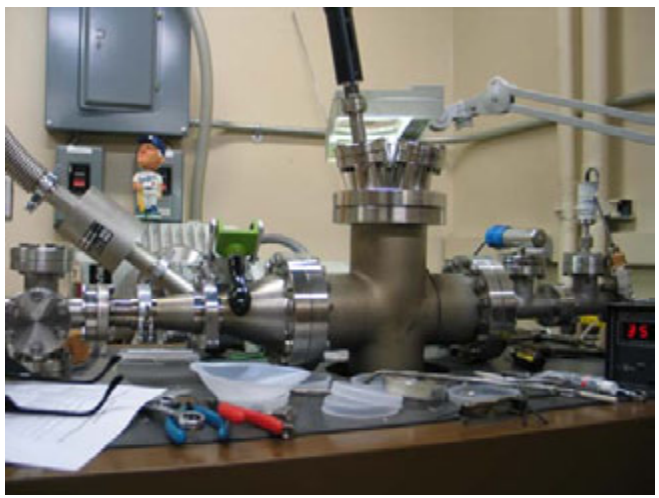
NIST (Terry Udovic)

Objectives

- To understand as to whether thermodynamically tractable reactions based on hydride destabilization, like Mg_2Si+2H_2<-> $2MgH_2+Si$ that should be reversible but appear not to be, are kinetically limited.
- To address short hydrogenation times associated with refueling, that will require short solid-state and gas-solid diffusion path lengths.
- To reduce characteristic length scales typically achieved via mechanical attrition (microns), down to nanoscale lengths necessary for relevant reaction kinetics via gas condensation syntheses.
- To address the problems associated with large, light-metal-hydride enthalpies (hydrogen fueling/refueling temperatures) and develop strategies to address thermodynamic issues surrounding the use of these materials through hydride destabilization.
- To understand issues related to grain growth and surface/interface energies, vital in order to understand the kinetics of hydrogenation/dehydrogenation reactions.
- To follow up on previously studied reactions with phase identification via x-ray diffraction and transmission electron microscopy.

Approach

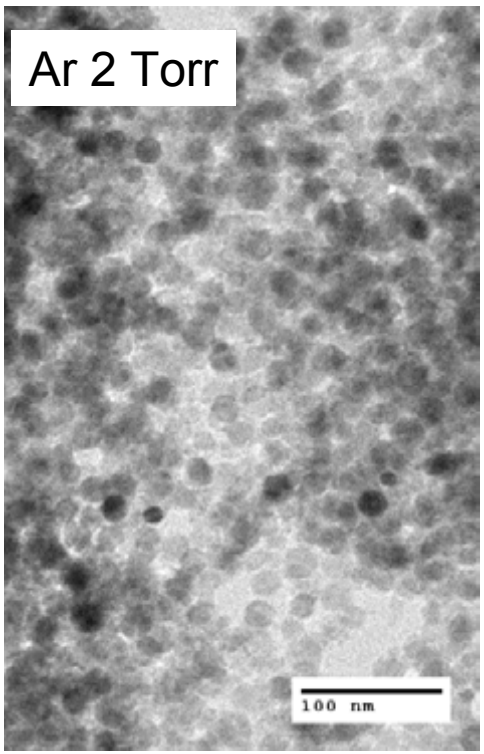
- Gas condensation used to synthesize appropriately sized particles at the nanoscale whereas mechanical attrition or ball milling typically yields micron sized particles (that typically have high contaminant levels).
- Kinetics are expected to go as any typical heterogeneous reaction <u>at least</u> as $1/d^2$ of particle size so hydrogenation/dehydrogenation rates for 100 nm sized particles will be 100 times faster, and 10 nm sized 10,000 times faster kinetics than for micron sized particles.
- Previous work has shown that alloys can also be produced using gas condensation.

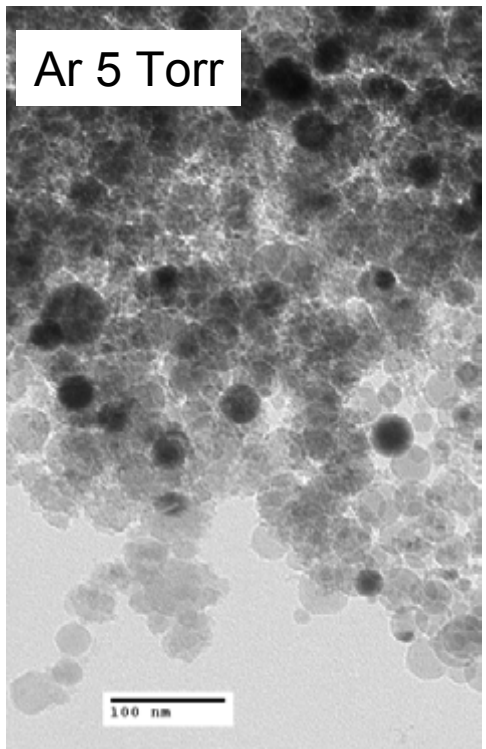


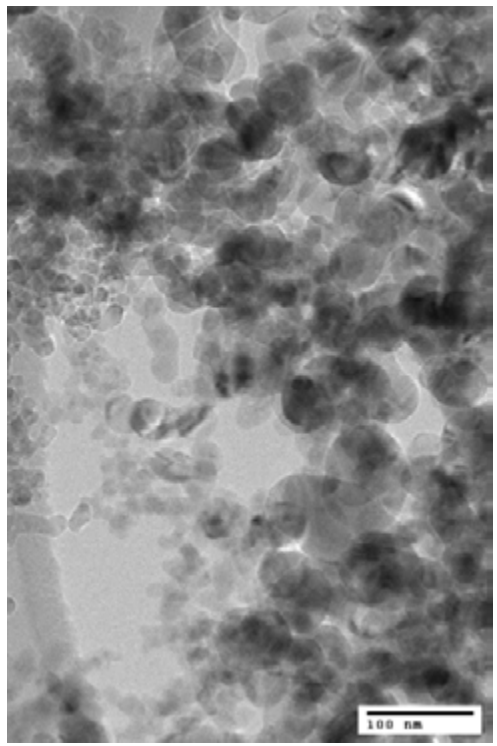
- Our small pilot batch synthesis system for fundamental feasibility studies shown at left.
- Yields presently on the order of ~50% of initial charge, improved from ~15% last year.

Accomplishments/Progress/Synthesis Results

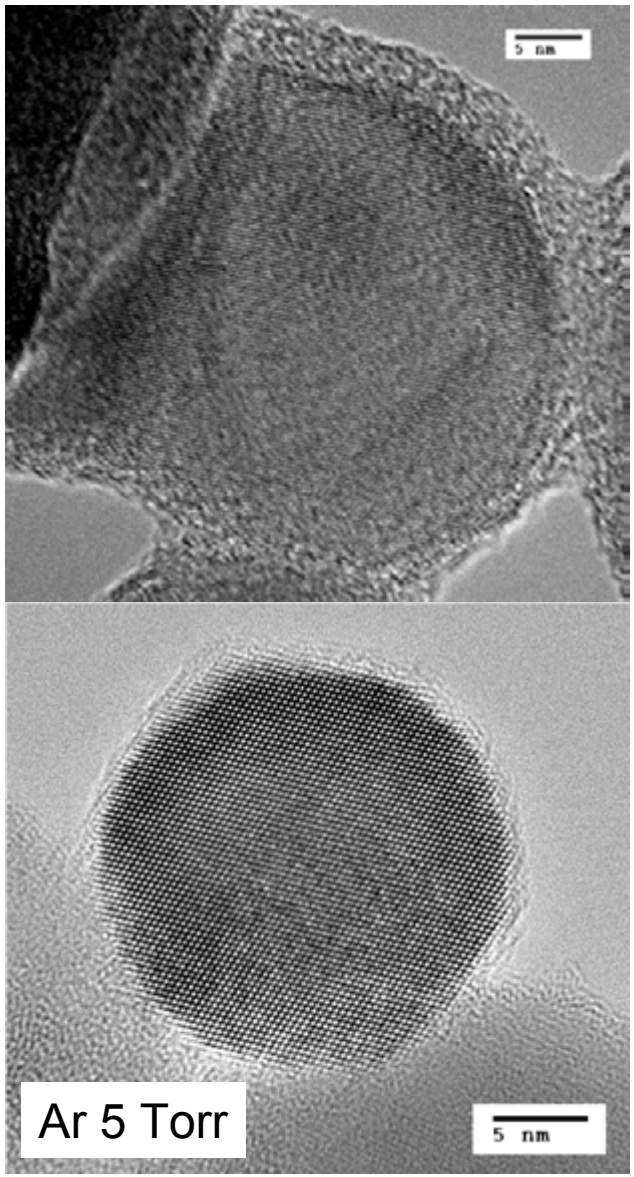
- We have encountered some difficulties with disproportionation in the direct synthesis of the Mg_2Si alloy. Our new plan is to synthesize precursors at the appropriate size scale for subsequent alloying. Two lower left transmission electron micrographs (TEM) show Si particle size distributions obtained under two different gas condensation pressure conditions using an Ar forming gas. Individual particles are resolved throughout the structure and no evidence of grain boundary necking is apparent.
- Lower right image shows a commercial Si product that was obtained as a 5nm size material. Size and size distributions are larger than 5 nm in the commercial material.







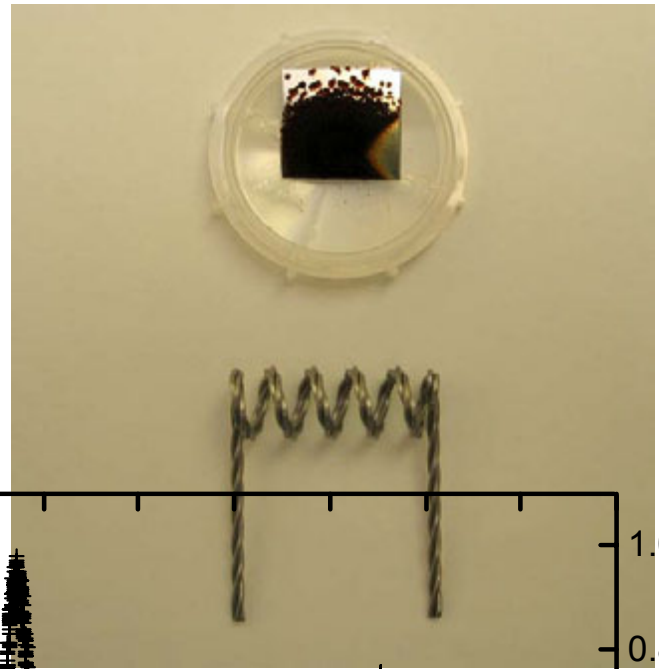
Accomplishments/Progress/Synthesis Results

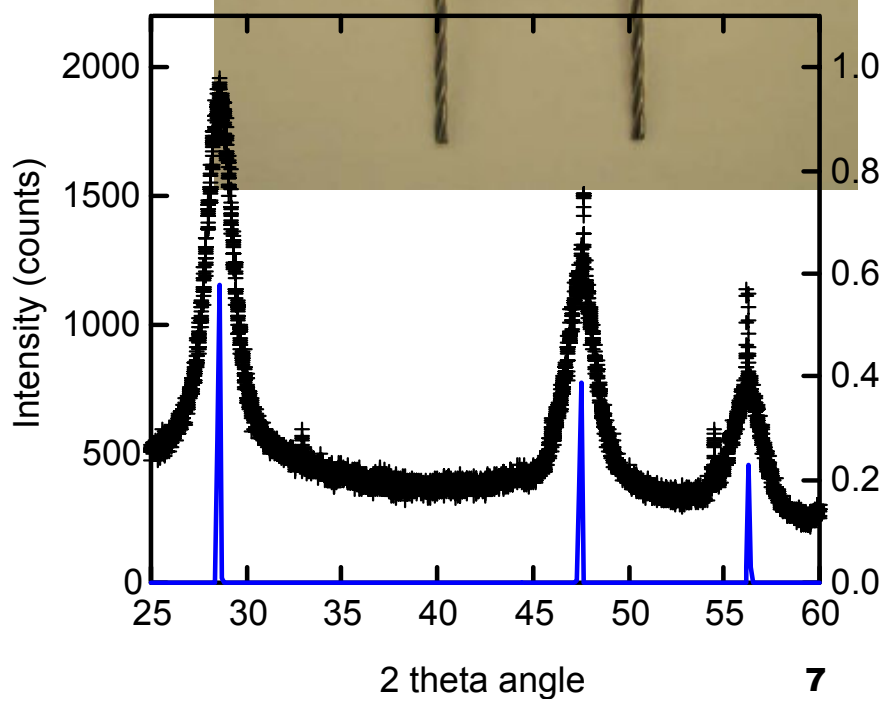


- Upper left micrograph shows the commercial Si material with a 4 nm oxide layer in the as-received product.
- The lower left image shows that a gas condensation produced particle has only a very thin amorphous or oxide layer, presumably as a consequence of forming gas hydrogen terminations at the surface that are able to temporarily suppress oxide growth. Processing with an initially oxide free layer should enable the alloying reaction to proceed without the need to overcome diffusion across the oxide layer.

Accomplishments/Progress/Synthesis Results

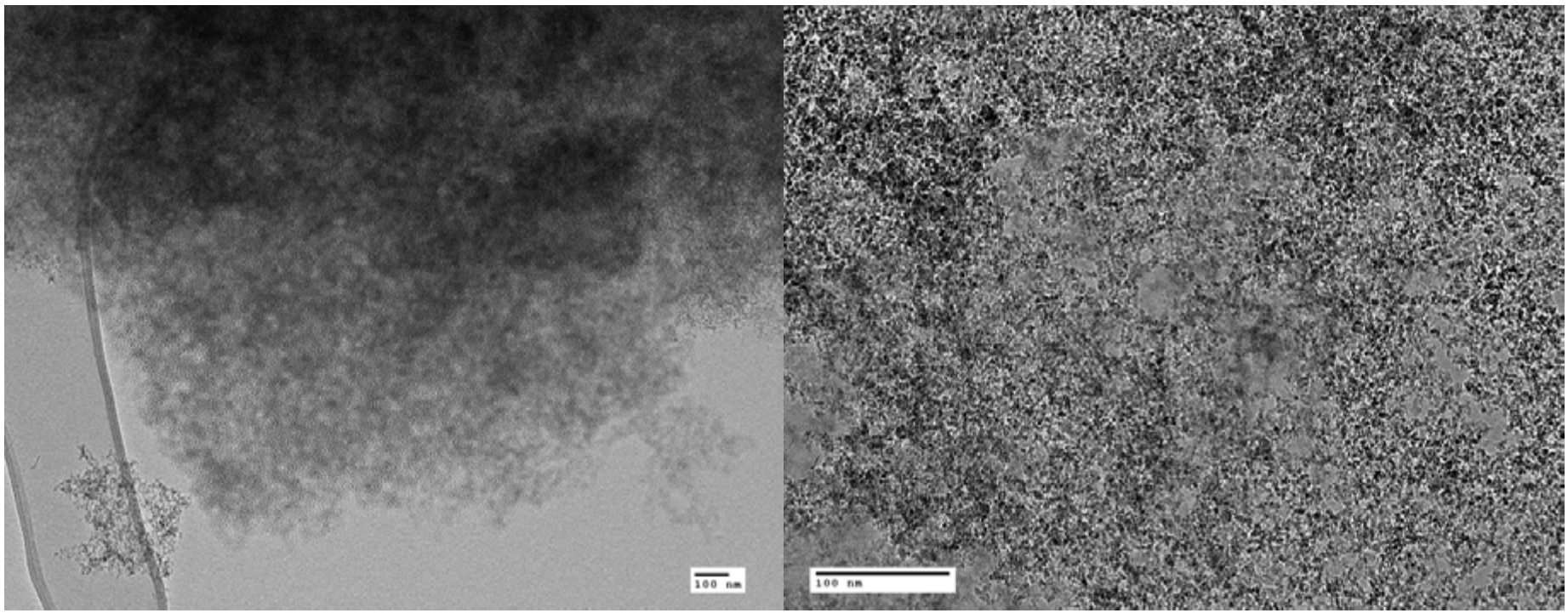
- Low yields have been problematic in the past with this technique but revisions to the reactor configuration have resulted in discernible yields as measured by x-ray diffraction as shown with a Si deposition onto a Si substrate shown to the right, along with a filament assembly that is able to withstand multiple depositions using smaller initial charges.
- The lower right hand figure shows x-ray line broadening of this Si sample compared to calculated diffraction peaks.
- Several runs are presently being evaluated by partner HRL laboratories, for Mg_2Si formation studies.





Microstructural analysis

Transmission electron micrographs from samples synthesized in a He forming gas show much smaller size and size distributions of Si particles than those shown previously from Ar forming gas synthesis.



13 Torr He forming gas synthesis

Planned Work for FY2006/2007

- Follow-up on direct Mg_2Si nanophase formation
- Continue to increase yields of elemental nano Mg and Si in order to study the reaction kinetics of intermetallic formation.
- Kinetic evaluation of this system.
- Synthesis of hydrides of other destabilized systems in progress based on computational work of J. K. Johnson at Pitt.

Summary:

- Relevance: Nanoscale hydrides and hydride precursors necessary to understand kinetic limitations, ultimately tied to refueling rates.

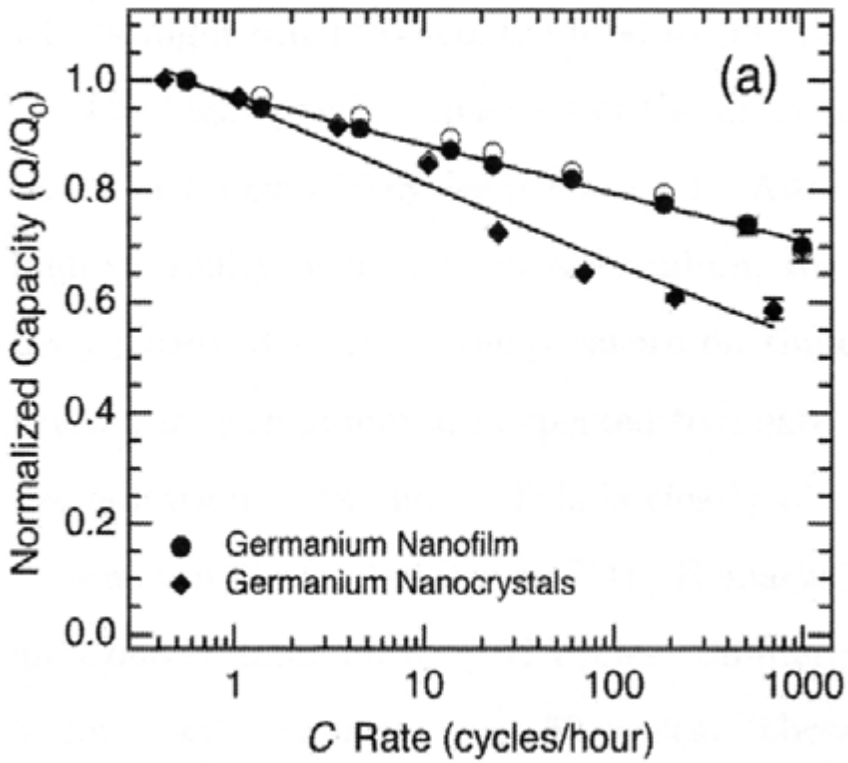
- Approach: Synthesis via gas condensation and ballistic deposition, produces particles smaller and purer than that achievable via mechanical attrition and size distributions are smaller than commercially available material.

- Technical accomplishments and progress: Quantifiable yields of nano Si as reaction precursor synthesized, attempts at direct nano Mg_2Si in progress. Microstructural (transmission electron microscope) and x-ray analyses of relevant phases based on hydride destabilization.

- Collaborations: HRL, JPL, U. Hawaii, Stanford, U. Pittsburgh, NIST

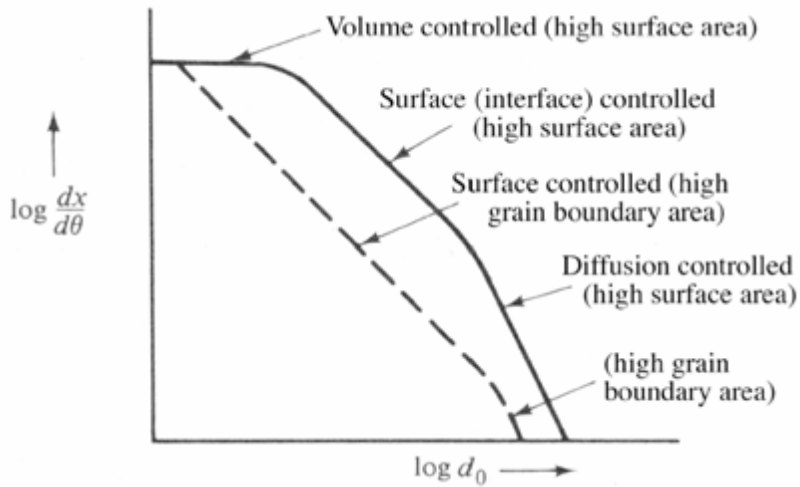
Background

Previous work by J. Graetz Caltech PhD thesis (now at BNL) showing the improvement to kinetic behavior at nanoscale dimensions showing high rate capability in Ge anode Li half-cell.



"Nanocrystalline and thin film germanium electrodes with high lithium capacity and high rate capabilities," J. Graetz, C. C. Ahn, R. Yazami, and B. Fultz, J. Electrochem. Soc., 151, A698 (2004).

"Highly reversible lithium storage in nanostructured silicon", J. Graetz, C. C. Ahn, R. Yazami, B. Fultz, Electrochem Solid St. 6 (9): A194-A197 (2003).



Schematic of different size regimes over which various diffusion mechanisms are expected to be important.

Background

Vapor pressure of metal derived from Clausius-Clapeyron equation and relies on latent heat of Evaporation. Data of relevance to both sime evaporation and gas condensation processes.

Data obtained from thermochemical databases of Hultgren and JANAF tables and generally presented in form

$\log(p) = AT^{-1} + B\log T + CT + DT^2 + E$

A and E dominant terms, e.g. for Li
$E = 10.99$ and $A = -8.07\times10^3$

Evaporation rate will be $\mu\ p(MT^{-1})^{1/2}f$

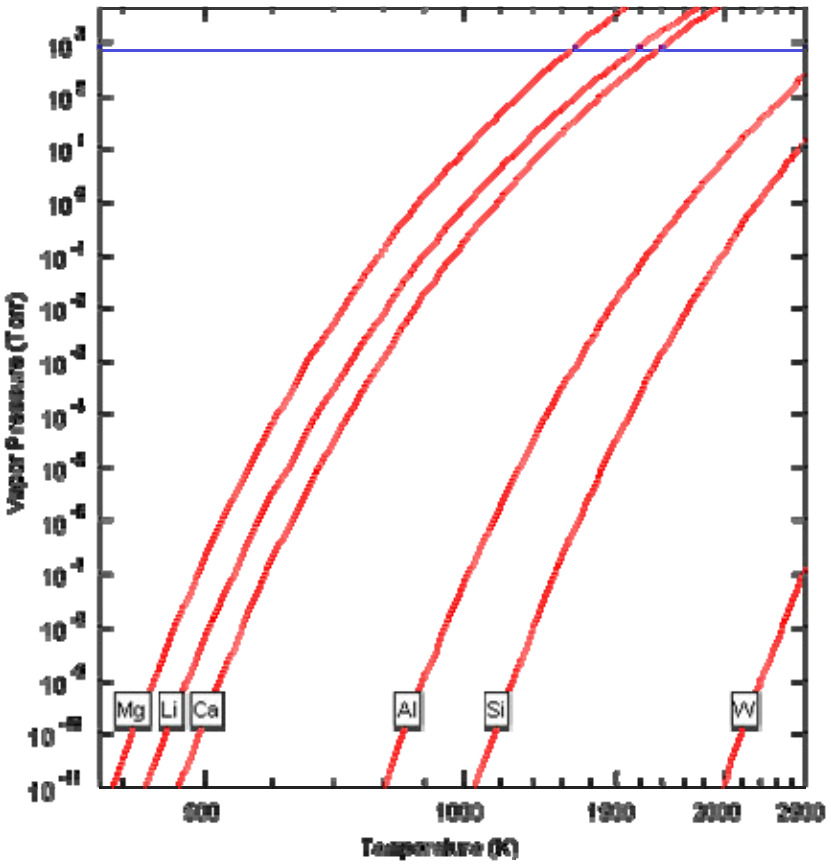
Where M molecular weight and f sticking coeff.

References:

Hultgren, et al, "Selected values for the Thermodynamic Properties of Metals and Alloys," Report of the Minerals Research Lab, UC Berkeley (1962-1969).

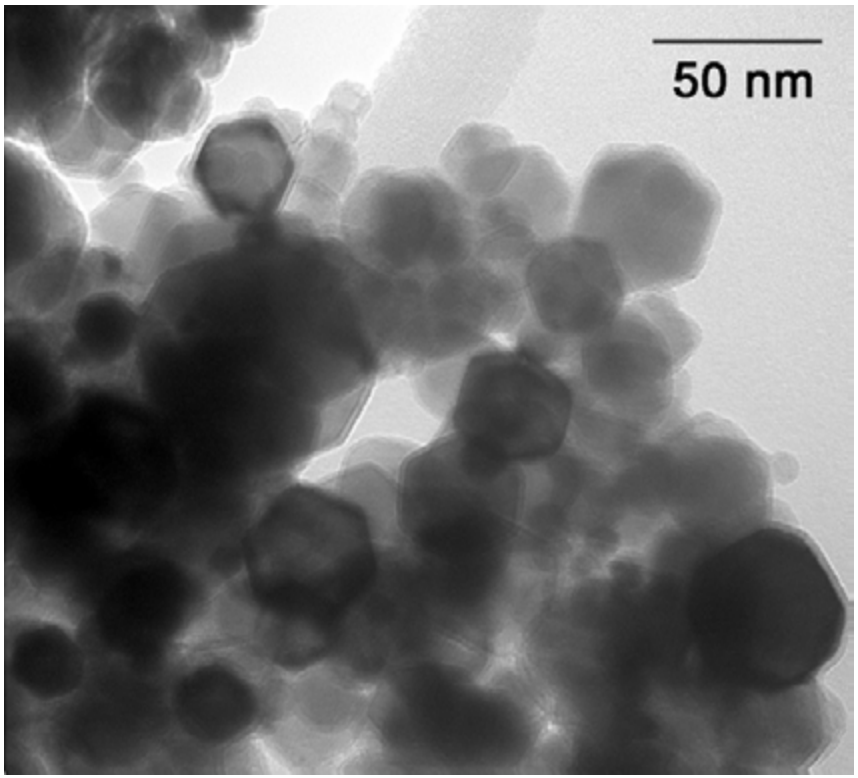
JANAF Thermochemical Tables

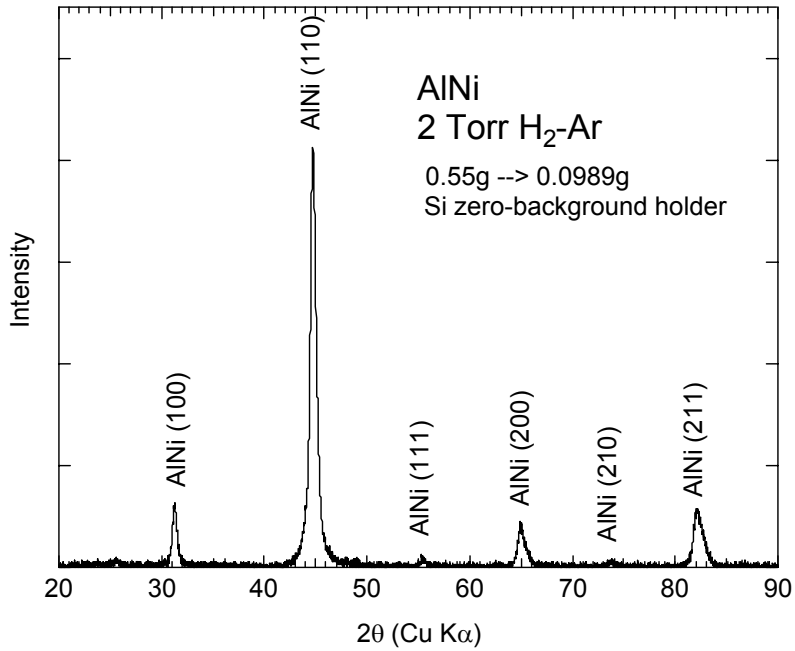
Honig and Kramer, "Vapor Pressure Data for the Solid and Liquid Elements," RCA Review, Princeton, NJ (1969).



Background

Our previous work on Al alloys shows that direct alloy formation via gas condensation is possible. This example from NiAl is consistent with other results from Fe_3Al and LiAl alloys. We have encountered difficulty in preparing Mg_2Si in this way but hope to overcome this in the next few months.





Publications and Presentations

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

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

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

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

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