Combinatorial Approach for Hydrogen Storage Materials

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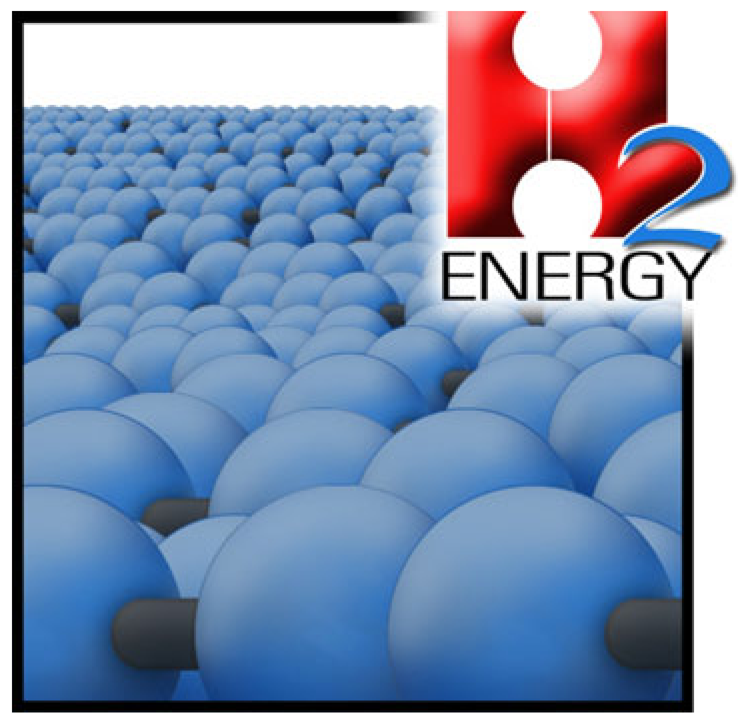
METAL HYDRIDE CENTER OF EXCELLENCE

ecomagination℠

imagination at work



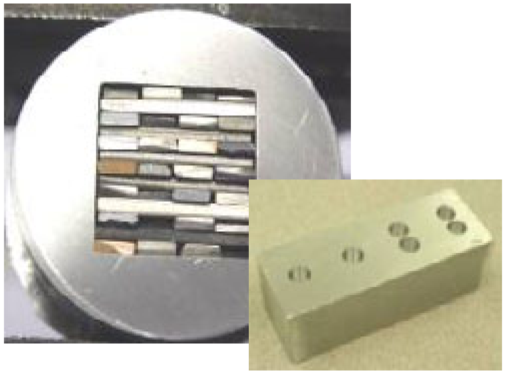
Outline

Approach: Parallel synthesis accompanied by high throughput screening for a desired property.

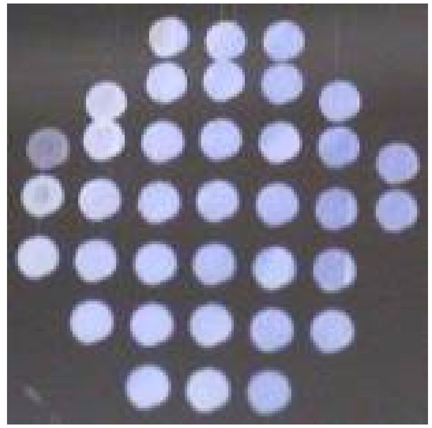
- Methods
  - Preparation/parallel synthesis
  - Analytical techniques
  - Scale-up
- Selected results
  - Al-Li-Si system
  - Al-Mg-Ti system
  - AlH_3 + Si
  - $Mg(BH_4)_2$
- Summary

Down-selection of the combi process

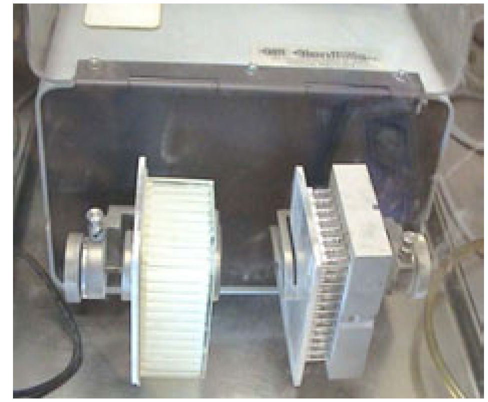
Production of multiple compositions



Diffusion multiples

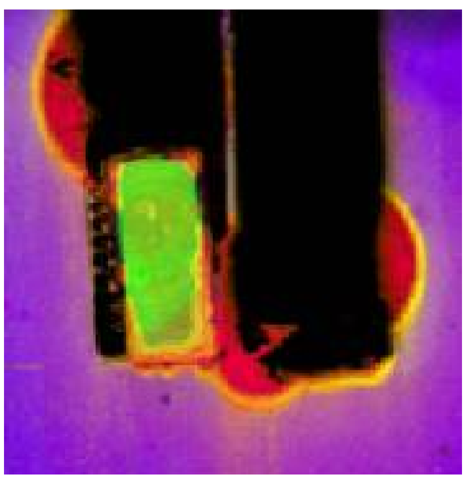


Co-sputtering



High energy 96-well Shaker

HTS Analytical Tools



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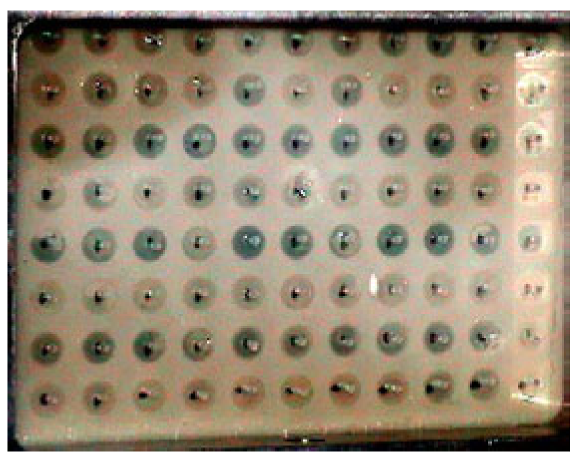
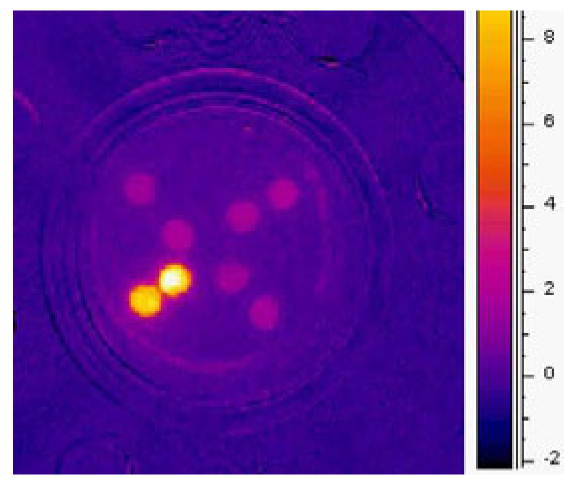


WO_3 sensor



Thermography

imagination at work

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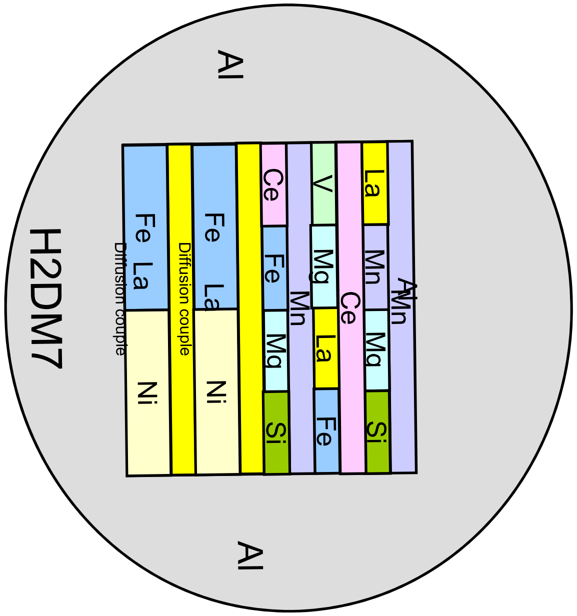
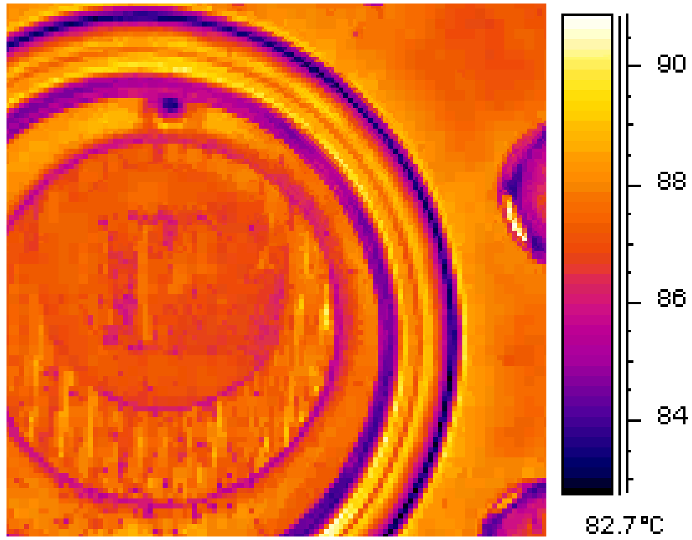
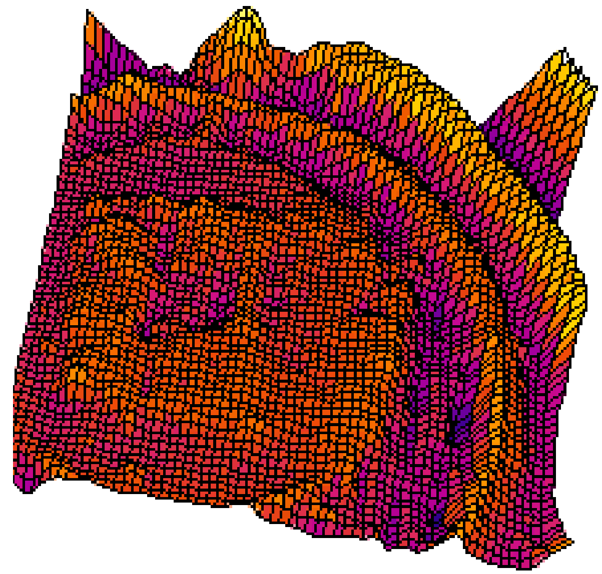
Hydrogen Sorption in Diffusion Multiples



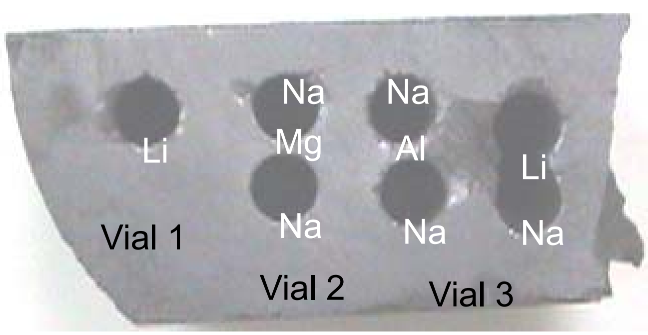
Traditional DM w/ LaNi several new concepts.



Activation 80 °C / 100psi H_2

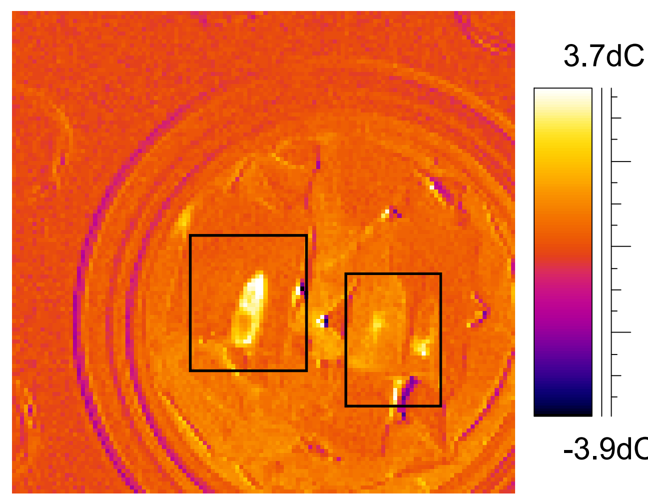


Cycling 80 °C / 100psi H_2



Si DM with Li and Na

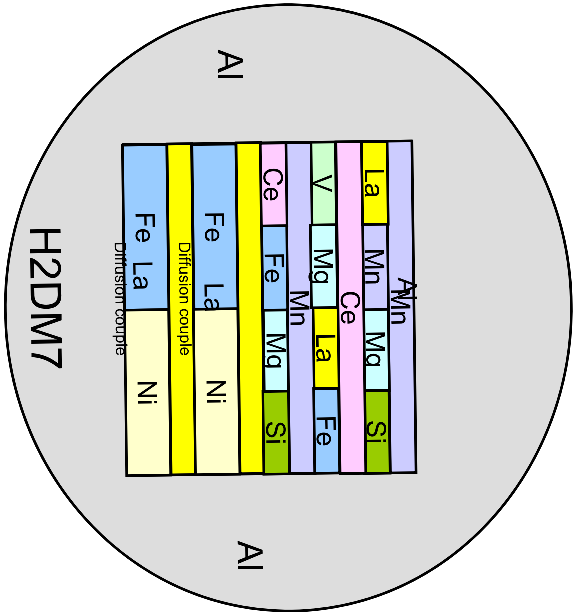
Sliced cross section



Subtracted Image

Rapid in-situ screening method but low spatial resolution

Hydrogen Sorption in Diffusion Multiples



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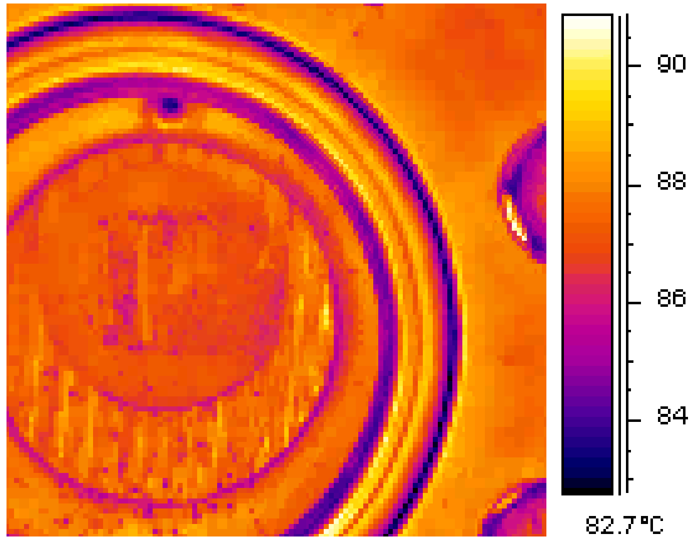

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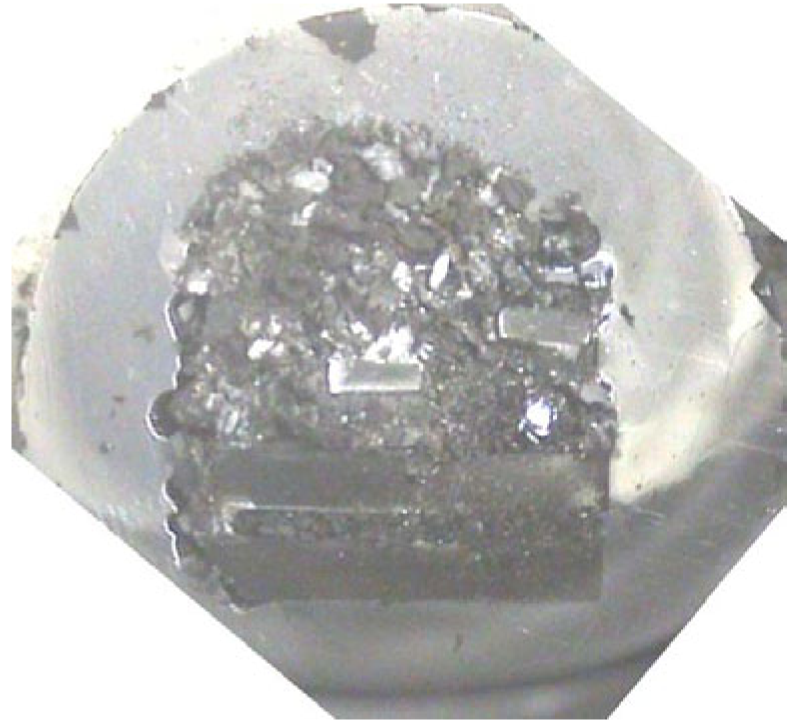

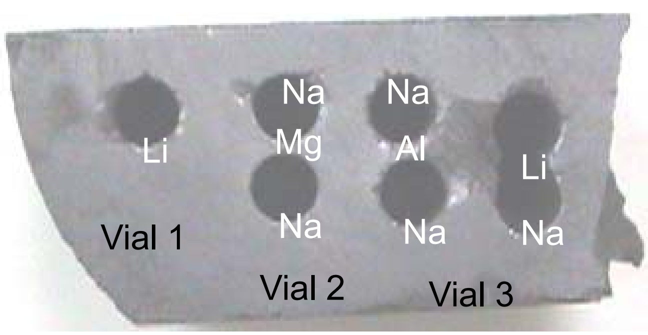

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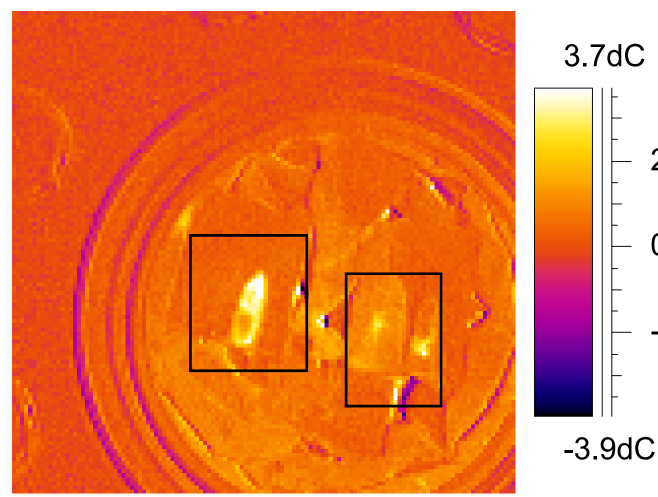

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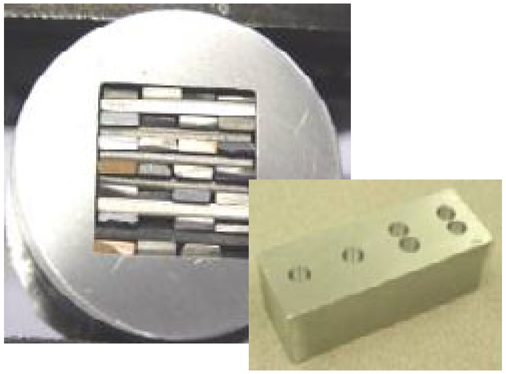
Down-selection of the combi process

Production of multiple compositions



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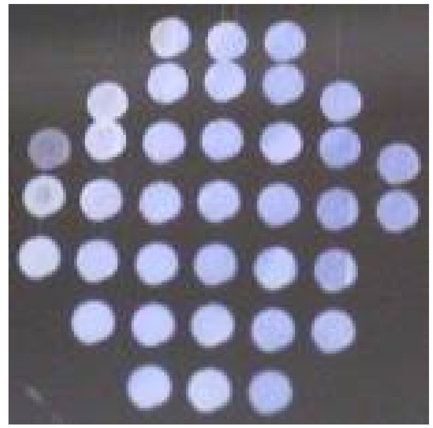

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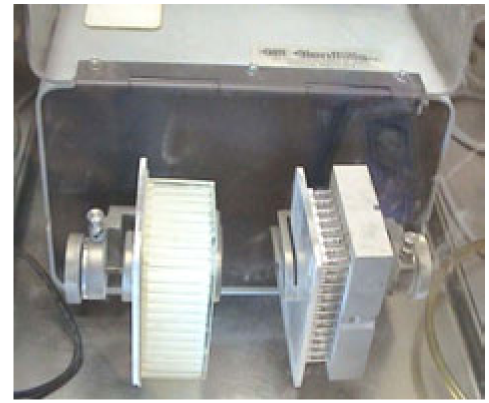

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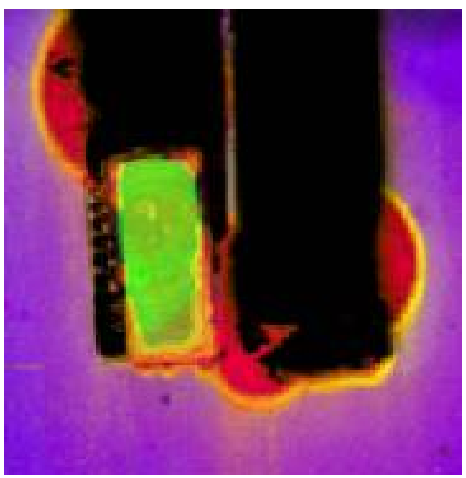

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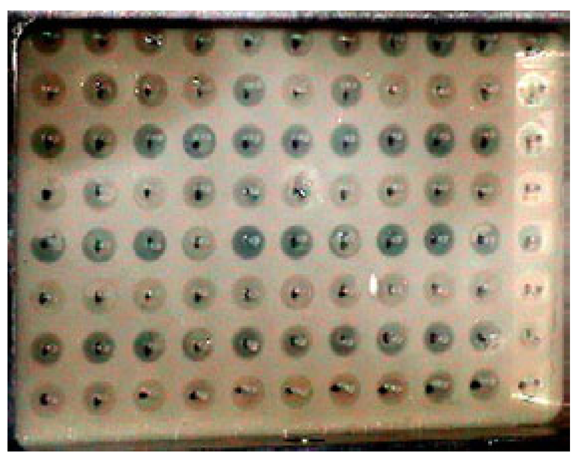

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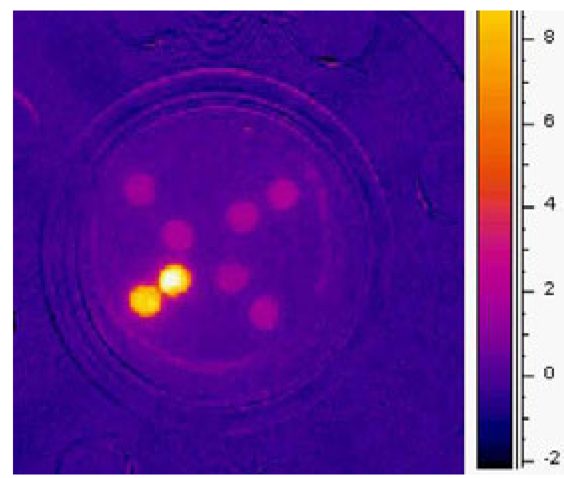
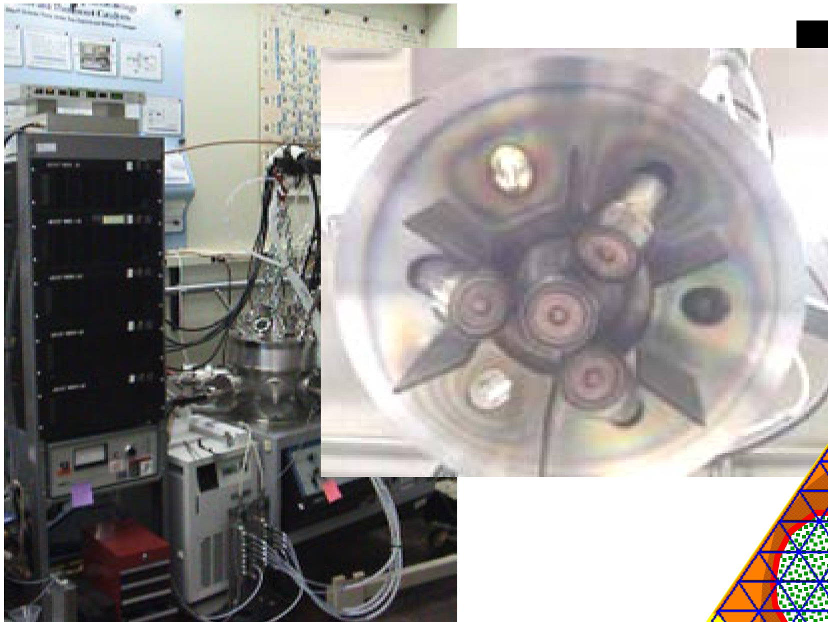
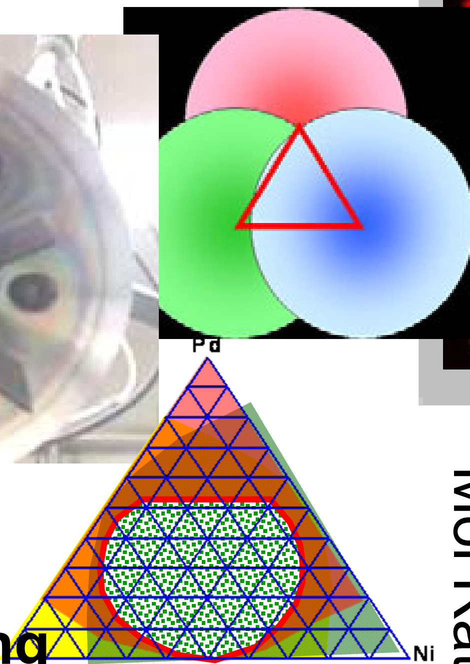
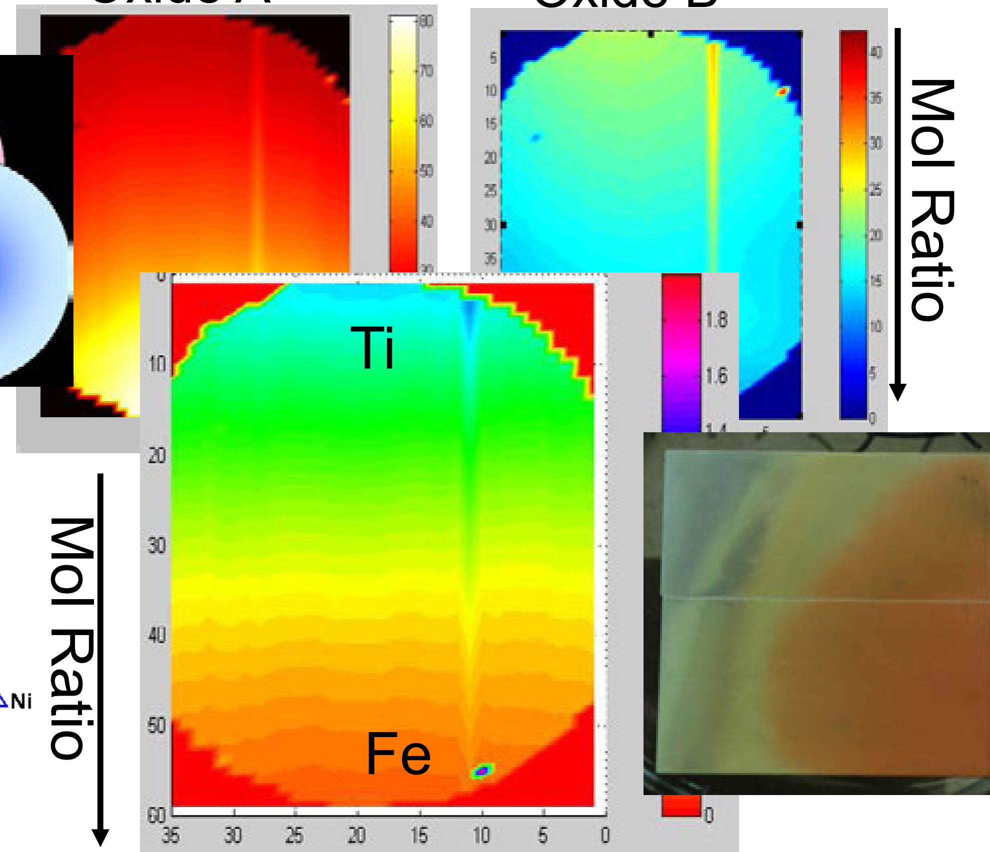


Thermography

Thin Film Sputtering

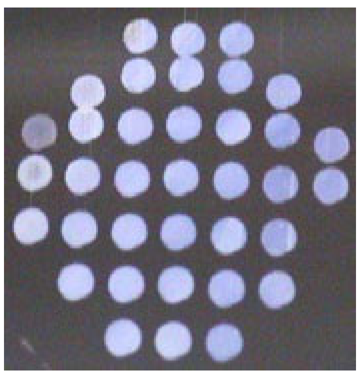




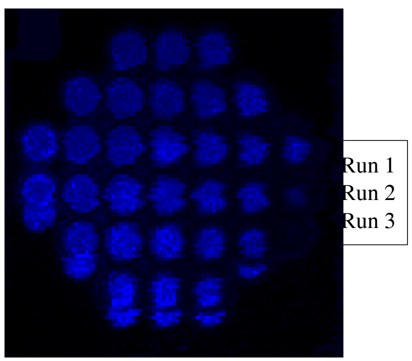


Multi-Target Co-sputtering

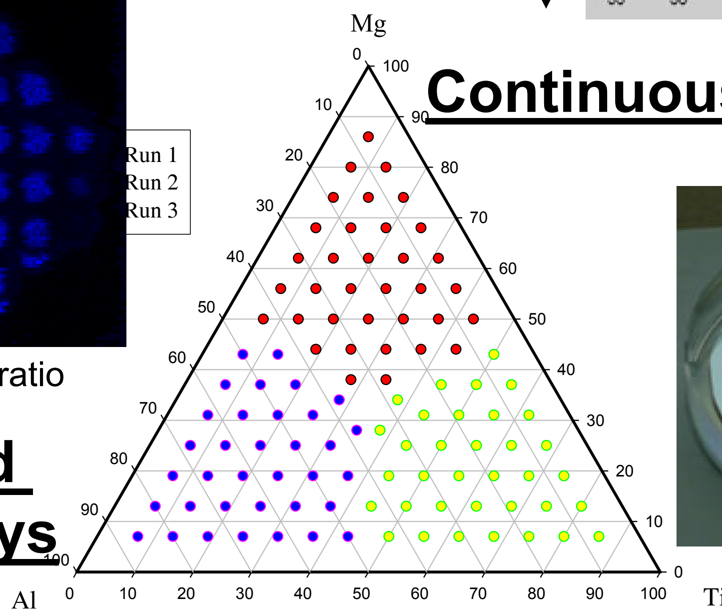
Start Mg_3-$Al_{0.03}$ End $Mg_{0.03}Al_3$



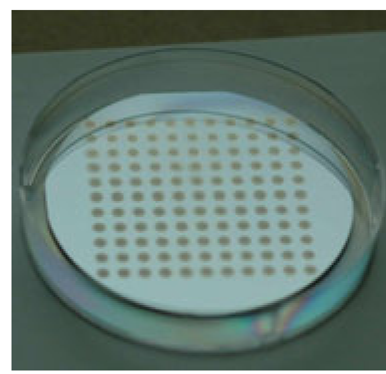
Sputtered Array

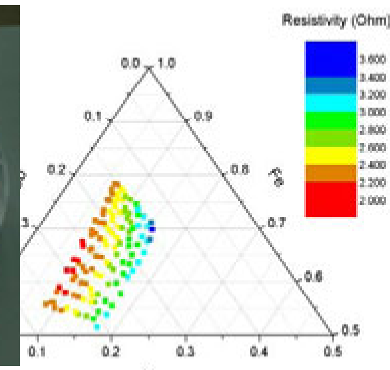


Imaging A/B ratio



Continuous Compositional Gradients





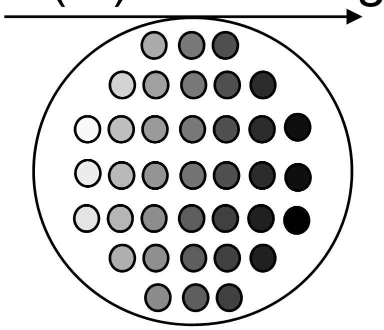
Spatially Resolved Programmed Arrays

Ti

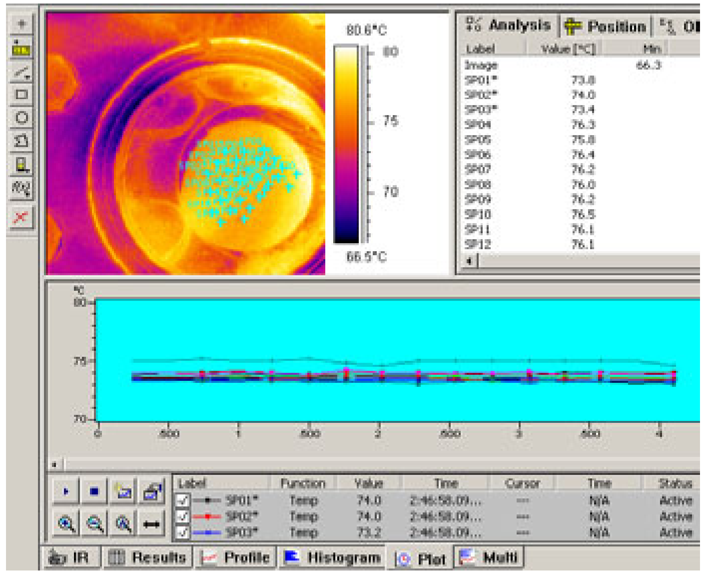
Reversible Catalyst Screening

Validation w/ $3NaAlH_4$ + Ti (catalyst) 120 °C → $Na_3AlH_6 + 3H_2 + 2Al$ (Endothermic)

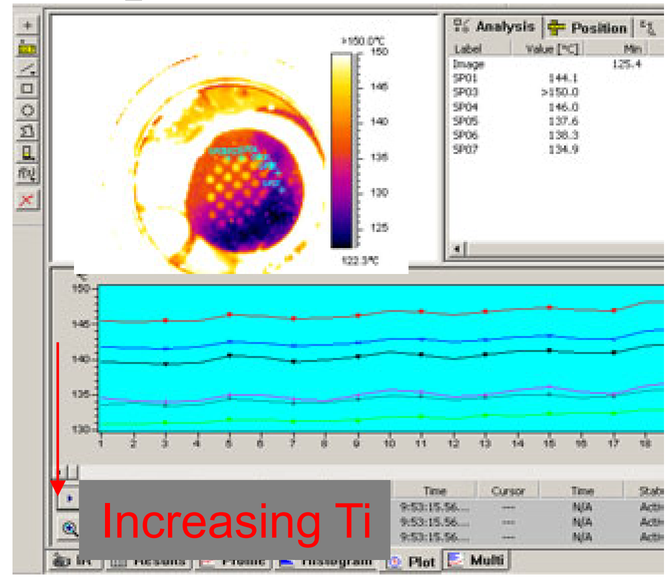
Ti(m) increasing



$NaAlH_4$ pellet

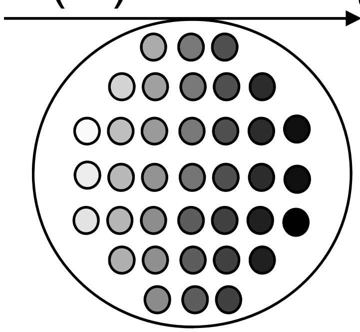


Equivalent emissivity at 80 °C

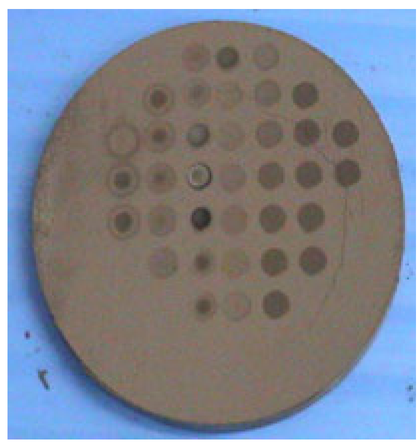


At 130 °, lower temperature contains , higher [Ti].
Evidence of decomposition by XRD and H2 pressure.

Ti(m) increasing



ZnB_2, MgB_2,



Mg, Mn,Ti on ZnB_2

- High pressure thermography.
- XRD

>200 catalyst composition screened

imagination at work

METAL HYDRIDE CENTER OF EXCELLENCE

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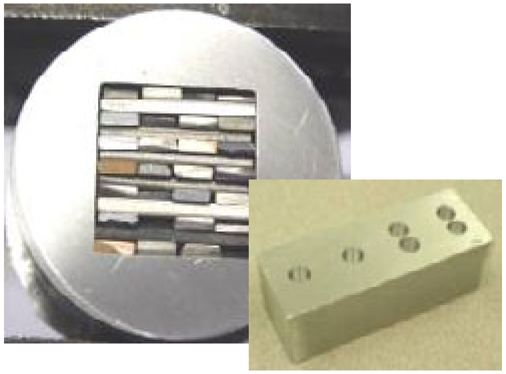
Production of multiple compositions



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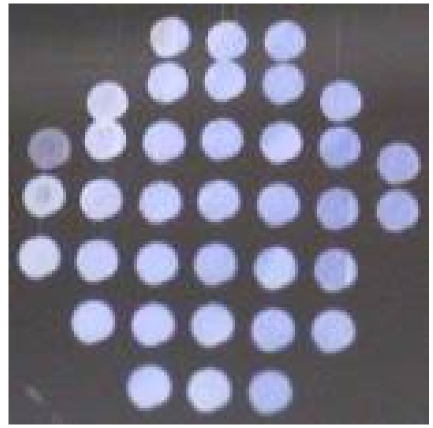

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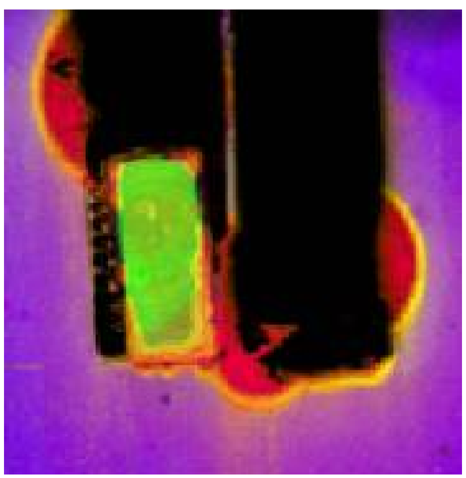

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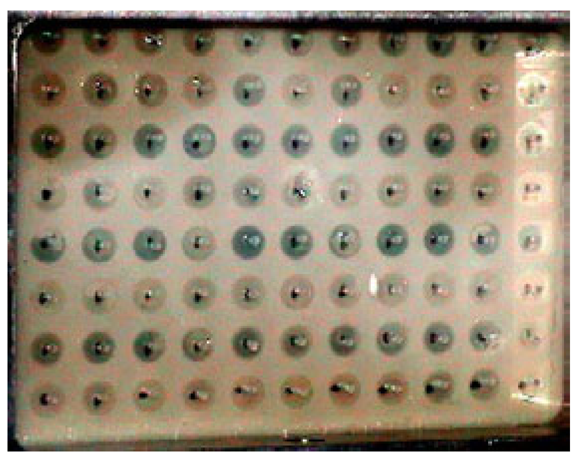

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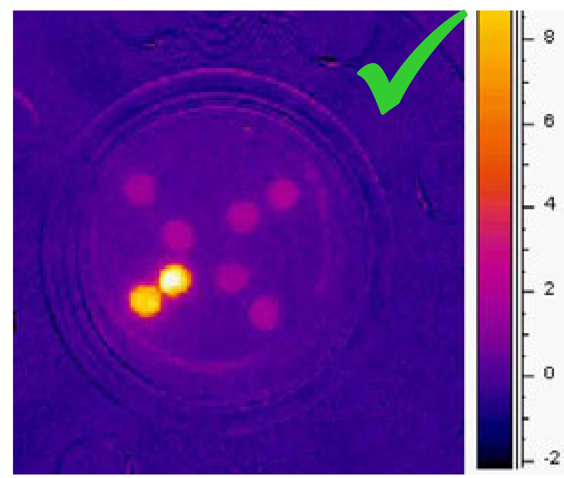
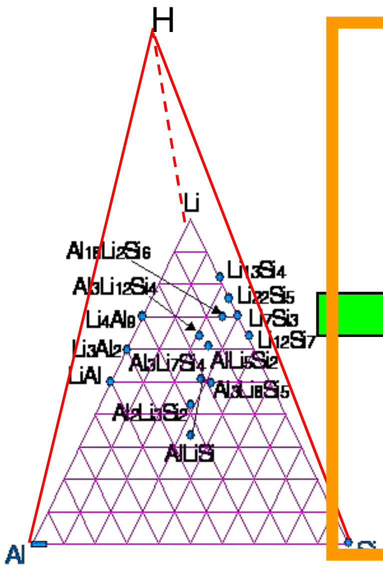
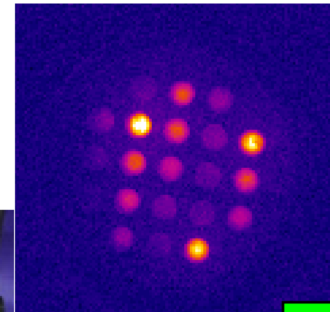
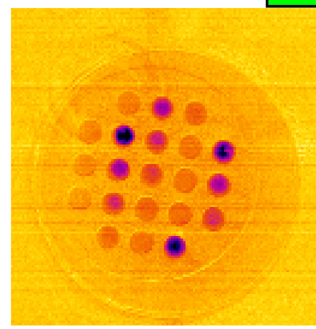


Thermography

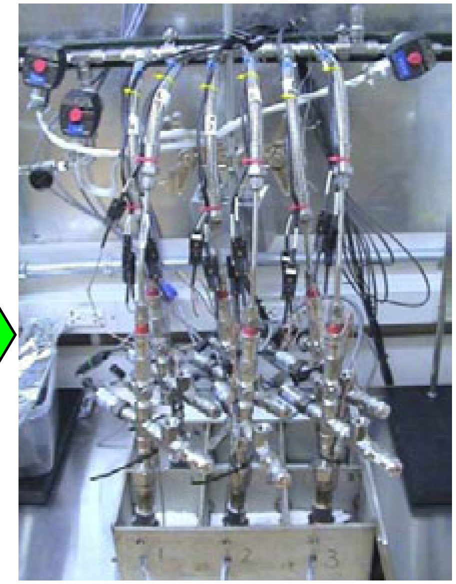
Approach



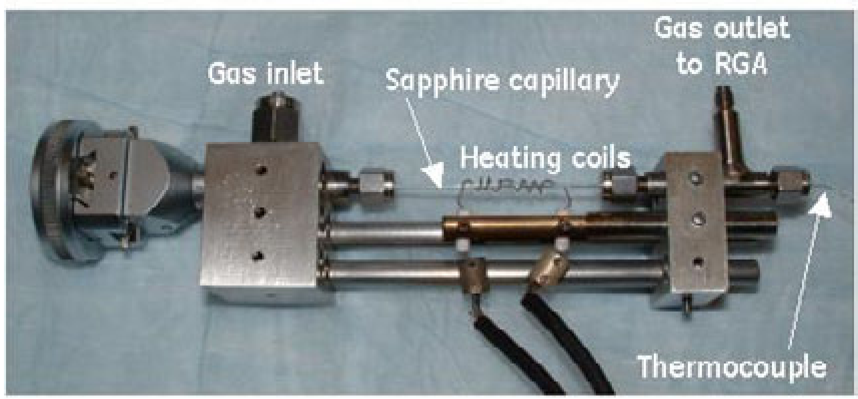




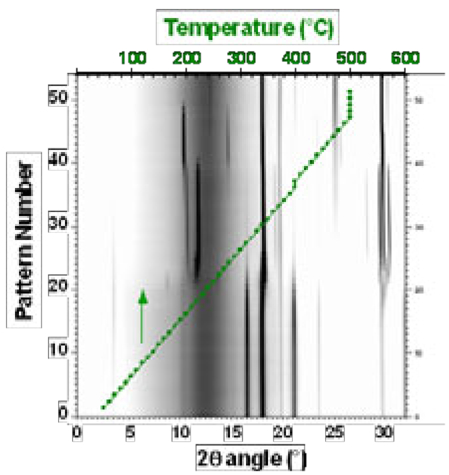
T: <400 °C P: <70 bar



T: <400 °C P: <140 bar



max T: 550 °C max P: 140 bar



Robust combinatorial/high-throughput methodology developed & validated by confirming the observations with bulk PCT tests

Multi-well Reactive Ball Milling

Entire process in glove box

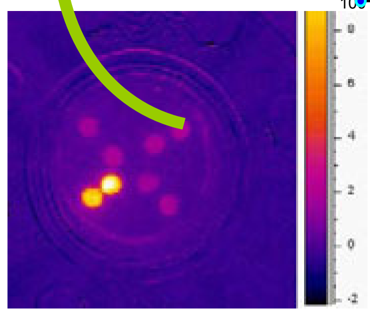
Catalyst Doping

- Validated with $NaAlH_4$, previously screened over 2000 catalyst.
- New MH candidates.

Synthesis

- Metal substitution in amides.
- Li – Alumides, AlLiMg
- Li – Silicides, LiSiMg

PCI Measurement



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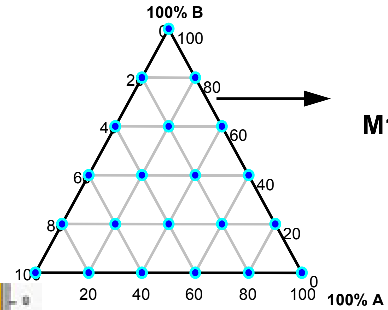
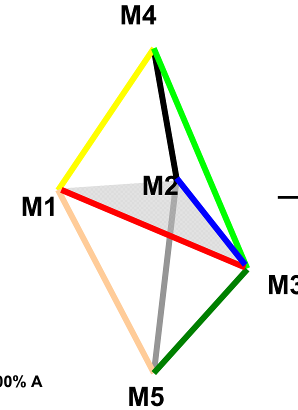




Catalyst/Reactant Mixtures

96-well sample holder

Optical image

96-well H_2 sensor for H_2 desorption 25 – 300 °C

High energy shaker 2x, 4x, or 96

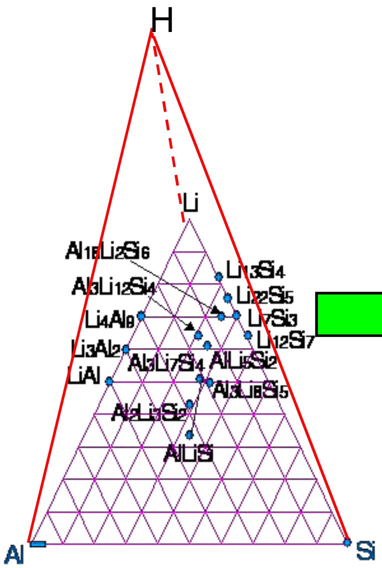
High T and P Reactor

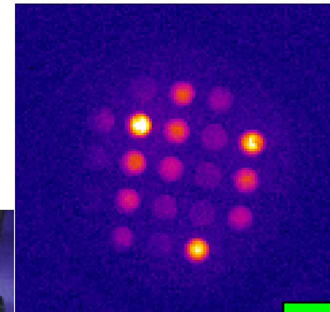
Improved method for the synthesis of ternaries.

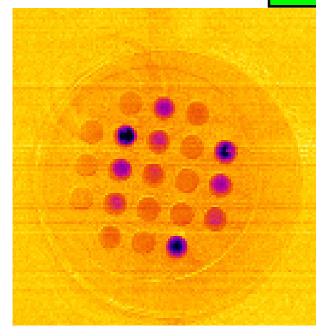
imagination at work

METAL HYDRIDE CENTER OF EXCELLENCE

Approach







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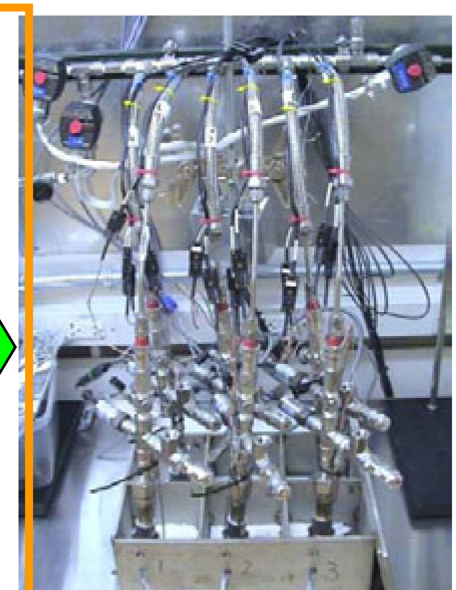

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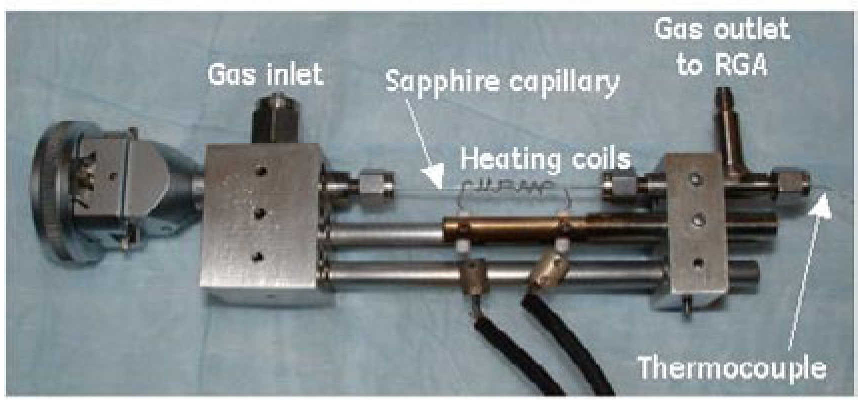

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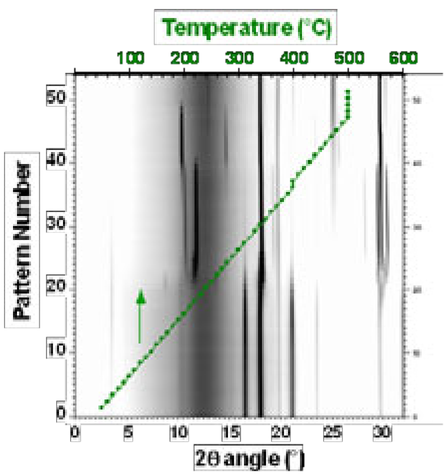

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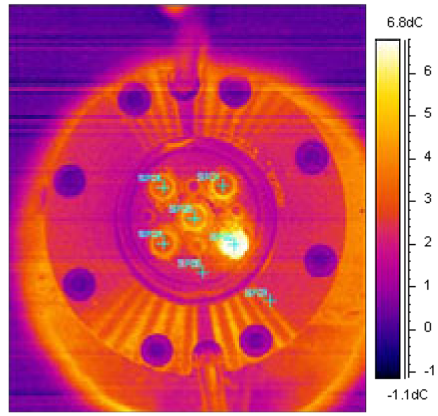
Hydride Screening with IR Imaging

Hydrogen Sorption and Desorption

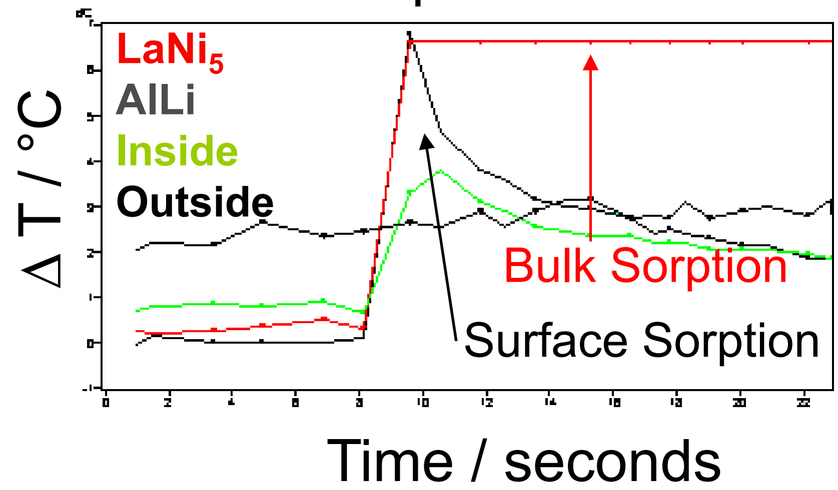
- Benchmarked with $LaNi_5$ $LaAlNi_5$, and FeTi powders, 100 mg.
- 10 replicates 3% rsd .
- Distinguish between surface absorption and bulk hydriding.
- Synthesis and hydride w/o sample removal.

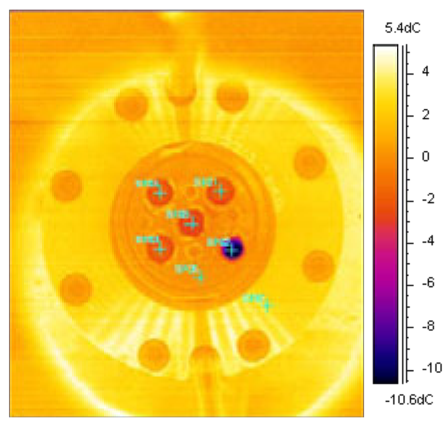
Risks

- Indirect measurement.
- Surface differences
- Resolution limited, need magnification lens for DMs

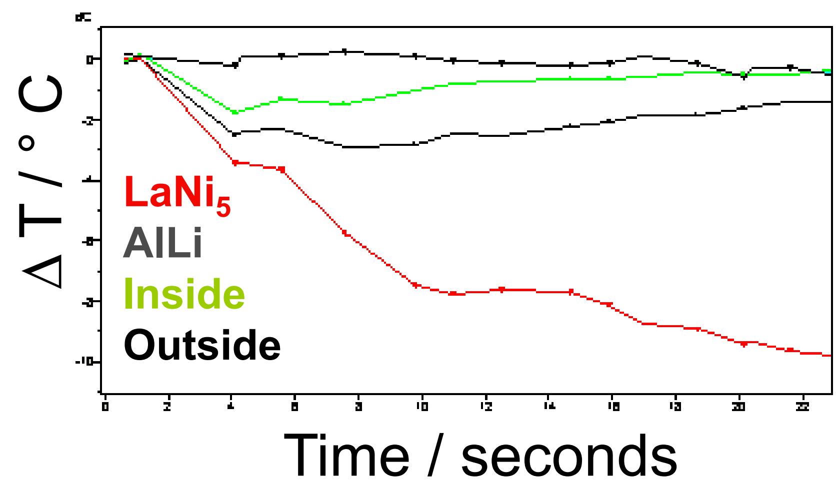


Sorption





Desorption



Surface sorption may mask hydrogenation

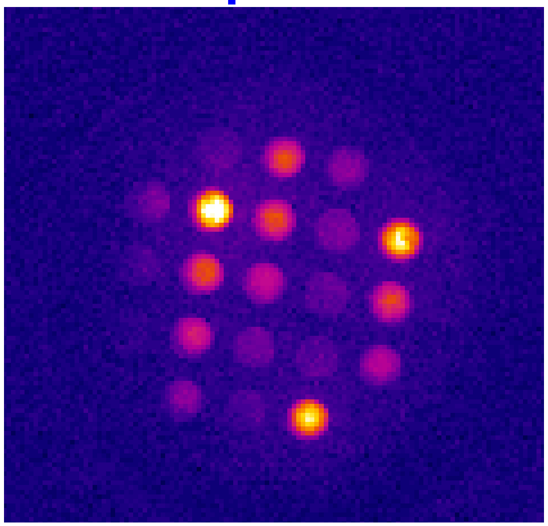
imagination at work

METAL HYDRIDE CENTER OF EXCELLENCE

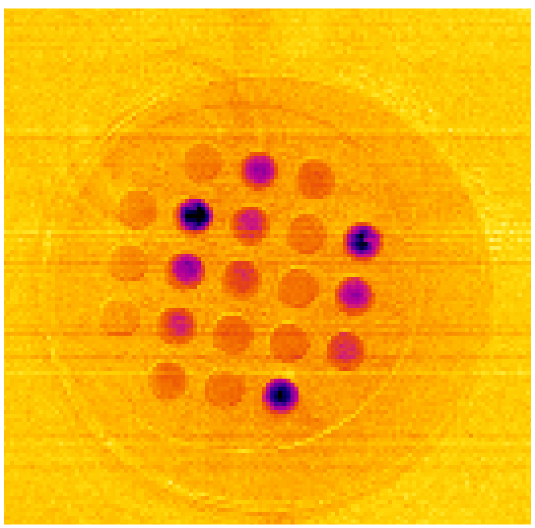
Thermographic Imaging

Mixed samples of $LaNi_5$ diluted with Al powder hydrided at 55 bar, 40°C.

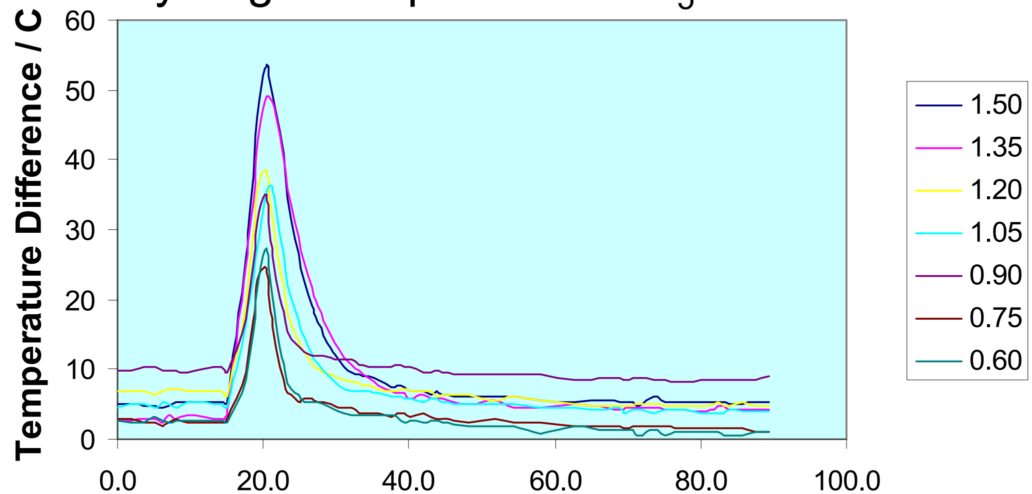
Sorption



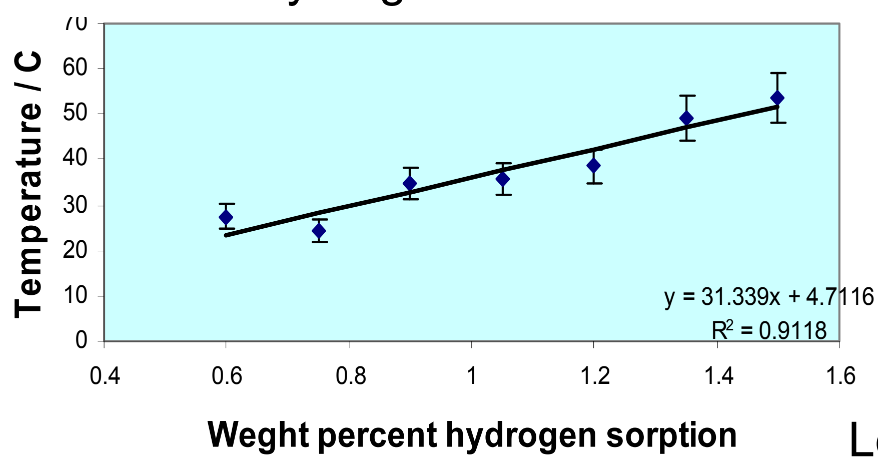
H_2 Desorption



Thermal camera response for the hydrogen sorption of $LaNi_5$



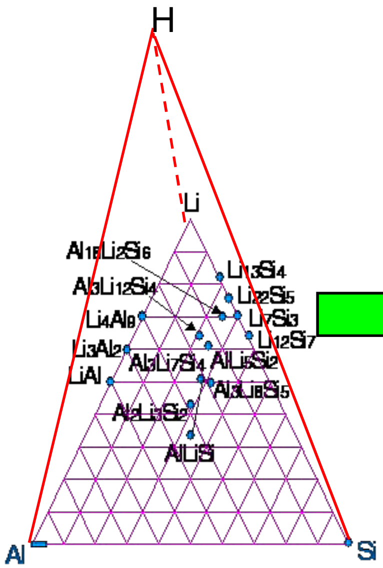
Linear response for H_2 sorption
0.3 wt% hydrogen detection limit.

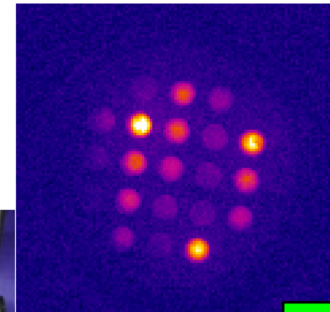


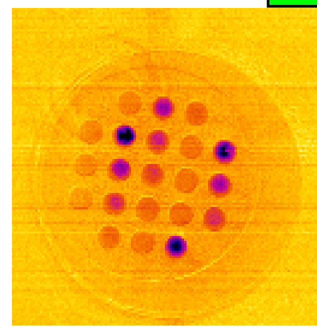
Lemmon

Capability to rapidly and quantitatively screen for reversible, hydrogen storage up to 400°C / 55 bar.

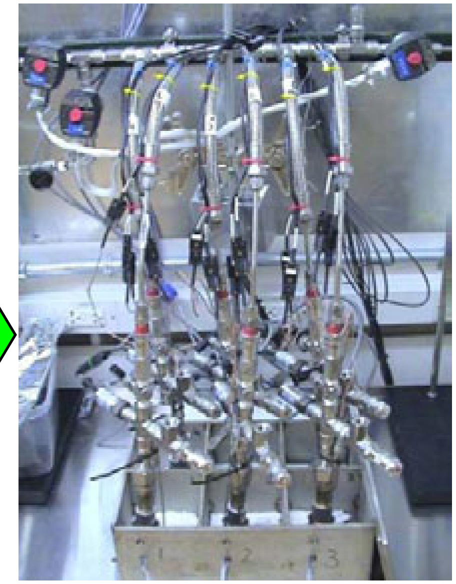
Approach



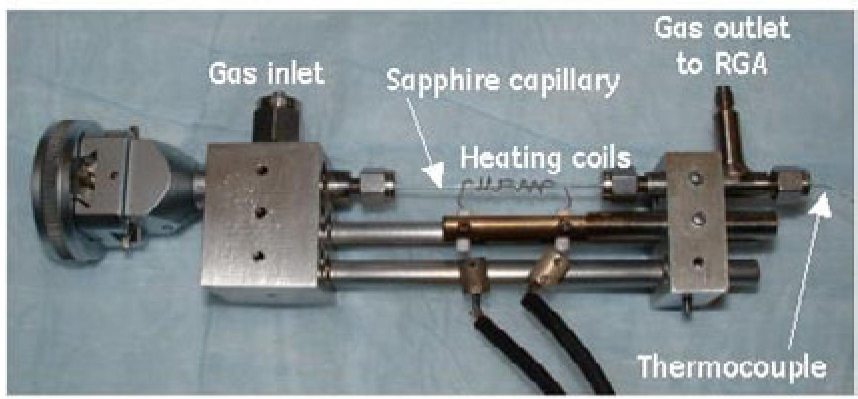




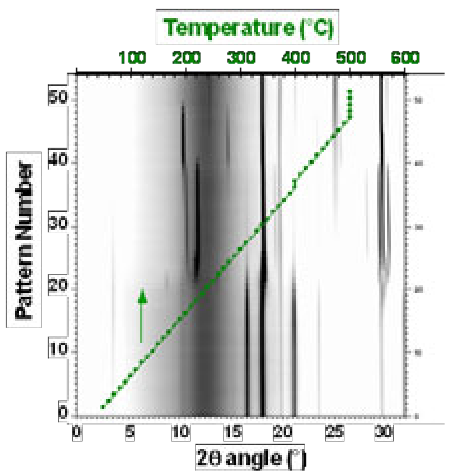
T: <400 °C P: <70 bar



T: <400 °C P: <140 bar



max T: 550 °C max P: 140 bar

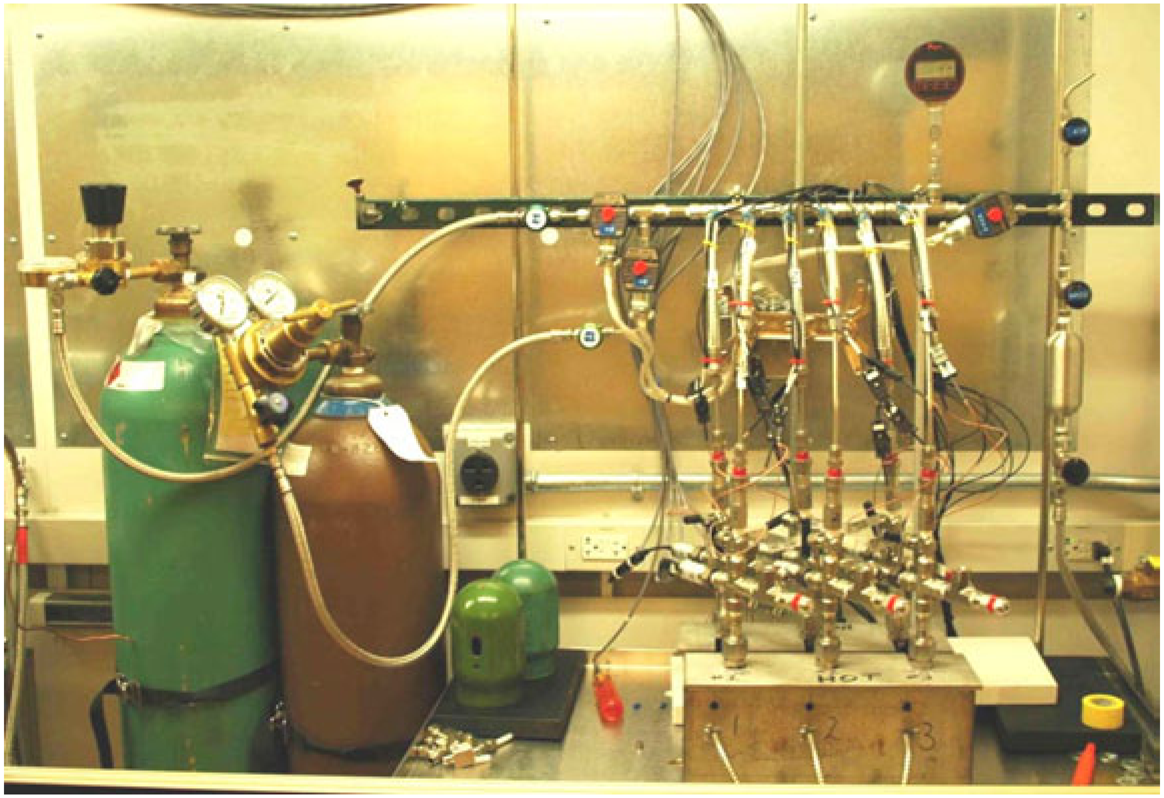


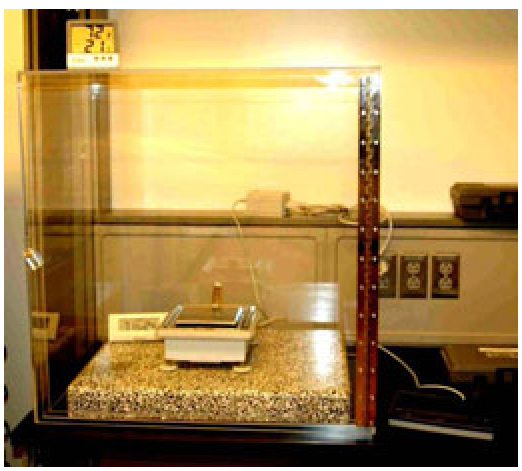
Robust combinatorial/high-throughput methodology developed & validated by confirming the observations with bulk PCT tests

imagination at work

METAL HYDRIDE CENTER OF EXCELLENCE

6-Pak Test Setup – secondary screening





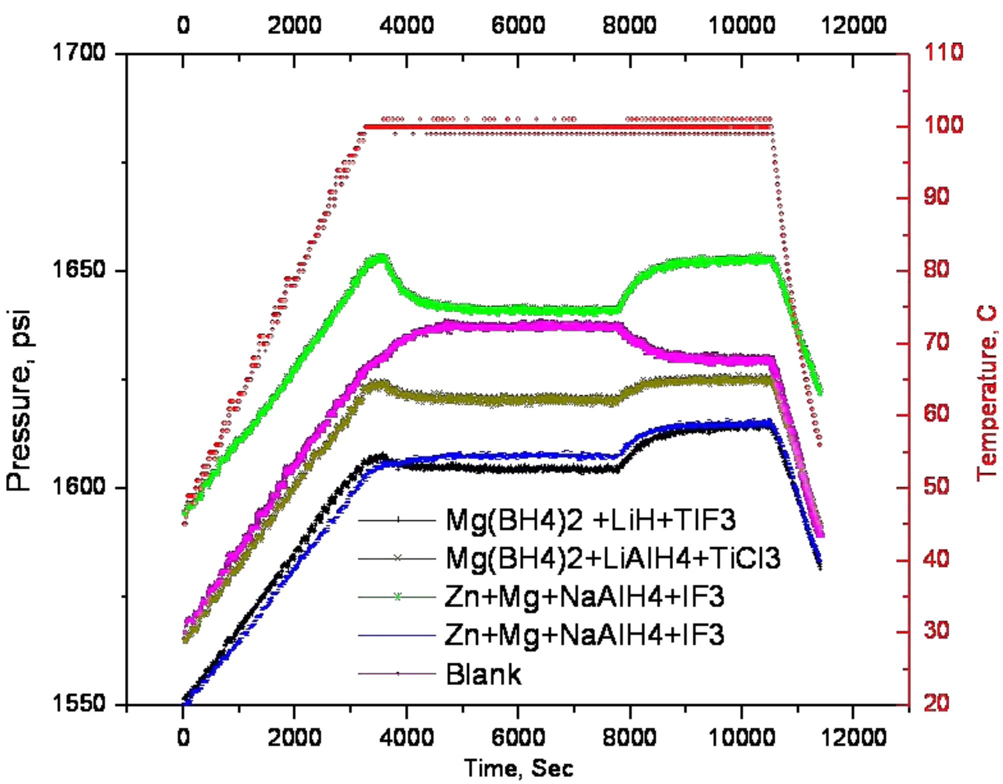
Capacity:
- Temp: RT~450°C
- Pressure: 0~1600 psi
- Resolution: 1 wt%

Features:
- 6 reactors/samples run simultaneously & independently
- 6 separate temperature/pressure controls
- Monitor/control through internet

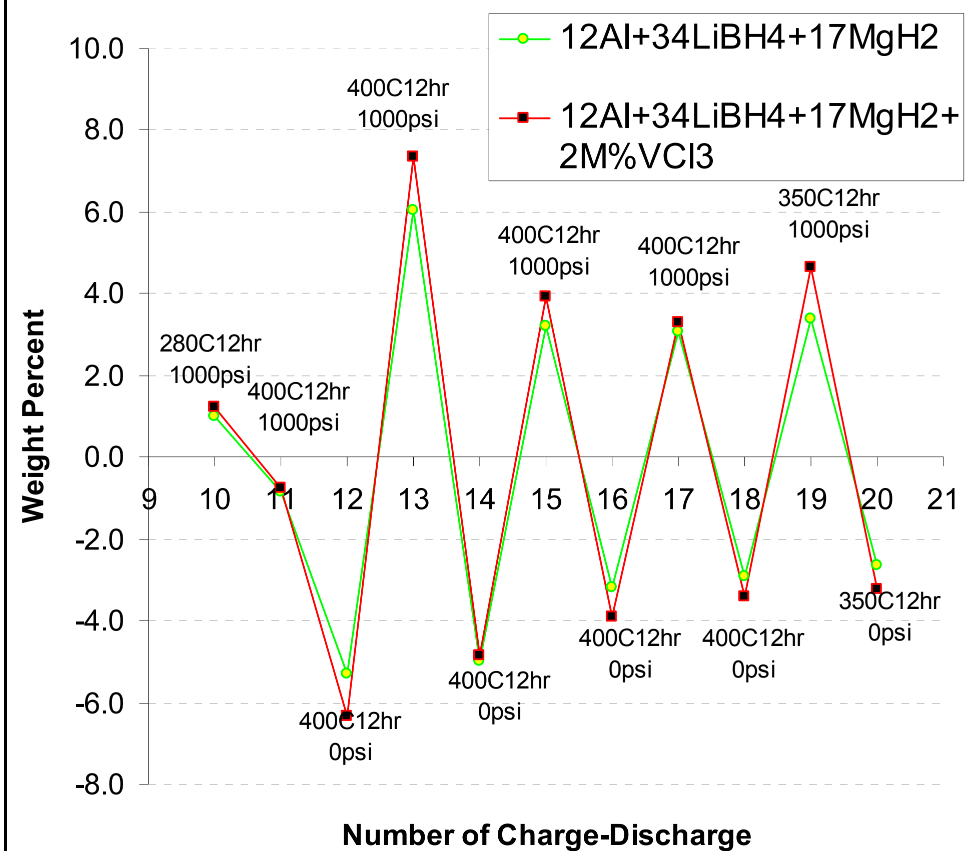
Cui, Raber, Rubinsztajn, Rijssenbeek, Lemmon

6-Pak example results

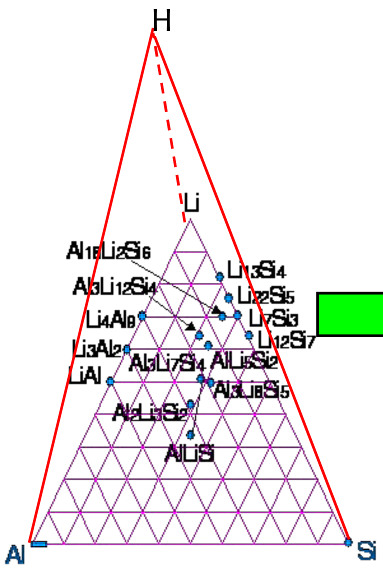
pressure change during H_2 uptake/release

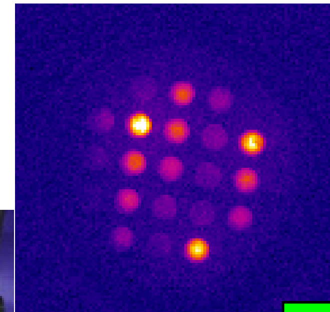


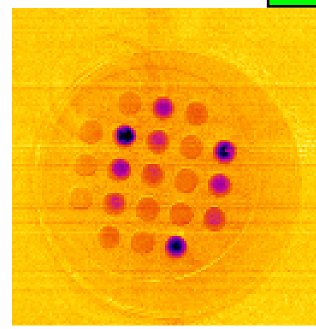
Weight change after H_2 charge/discharge

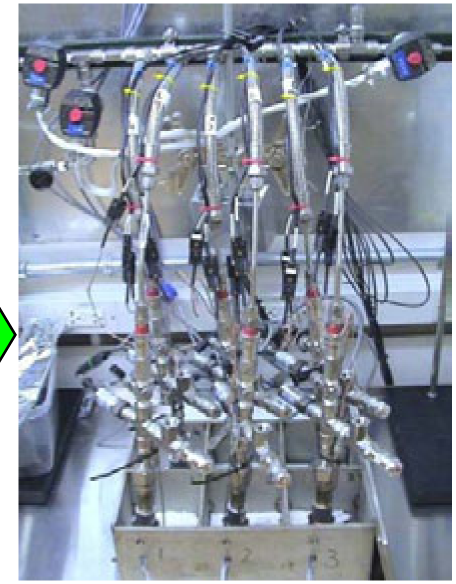


Approach



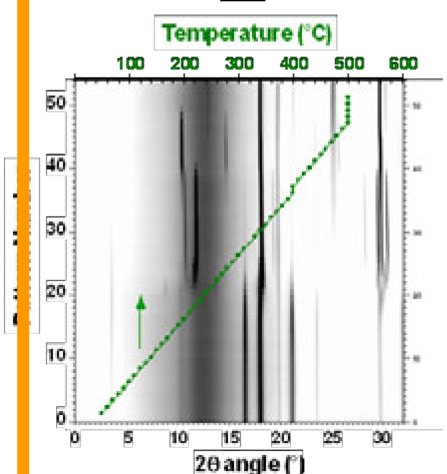


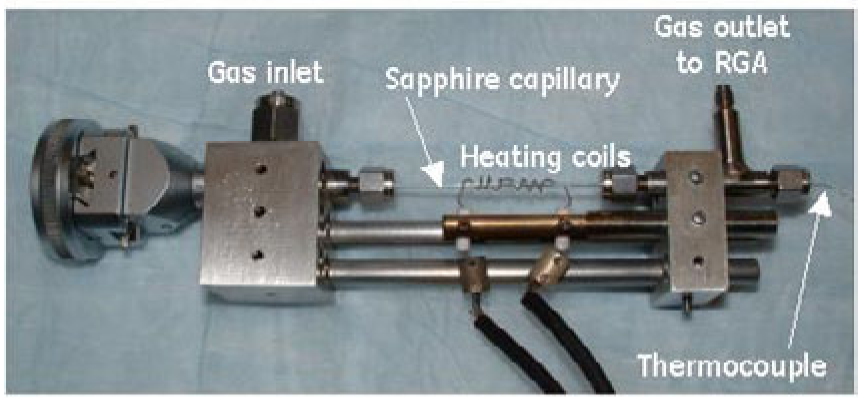




T: <400 °C P: <140 bar

T: <400 °C P: <70 bar



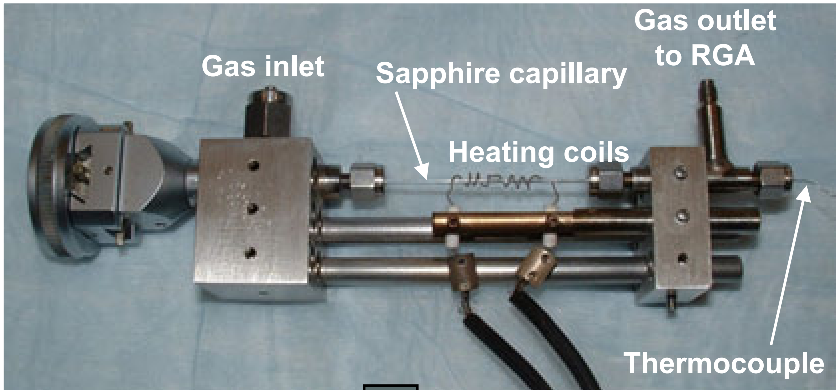


max T: 550 °C max P: 140 bar

Robust combinatorial/high-throughput methodology developed & validated by confirming the observations with bulk PCT tests

Combined *In-situ* XRD and gas analysis

Sample holder



max T: 550 °C max P: 140 bar

Diffraction setup

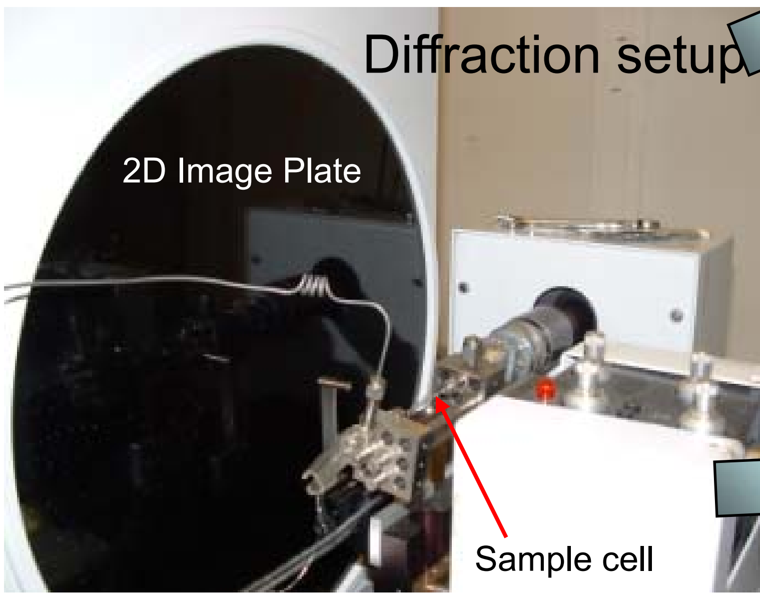
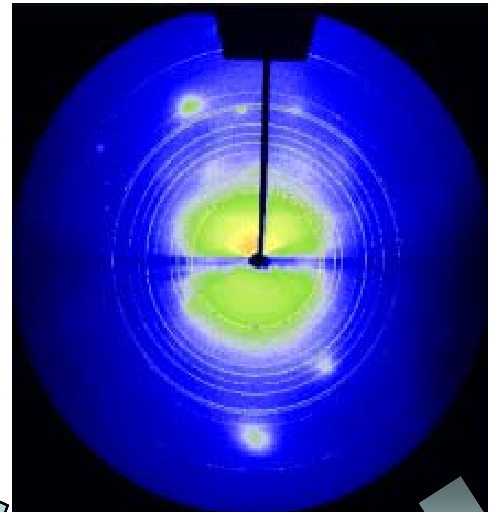
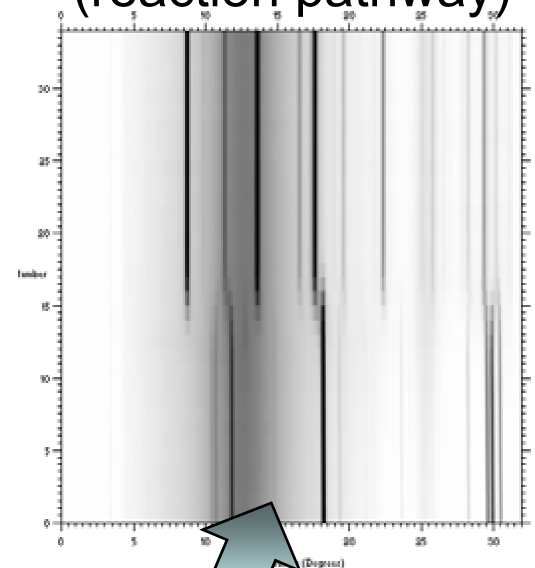


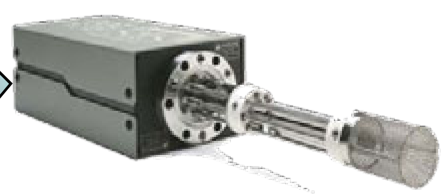
Image plate readout

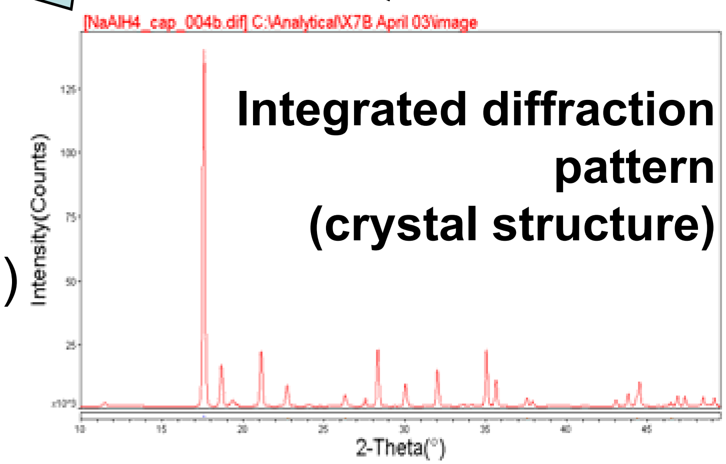


Time resolved patterns
(reaction pathway)



RGA (gas analysis)

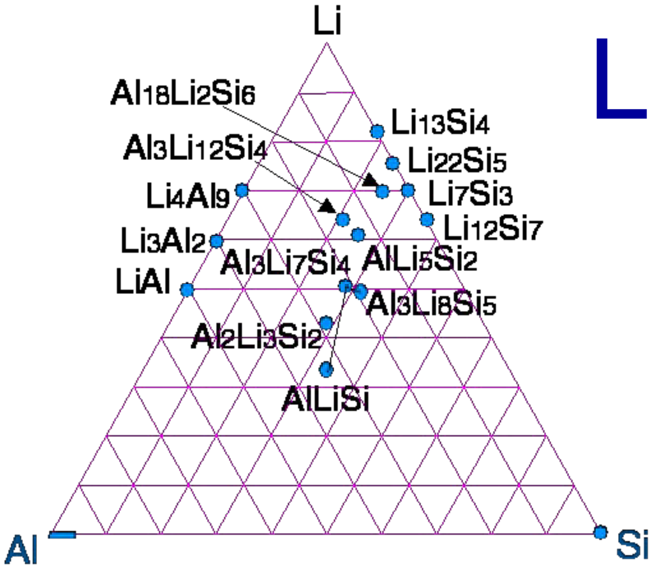




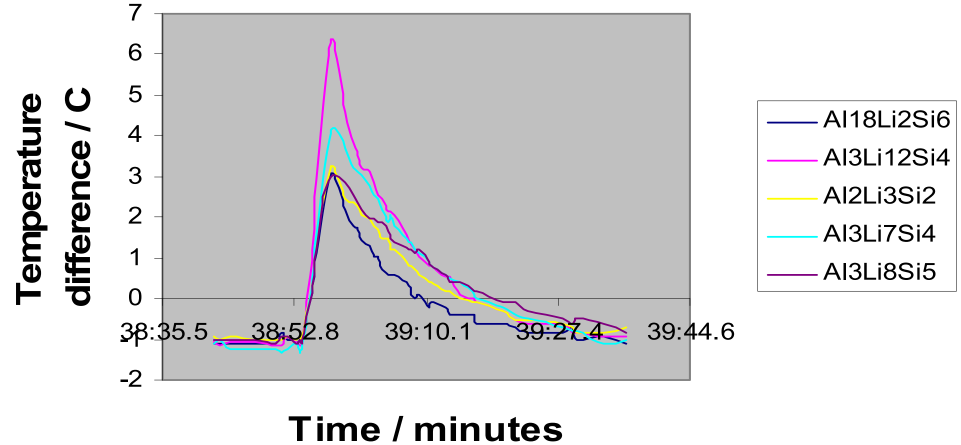
Integrated diffraction pattern (crystal structure)

Unique apparatus to provide unmatched information about reaction pathways / mechanism

Li-Al-Si System

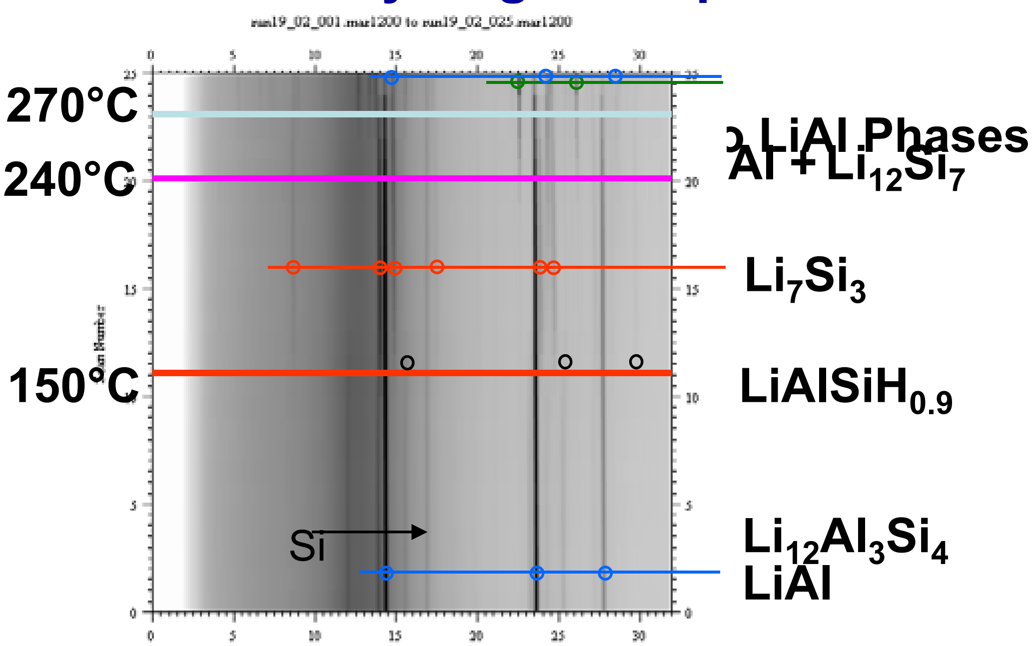


Thermal camera response for H_2 sorption, 150°C, 55 bar.

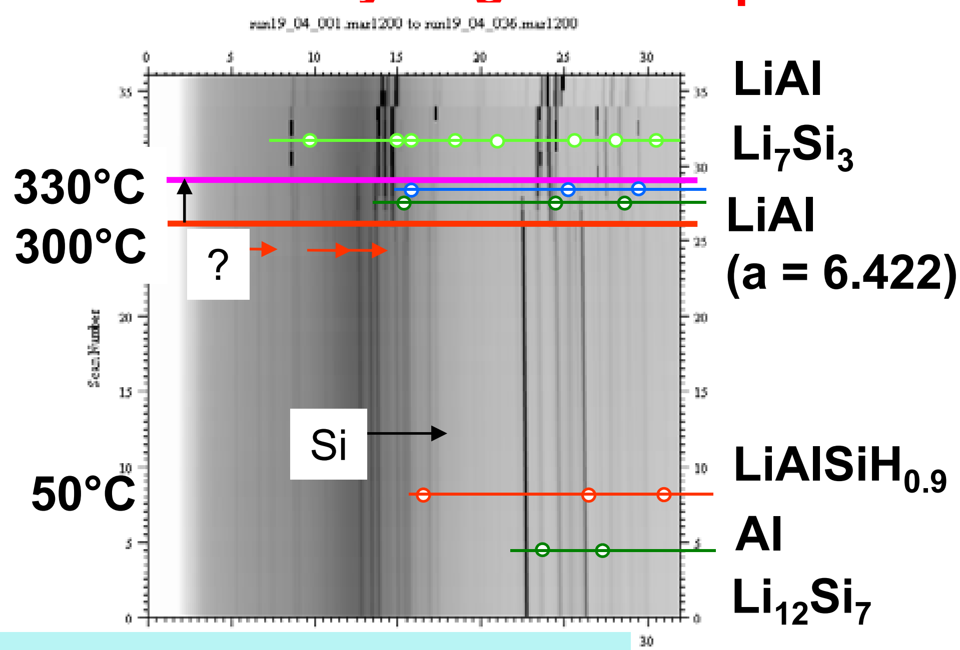


$$Li_{12}Al_3Si_4 + H_2 \Leftrightarrow AlLiSiH_{0.9}$$

In-situ XRD: Hydrogen Sorption



In-situ XRD: Hydrogen Desorption

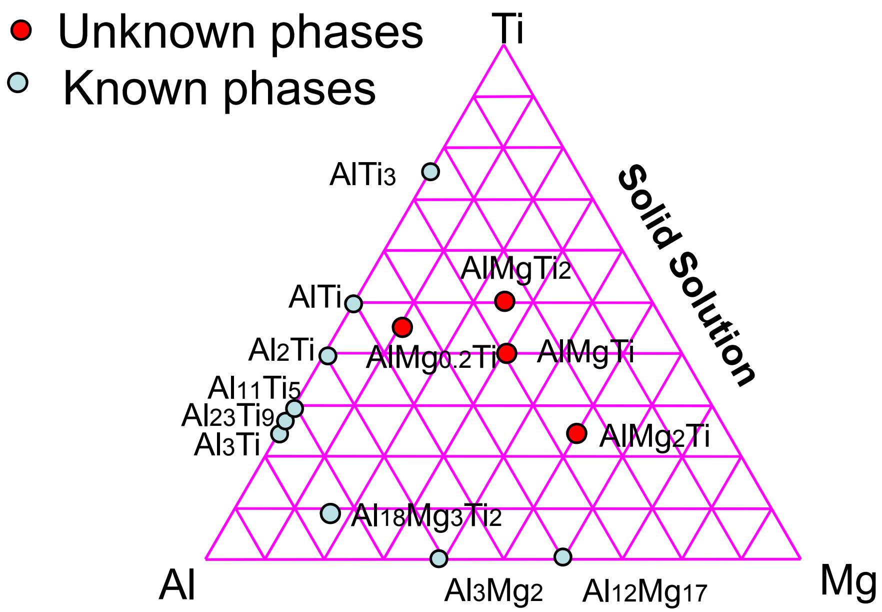


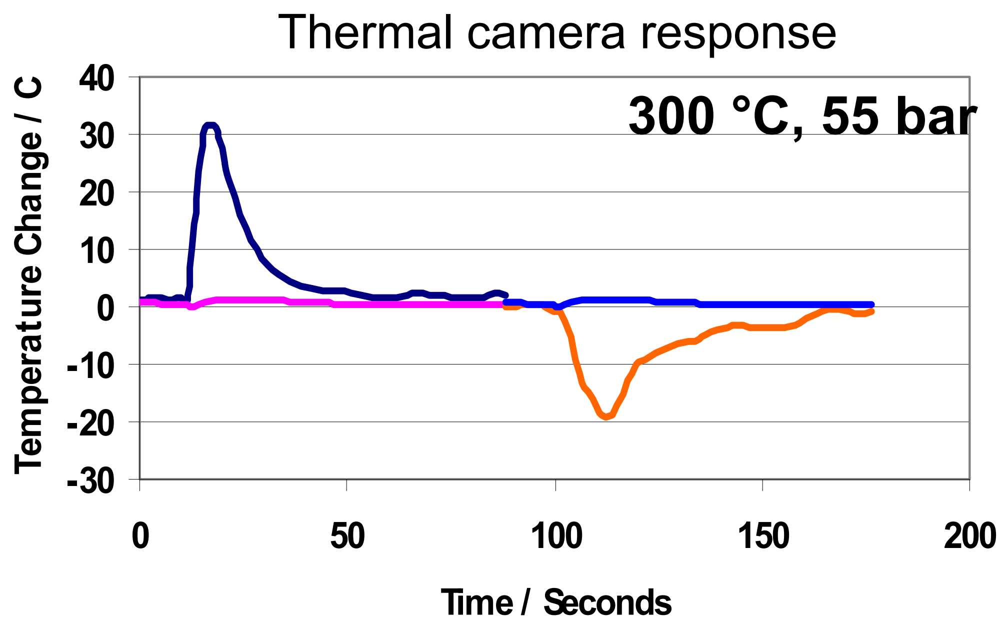
- New intermetallic compound reversibly absorbs up to 1.2 wt % H_2 at 150°C, 55 bar (desorption at 300°C)
- Found using diffusion multiple

imagination

METAL HYDRIDE CENTER OF EXCELLENCE

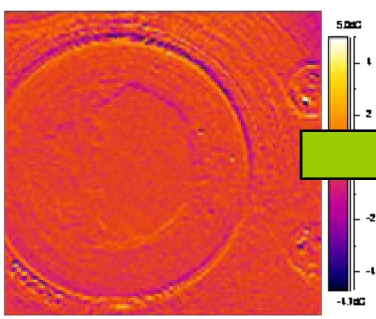
Al-Mg-Ti System



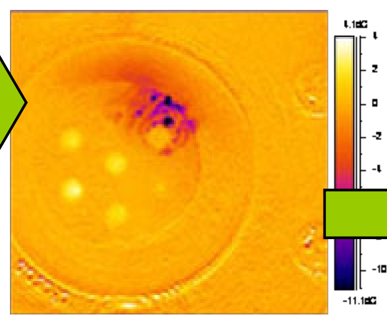


Thermographic Images: Hydrogen Sorption 55 bar, 300°C, blank subtracted.

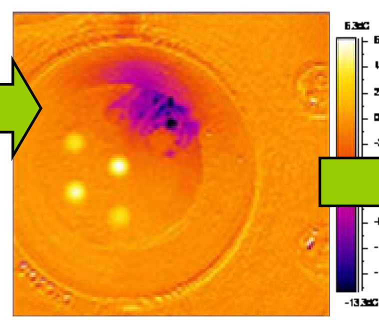
40 seconds



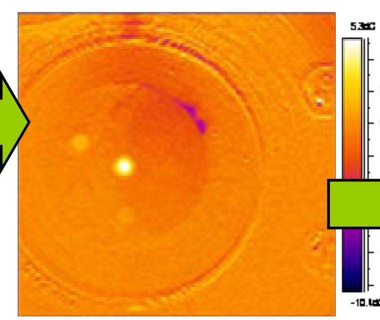
Before H_2 addition.



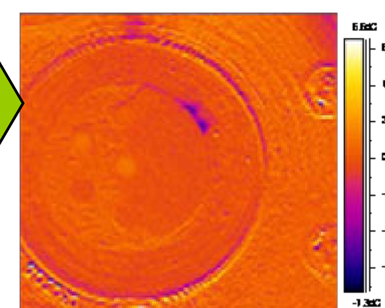
Immediate surface sorption.



10 sec after H_2 addition



30 sec after H_2 addition

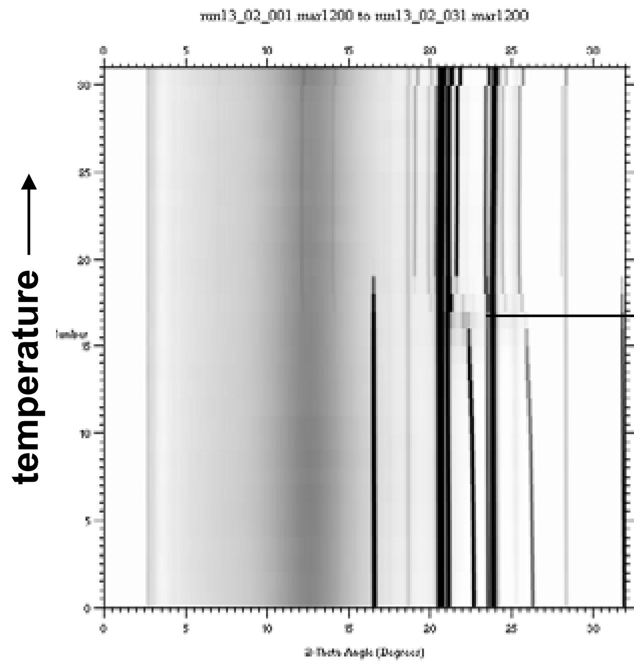


40 sec after H_2 addition

imagination at work

AlH_3 + 2 MgH_2 + TiH_2 *in-situ* XRD

Hydrogen Desorption

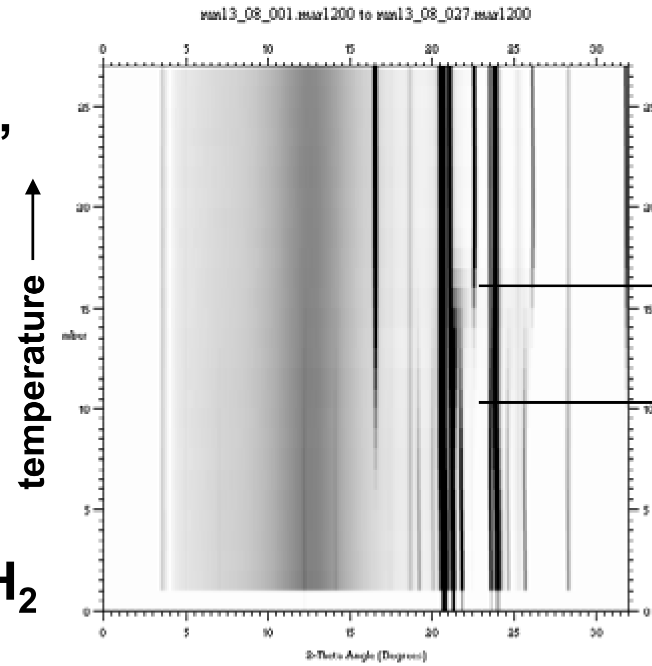


$Al_{12}Mg_{17}$, Mg, TiH_2
WC, MgO

290 °C

Al, MgH_2, TiH_2
WC, MgO

Hydrogen Sorption (130 bar)



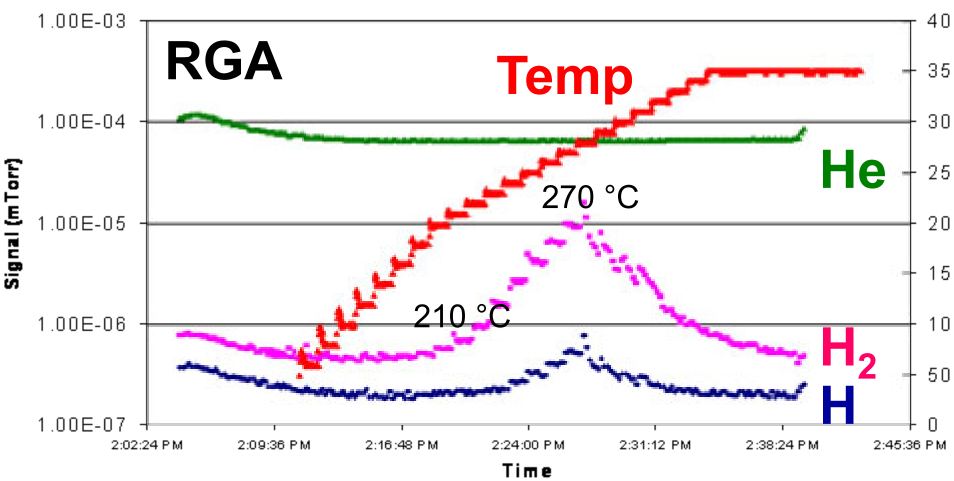
Al, MgH_2, TiH_2
WC, MgO

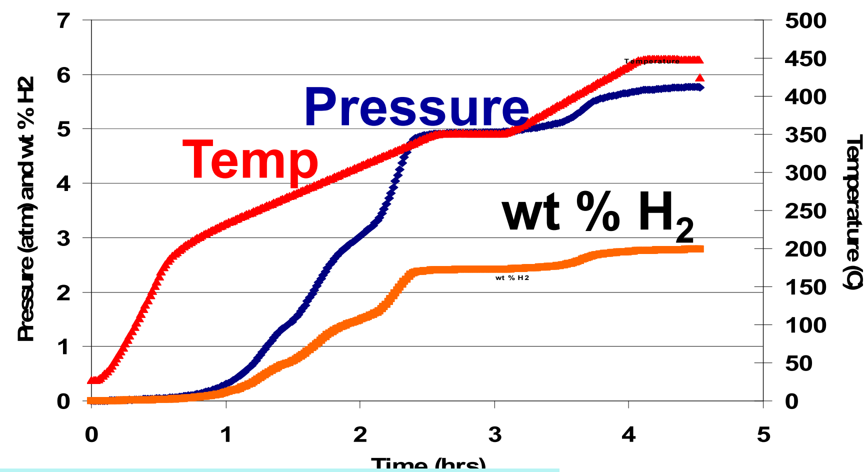
230 °C

185 °C

$Al_{12}Mg_{17}$, Mg, TiH_2
WC, MgO

MgH_2 + 0.71 Al ↔ $MgAl_{0.71}$ + H_2





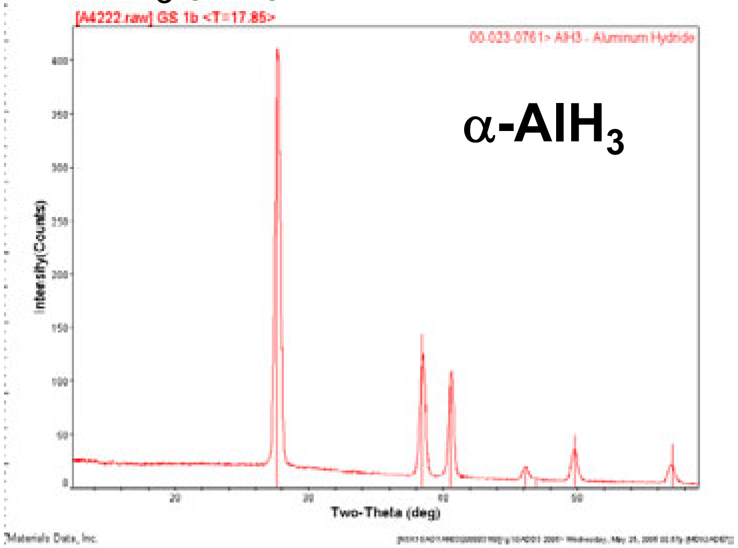
- Reduced T & wt.% but faster kinetics
- Found independently using multi-well shaker

imagination at work

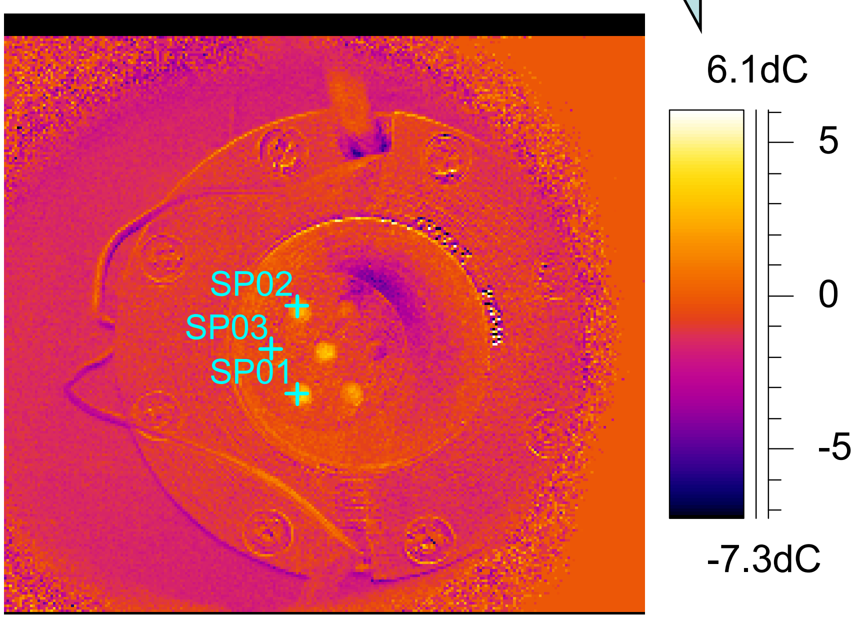
METAL HYDRIDE CENTER OF EXCELLENCE

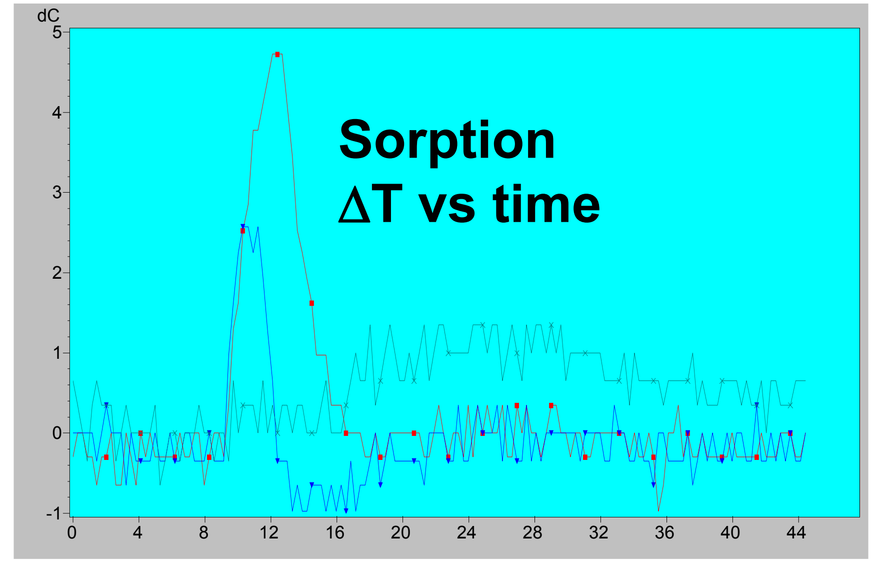
AlH_3 Doping

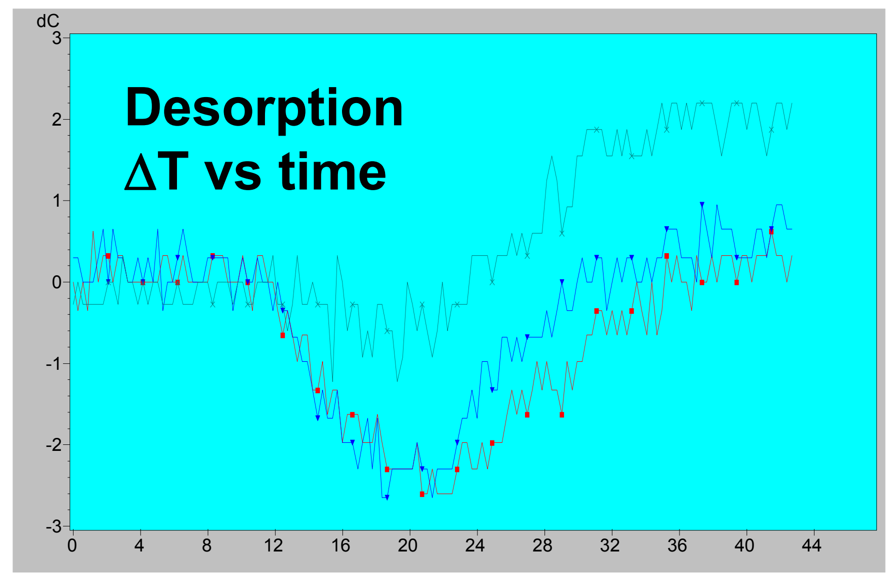
AlH_3 prepared in-house



Doping







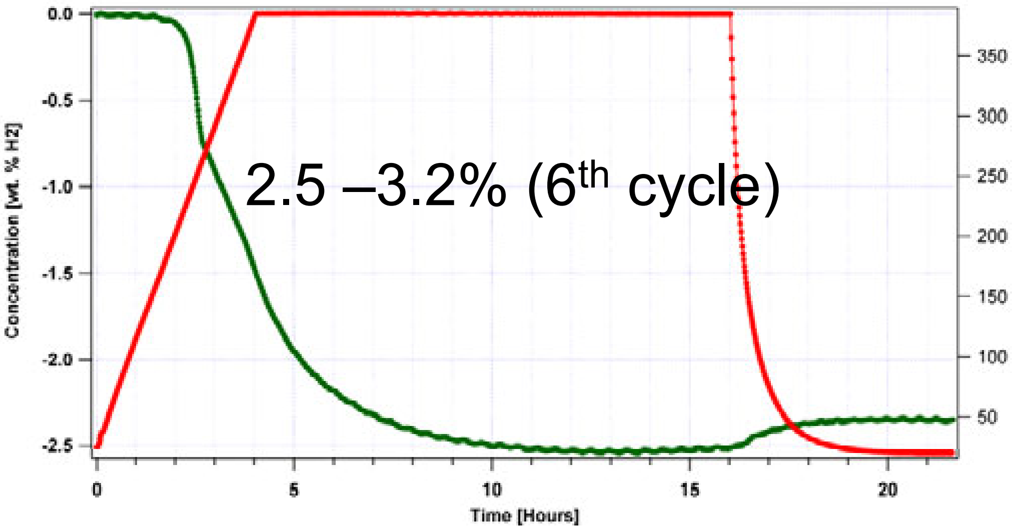
Over 100 composition investigated, only Si demonstrates reversibility.

imagination at work

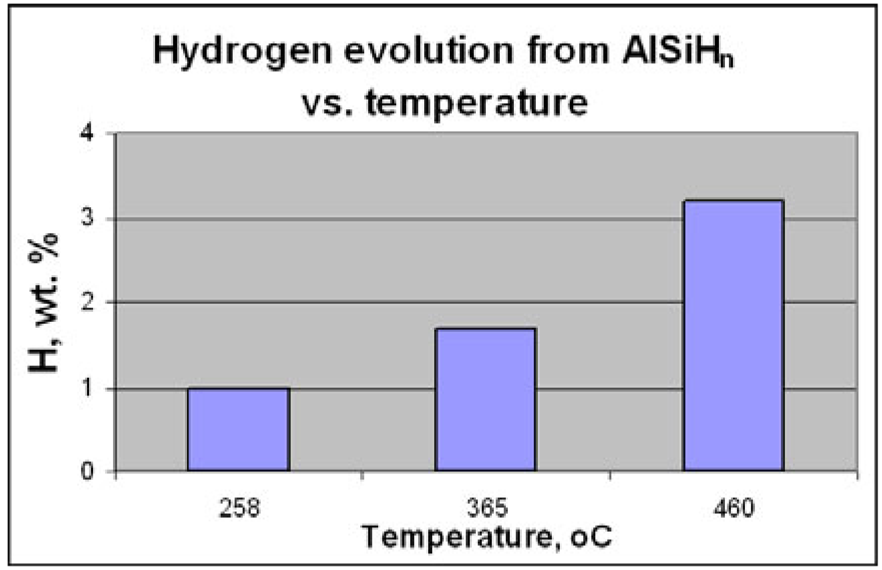
METAL HYDRIDE CENTER OF EXCELLENCE

Reversible AlH_3 + Si

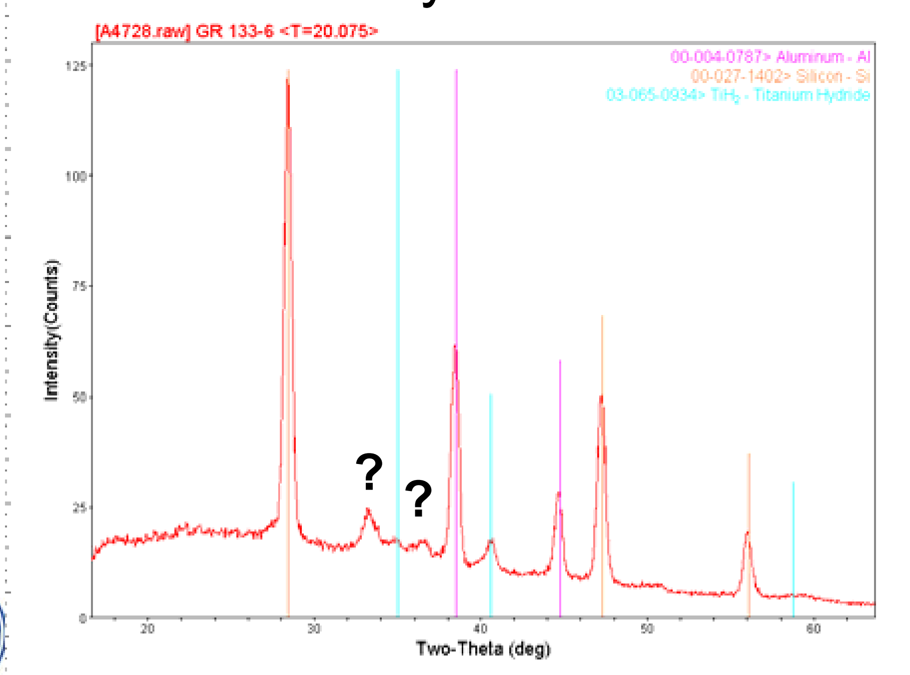
H$_2$ Desorption, 460C 1st Cycle



2.5 –3.2% (6th cycle)

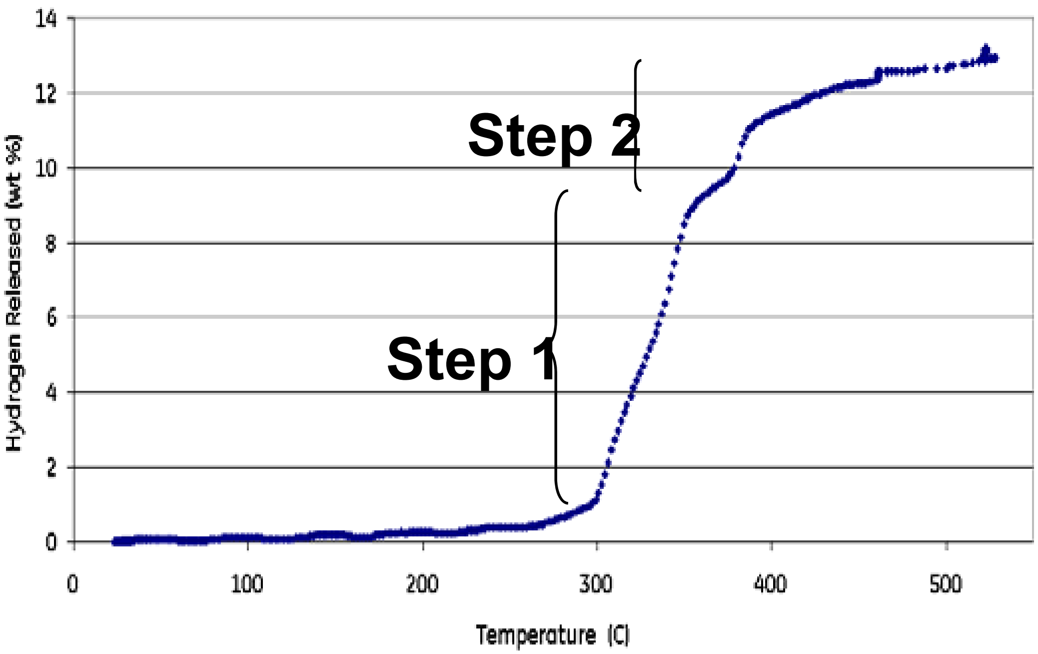


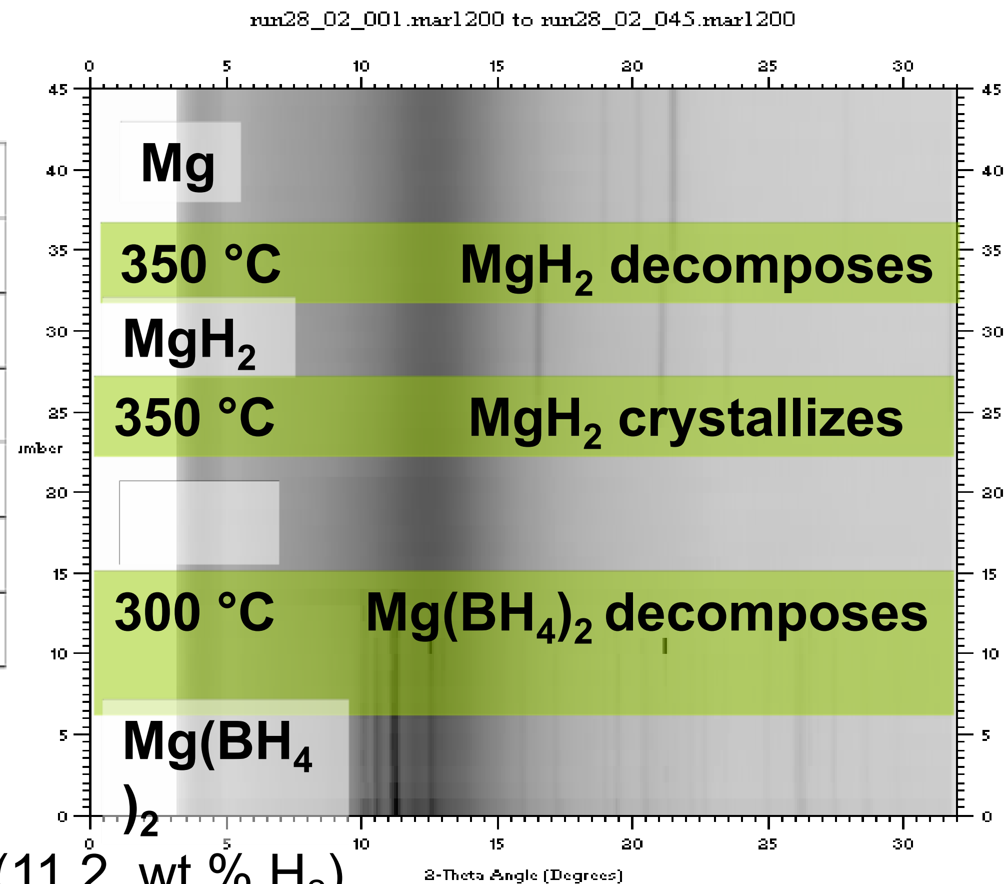
XRD Hydride State



- **Reversible store ~3 wt.% (400-460°C)**
- **Found using multi-well shaker**
- **Surprising finding**
- **Don’t understand what’s going on yet**
- **Shows the power of Combi/HTS**

Thermal decomposition of $Mg(BH_4)_2$





Step 1. $Mg(BH_4)_2 \rightarrow 2\,B + MgH_2 + 3\,H_2$ (11.2 wt % H_2)

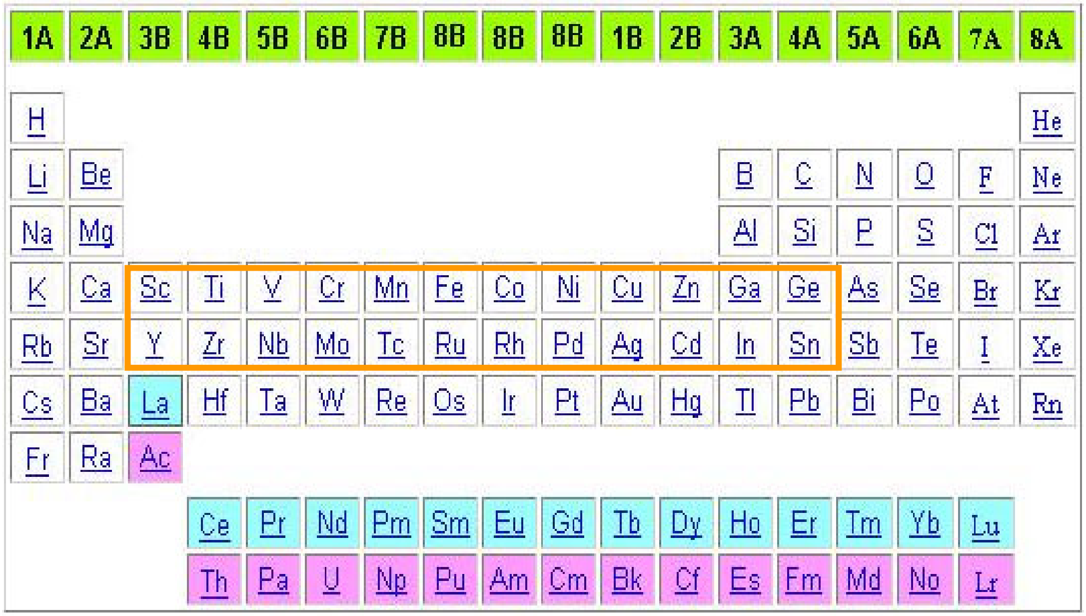
Step 2. $MgH_2 \leftrightarrow Mg + H_2$ (3.7 wt % H_2)

- Partial recharging possibly produced MgH_2 but with much lower T_{des}
- T_{des} decreased with Zn and Ti doping
- $Mg(BH_4)_2$ prepared in gram quantities – dopant & catalyst screening ongoing

Substitution and Catalyst Screening of $Mg(BH_4)_2$

Catalyst Doping

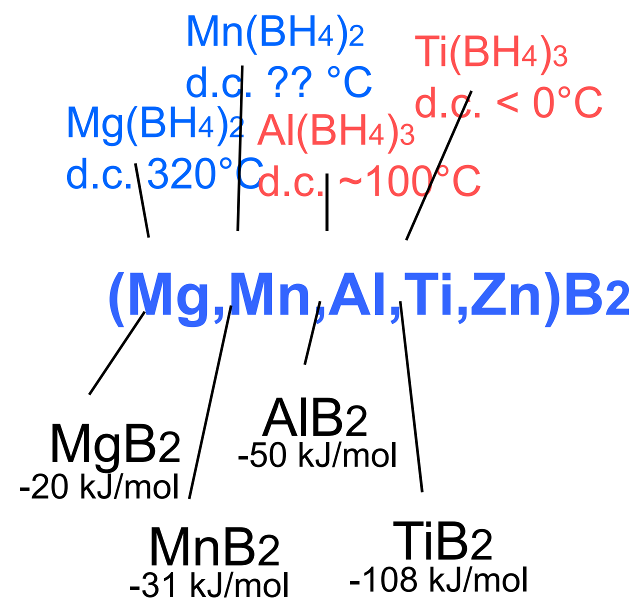
As chlorides and metals.



Also with addition of other hydrides

Substitution Concepts

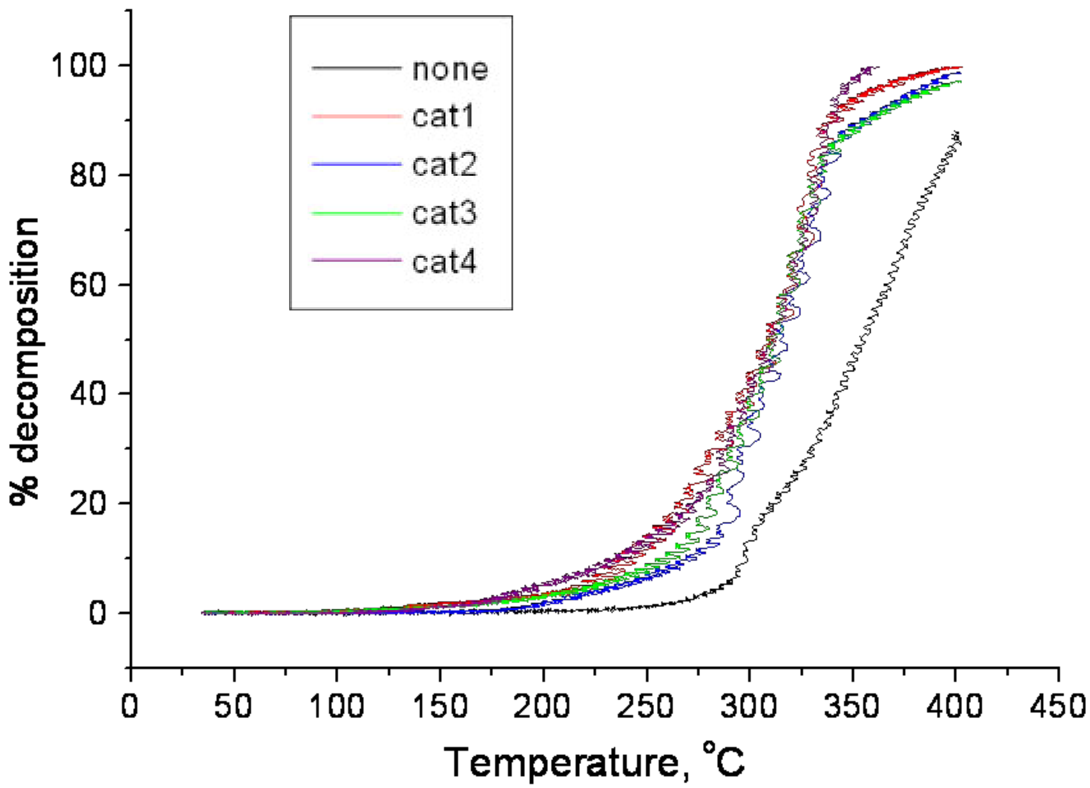
Promising concept to form metal boride alloys.



Over 100 combinations of single, binary and ternary compositions screened..no reversibility demonstrated for the first step.

Catalyst Screening for $Mg(BH_4)_2$

Hydrogen desorption from catalyzed $Mg(BH_4)_2$

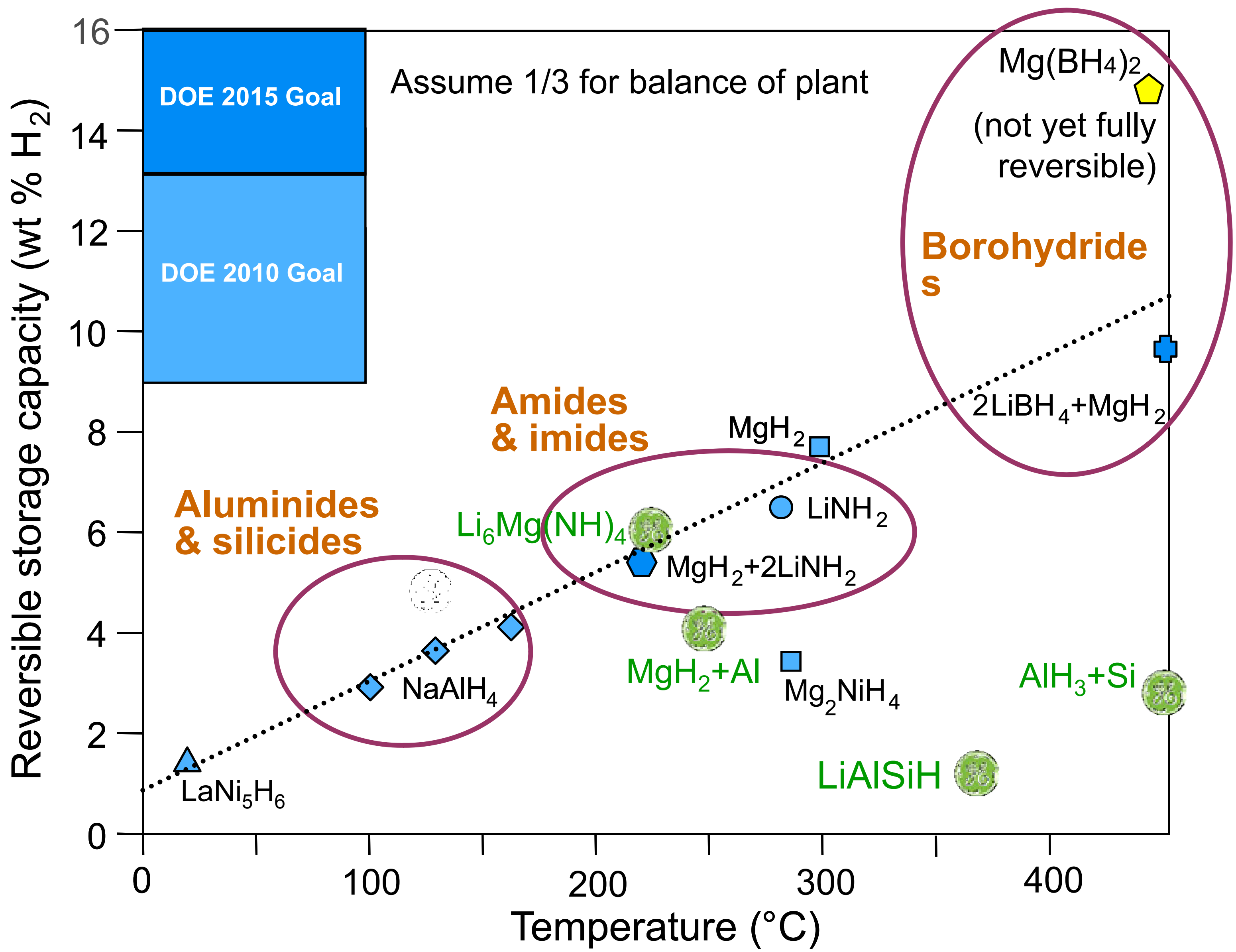


- Catalysts decrease the decomposition temperature by 50 – 70 ^{o}C and improve hydrogen desorption kinetics
- Found using 6-pack unit

imagination at work

METAL HYDRIDE CENTER OF EXCELLENCE

Metal hydrides against DOE targets



imagination at work

METAL HYDRIDE CENTER of EXCELLENCE

HTS Challenges

- High sensitivity to O_2 and moisture
- High reactivity of metals – materials corrosion
- Low spatial resolution
- Combining high temperature and high pressure
- Parallel wet synthesis/desolvation
- Catalyst/dopant introduction in metal hydride phase
- Quantification of adsorbed/desorbed H_2 at small scale
- Scale up of HTS findings

New methods for parallel wet synthesis of complex hydrides and analysis of their hydrogen storage characteristics needed

Summary

- Developed effective HTS methodologies
- Down-selected parallel ball milling and thermal imaging
- Successfully scaled materials and validated methodology
- Screened the aluminide and silicide compositional space
  - Low weight percent
  - Disproportionate
- Found low temperature $Al_{12}Mg_{17}$, with improved kinetics compared to MgH_2
- Discovered reversible AlH_3 + Si system
- Lowered the decomposition temperature of $Mg(BH_4)_2$ with some catalysts