Combinatorial approaches for hydrogen storage materials

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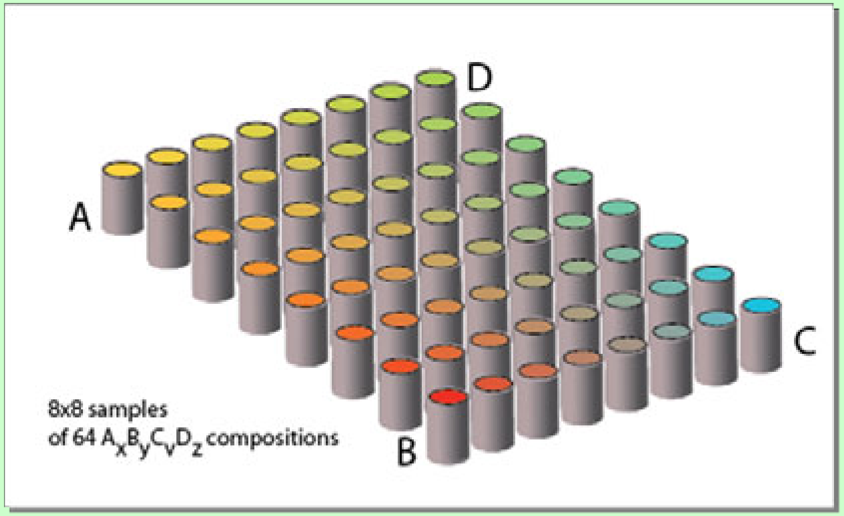
Two Main Challenges to Combinatorial Analysis of Hydrogen Storage Materials

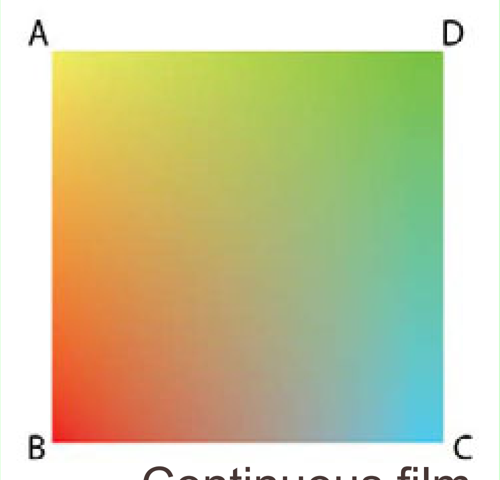
- Design and fabrication of appropriate materials libraries

- Rapid, quantitative measurements of hydrogenation phenomenon

We are attacking both of these problems at NIST

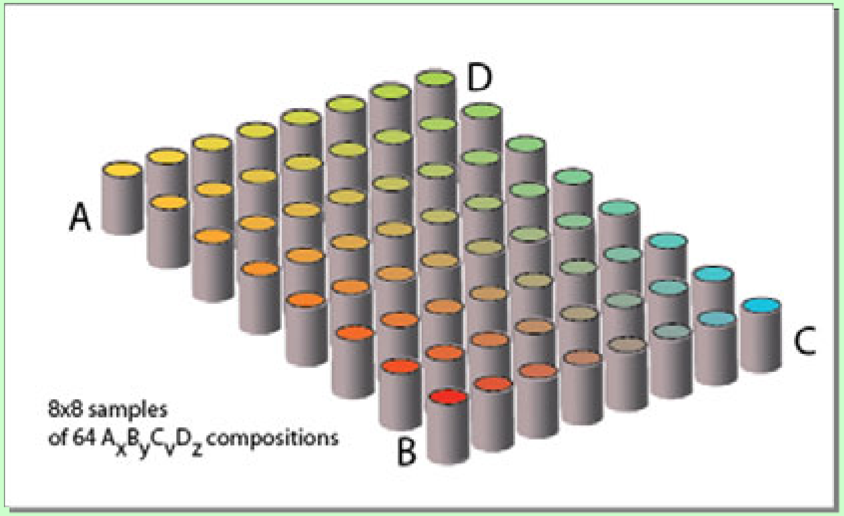
Combinatorial Library Fabrication



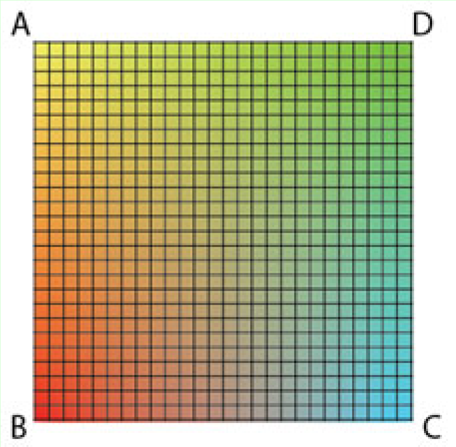


Continuous film

Combinatorial Library Fabrication

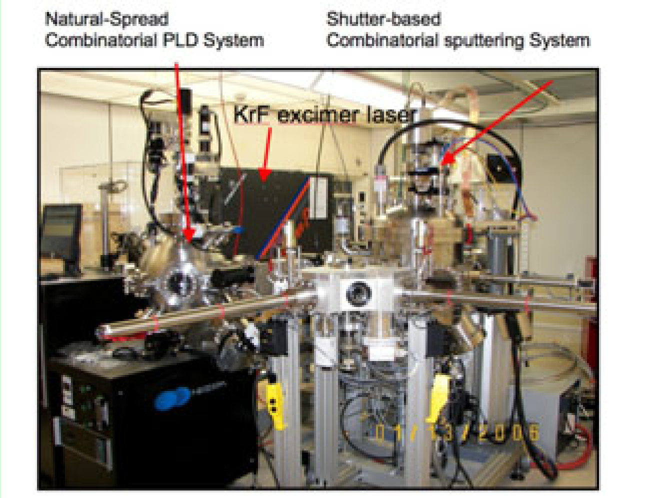


E-beam system with automated moving shutter/mask control



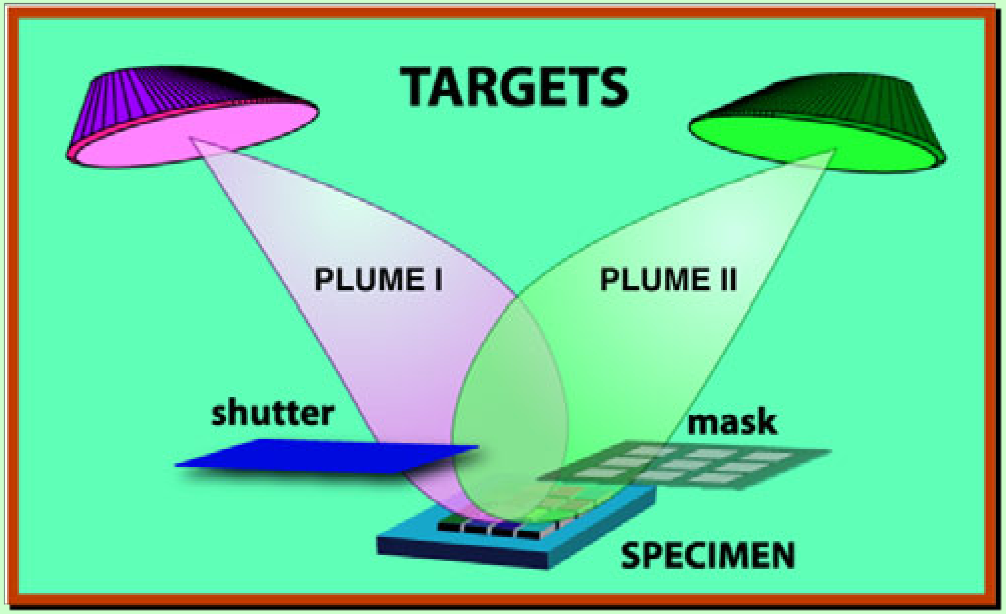
676 samples

Density of samples are determined by the spatial resolution and sensitivity of a measuring probe

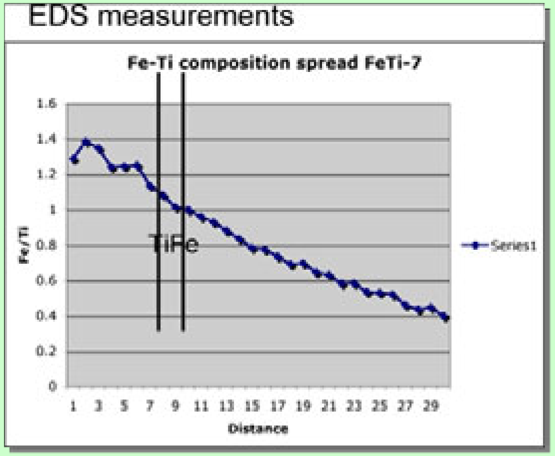


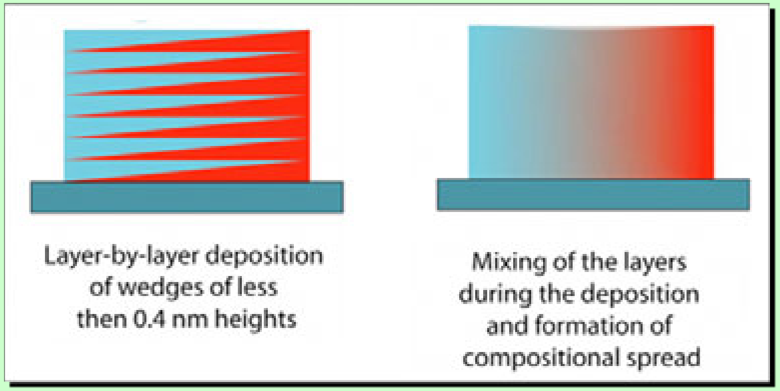
Dual PLD/Sputtering

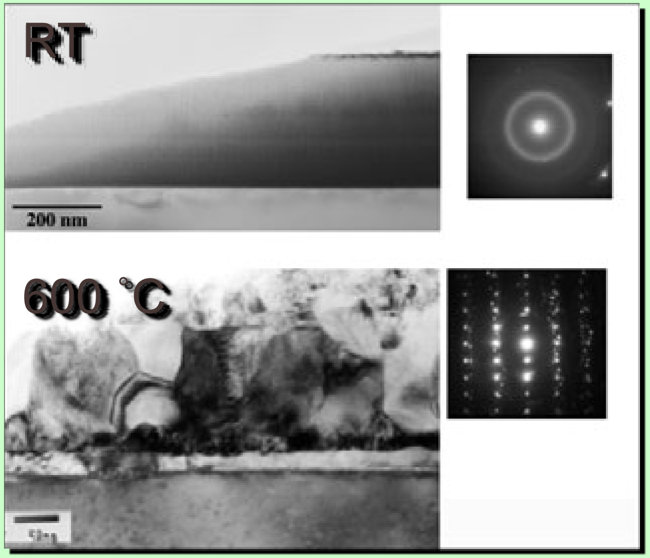
Combinatorial Library Fabrication



Fe-Ti Film







NIST Success in Combinatorial Methods

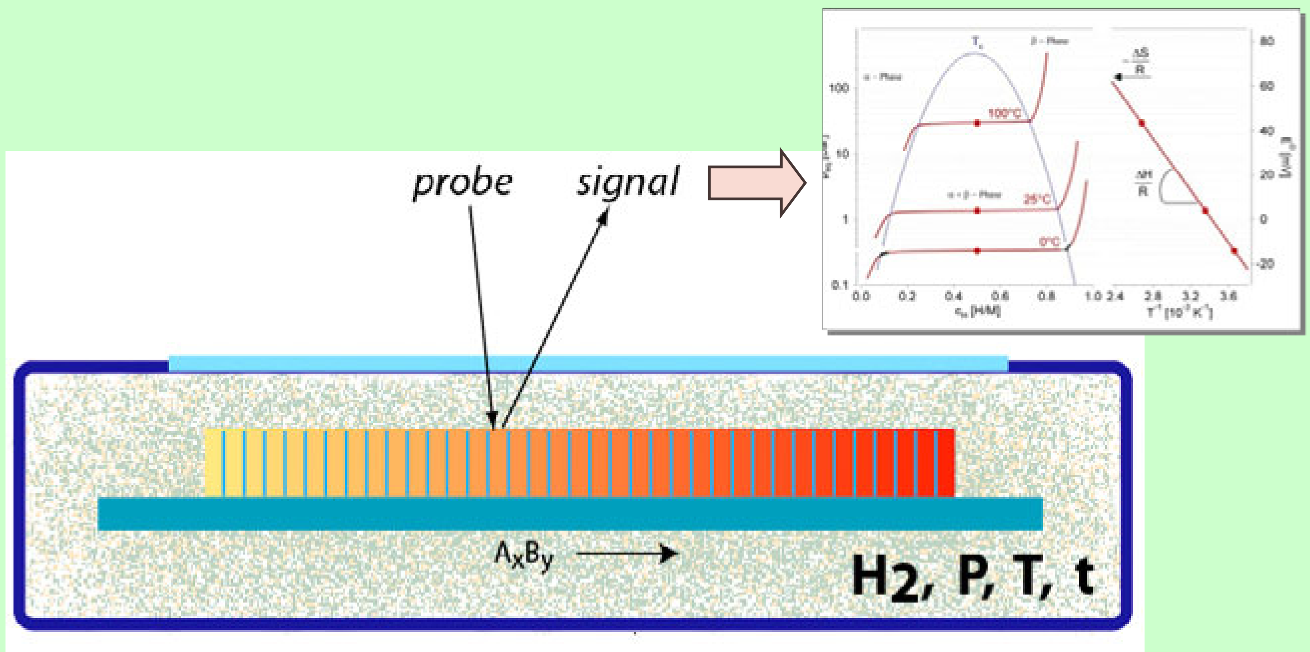
Studied systems	Properties	Synthesis	HTP Tools
*** $BaTiO_3$ - $SrTiO_3$**	High dielectric material for microwave	PLD, Precursors, multilayers	Scanning microwave microscope
*** ZnO-MgO**	band gap of ZnO semiconductor	PLD multilayers	Optical transmission
*** $LaMnO_3$ - $CaMnO_3$**	CMR material, magnetic diagrams	PLD multilayers	Magneto-optical imaging
*** $BaTiO_3$-$CoFeO_4$**	Multiferroic material	PLD multilayers	Scanning SQUID Scanning microwave microscope
Metals on GaN	Electric contacts	e-beam	Electrical measurements
*** $Fe_{(1-x)}Ga_x$ (x=0-0.4)**	Magnetostriction	Sputtering Co-deposition	Micromachined cantilevers
Fe_2Ti-FeTi-Ti_2Fe	Hydrogenation	e-beam multilayers	IR imaging
Mg-Mg_2Ni-MgNi	Hydrogenation	e-beam multilayers	IR imaging
$LaNi_5$, FeTi, Pd	Hydrogenation	PLD, Sputtering	Nanocalorimetry
TaN - AlN	Advanced gate stack for Si CMOS	Reactive Sputtering	Automated C-V analysis
$(Ca_{1-x-y}Sr_xLa_y)_3Co_4O_9$	Thermoelectric (Seebeck coefficient)	PLD	Automated Seebeck coefficient measurements

* - in collaboration with Prof. I. Takeuchi, UMD

High-throughput metrology for combinatorial analysis of hydrogenation

Ultimate Goal

To measure the hydrogenation process in a library element (A_XB_Y)
(amount of H in the material at given P, T and time)



High-throughput metrology for combinatorial analysis of hydrogenation

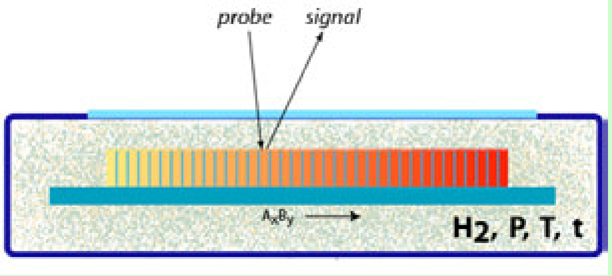
Ultimate Goal

To measure the hydrogenation process in a library element ($A_X B_Y$)
(amount of H in the material at given P, T and time)

Indirect measurements of H concentration:

Changes in physical properties due to hydrogenation; in-situ; correlation between the amount of hydrogen and the physical property:

- ➓ Optical transmission (metal-to-insulator) *Prof. Griessen group*;
- ➓ Cantilever bending (stress changes) *Ludwig*;
- ➓ IR emissivity *GM, GE, NIST*;
- ➓ Micro-R*aman NIST;*
- ➓ *MOKE (NIST-Boulder)*;



Limitations:

- Not universal (material-dependent)
- Difficult to estimate the amount of hydrogen

Thin-Film Nanocalorimetry of Hydrogen Absorption

- Calorimetric signatures:
  ΔH (absorption) -> exothermic
  ΔH (desorption) -> endothermic

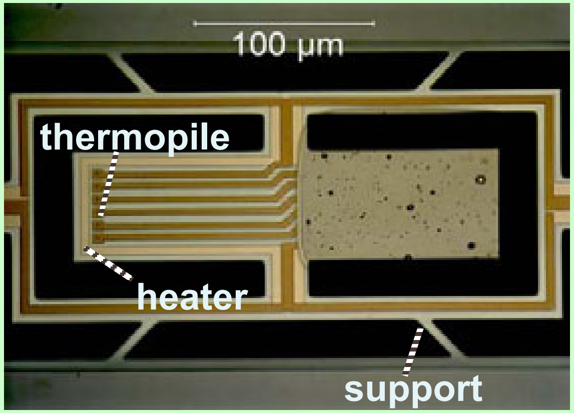
- Sensors will measure:
  1) enthalpy,
  2) activation energy
  of hydrogenation in thin-films

- Sensor size is suitable for combinatorial arrays

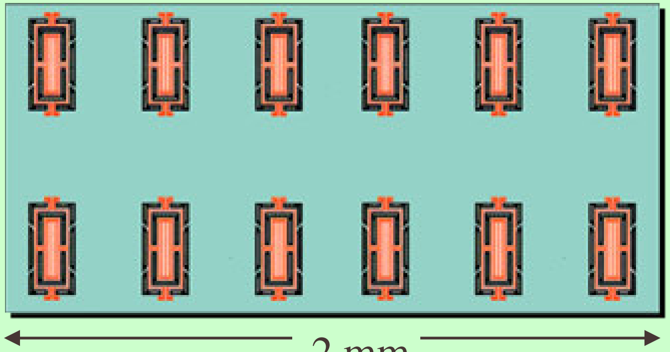
L. Cook, M. Green (MSEL, NIST)
R. Cavicchi (CSTL, NIST)

MEMS DSC Sensor

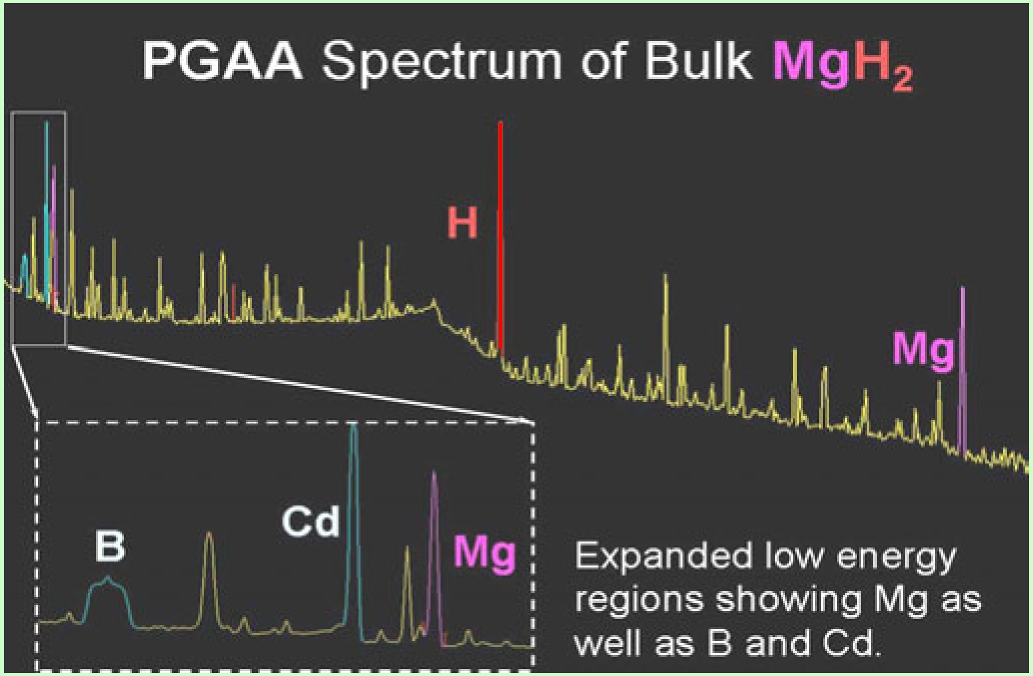
Reference side (uncoated) | Sample side (PLD-$LaNi_5$)



Propose Array of DSC Sensors



DIRECT Measure of Hydrogen Content
Prompt Gamma Activation Analysis



Technique Features:

- Quantitative
- Multi-element Analysis (H)
- Non-destructive
- Easy Sample Preparation

PGAA: non-destructive, multi-elemental analysis technique

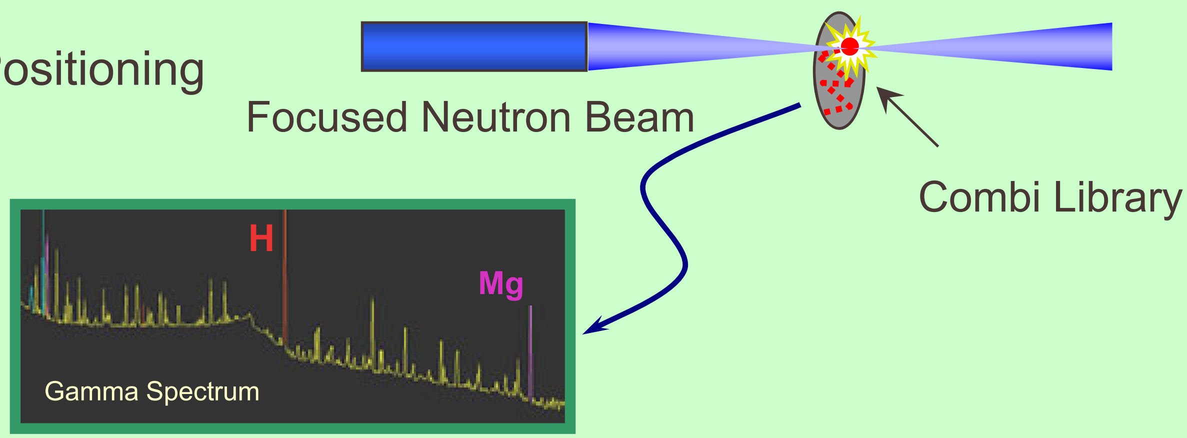
- Neutron Beam irradiation of sample → γ-ray emission
- γ-ray spectra give elemental composition and concentration (even hydrogen!)
- Quantitative when calibrated with elemental standards

Chemical Science and Technology Laboratory (NIST: CSTL)

Making the PGAA Combi

Three Analytical Challenges

- **Analysis of thin film specimens**
  - Target: Library Arrays
    0.3 μm to 4 μm thick films
  - Elemental: phase diagrams
- **Spatial Mapping**
  - Neutron Optics
  - Gain in Quantitation
  - Gain in Resolution
- **Environmental Control**
  - Temperature
  - Pressure
  - Absolute Positioning



Summary

NIST Library Fabrication

- Library deposition facilities suitable for metallic specimens in place
- New chambers will work with Li, Ca, B → borates, amides…

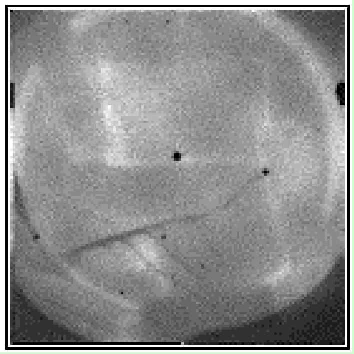
NIST Measurements

- In-situ Combi Prompt Gamma Activation Analysis (PGAA)
  - Quantitative H concentration measurements
  - Simple for interpretation, equivalent to the standard PCT measurements.
  - Leverages upgrade of NIST Center for Neutron Research
  - Lots of potential, challenges for combi
- Nanocalorimetry arrays
  - Rapid screening of hydrogen absorption
  - Parallel tracking of storage material kinetics

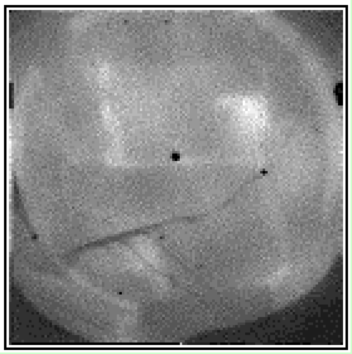
Infrared emission characterization of hydrogenation

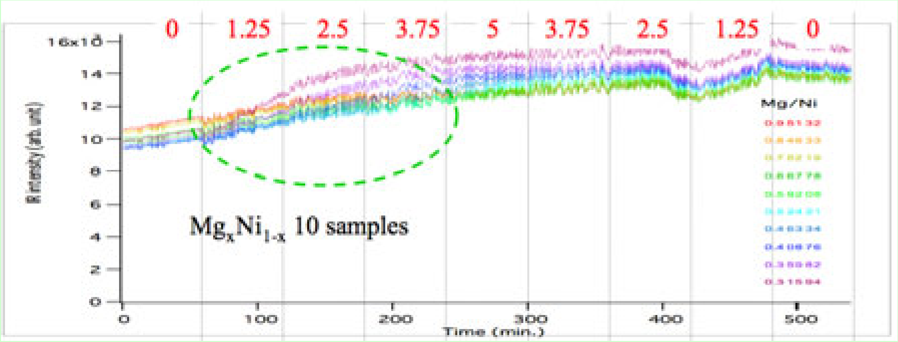
Example of hydrogenation of the Mg_7Ni-$MgNi_2$ compositional spread

IR image at 200 ˚C, P=0 atm

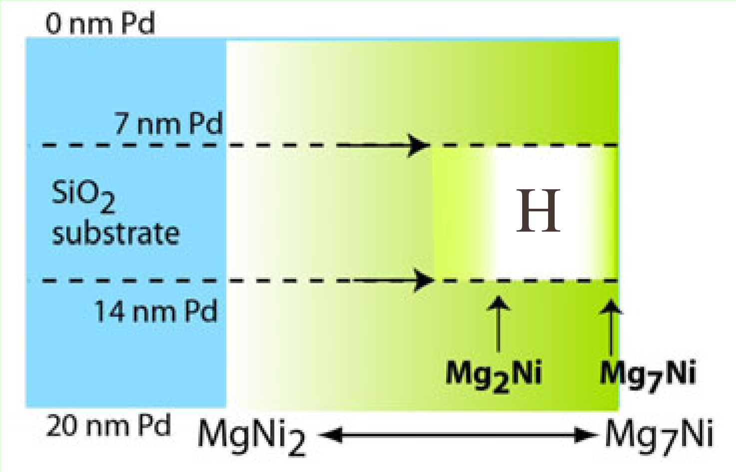


IR image at 200 ˚C, P=2.5 atm





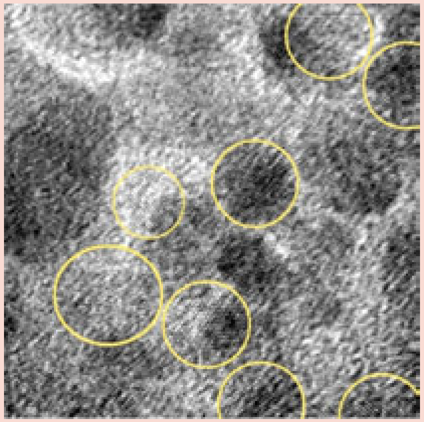
Evolution of IR intensity with time for different compositions of the film (200 ˚C at different pressures of H_2).



Schematic drawing showing that the maximum increase in IR intensity occurred for the compositions ranging between Mg_2Ni and Mg_7Ni, and Pd coating thicker then 7 nm. According to TEM, thinner Pd coating doesn’t cover Mg-Ni film and therefore oxidation prevents hydrogenation of the film.

NIST Hydrogen Storage Initiative - M^3 of MSEL Tasks

Materials



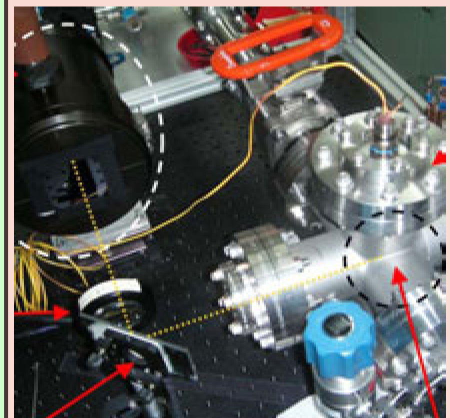
Combinatorial thin films of light-weight alloys

Metal-doped carbon-based thick porous films

Light-weight TCP intermetallic compound and quasicrystals

Mg bulk and rapidly solidified alloys

Measurements



High-throughput metrology for combinatorial search

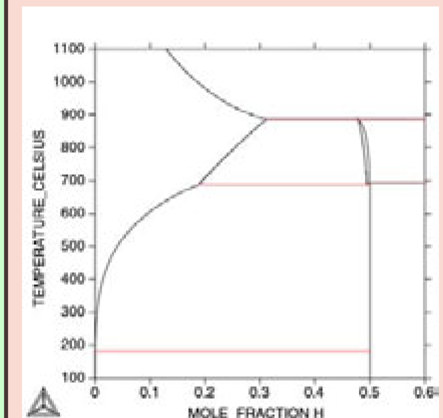
- In-situ IR emissivity
- In-situ micro-Raman
- In-situ PGAA of films
- In-situ MOKE of films

TEM of hydrogenated materials

Nanocalorimetry

In-situ synchrotron studies, SANS, x-ray

Modeling



CALPHAD

Thermodynamic modeling

Thermodynamic database to support experiments

HIGH THROUGHPUT/COMBINATORIAL SCREENING OF HYDROGEN STORAGE MATERIALS

OBJECTIVES

- **Assess the potential for High Throughput Screening/Combinatorial methods to benefit and accelerate Hydrogen Storage Materials R&D**
- **Identify the advantages and disadvantages of the application of High Throughput/Combinatorial techniques to Hydrogen Storage Materials R&D**
- **Match High Throughput Screening/Combinatorial techniques with specific types of Hydrogen Storage Materials**
- **Identify the technical challenges and limitations associated with applying these techniques to Hydrogen Storage Materials R&D**
- **Recommend appropriate ŅNext Steps,Óif any, to advance the application of these techniques to hydrogen storage materials**

PRELIMINARY AGENDA

9:00am Welcome/Introductions/Objectives - Ned

9:10am Status of Hydrogen Storage Materials R&D - Sunita

9:30am Summaries of Present High Throughput Screening/Combinatorial Activities (20 minutes each)

- Intematix
- UOP
- GE Research

1030am Break (15 minutes)

- NIST
- UCF/DoD
- Symyx Technologies
- Others from the Audience (30 minutes)

12:00pm Lunch

1:00pm Breakout Group Discussions Š Led by Carole, Grace, Ned
(3groups-metal hydrides, adsorbents, chemical hydrogen storage)

- Benefits of Hi ThruPut Screening/Combinatorial Techniques
- Challenges/Disadvantages
- Matching of Techniques w/ specific storage materials

2:30pm Break

2:45pm Breakout Group Summaries Š Sunita or Ned
Action Items
Open Discussion
Next Steps

4:00pm Adjourn