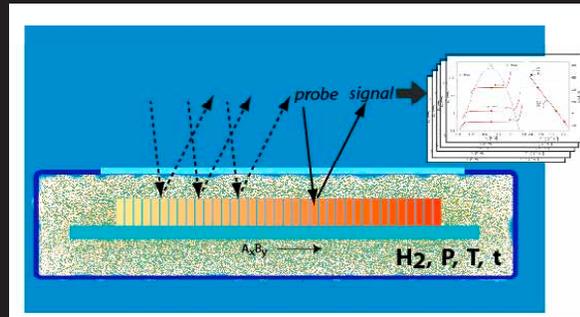


Hydrogen Storage

Objective

The goal of this project is to develop the metrologies necessary for rapid, high-throughput measurement of the hydrogen content of novel materials proposed for hydrogen storage and for electrodes in Ni-MH batteries. The project focus is bringing direct methods including volumetric measurements and Prompt Gamma Activation Analysis to the stage where they can be used as reference methods for calibration of indirect methods including infrared (IR) and Raman spectroscopies that are more readily available to the research community.



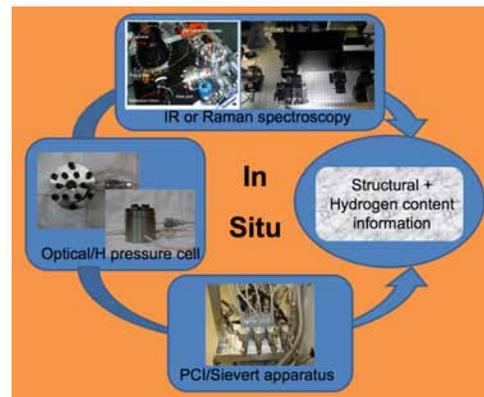
Impact and Customers

- Hydrogen is promoted as a petroleum replacement in the hydrogen economy, presenting an attractive alternative for fueling automobiles and trucks while maintaining a healthier global environment. A major roadblock associated with the use of hydrogen is the inability to store it efficiently.
- High throughput measurement tools for determining hydrogen absorption and desorption characteristics will accelerate discovery of new materials that can store hydrogen in a useful manner.
- Correlation of direct and indirect measurements of the hydrogenation process, and high throughput methods to accelerate the measurement process, for instance through study of combinatorial samples, are essential in developing a high throughput methodology.
- Industrial R&D, academia, and national labs are potential customers to use the developed methods as fast screening tools in their research of novel materials for hydrogen storage.



Approach

The evaluation of candidate storage materials is complicated by a lack of readily available methods for the direct measurement of hydrogen content. MSEL is working with researchers from CSTL, NCNR, and PL to provide measurement tools to fill this gap. Prompt Gamma Activation Analysis (PGAA) and volumetric Sievert PCI measurement are direct methods for measuring hydrogen but are not commonly accessible. Infrared (IR) and Raman imaging/spectroscopy methods, being developed at NIST, could be made widely available but are not capable of directly measuring hydrogen content. Using measurements of hydrogen content with PGAA and PCI to calibrate IR and Raman imaging/spectroscopy methods, NIST will provide accurate screening methods, widely usable by industry, with the high spatial resolution needed for the development of storage materials. These methods are being tested on combinatorial thin films that the Metallurgy Division prepares using a multilayer deposition technique in a customized electron beam evaporation deposition chamber. Currently the focus is on Mg-based films and complex borohydrides, which are of great interest to the hydrogen storage community.



Accomplishments

The Metallurgy Division has successfully demonstrated an in-situ IR emissivity imaging method that is able to capture the reaction between Mg-transition metal (TM) alloys and hydrogen gas and is sensitive to variations in composition, heat treatment and alloying.

We have this year developed a method to measure in-situ growth rates of hydride phases during metal-hydride phase transformations in thin films. The method relies on infrared emission imaging of wedge-shaped thin films during hydrogen loading and reveals the effects of alloying on Mg hydride growth rates (Figure 1). For example, it was found that the hydrogenation rate is increased by an order of magnitude when 3.1 at. % of Fe is added to Mg and that the thickness of the hydride layer is more than twice that of the hydride layer in pure Mg. The measurements can be used to guide the design of powder dimensions for hydrogen storage applications.

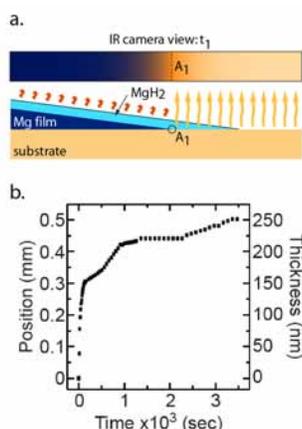


Figure 1 (a) Schematic of the wedge-shaped film during hydrogenation, forming a layer of IR-transparent hydride phase (MgH₂). Strong IR emission from a substrate through the fully hydrogenated region but not through untransformed film establishes a boundary A1 that corresponds to the hydride layer thickness at that particular time. (b) Plot from the hydrogenated Mg_{98.4}Ti_{1.6} film shows propagation of a hydride/

metal front (through approximately the A₁-boundary position) as a function of hydrogenation time.

Continuing earlier work toward quantifying hydrogen storage measurement techniques, a combined optical/Sievert's apparatus cell was built. The optical cell can attain pressures as high as 5.5 MPa and temperatures up to 723 K and can measure changes in the hydrogen content of a sample down to 0.5 μg. The new instrument allows simultaneous acquisition of volumetric data (hydrogen content) and either normalized IR emissivity (NIRE) or Raman spectroscopic data of powders or thin films during hydrogen loading/unloading. In-situ measurements of the NIRE of a stack of Mg thin films confirmed previous ex-situ PGAA/in-situ NIRE results that indicated NIRE response saturates before the films have completely hydrogenated. Measurements on Mg powders, however, show good correlation between NIRE response and hydrogen content.

The use of Raman spectroscopy to investigate the high temperature and pressure behavior of technologically interesting powder samples was an emphasis of this year's work. Simultaneous volumetric and Raman spectroscopic measurements on the mixed Li₄BN₃H₁₀ and Mg(NH₂)₂ powder system were used to assess the use of Raman spectroscopy as a semi-quantitative technique for monitoring hydrogen content and the chemical/structural changes during hydrogen desorption. (Figure 2) By observing the Raman peak intensities of Li₄BN₃H₁₀ and Mg(NH₂)₂ as a function of temperature and correlating this with known hydrogen desorption of these powders the behavior was seen to be decomposition of both phases into Li₂Mg(NH)₂. It was also demonstrated in this system that upon rehydrogenation at 8 MPa and 423 K the Raman modes indicate partial reversibility of reactions. Further, it was found that monitoring the Raman peak intensity of the product phase Li₂Mg(NH)₂ during hydrogen desorption in this system provided a satisfactory fit to the volumetric response of the powder.

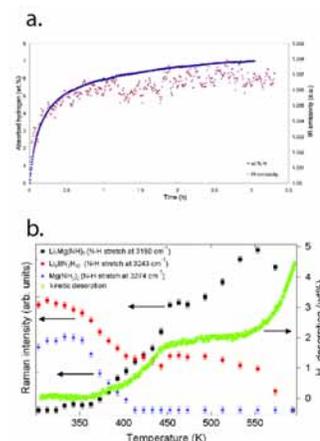


Figure 2 (a) Comparison of NIRE and Sievert's response of Mg powder during charging at 573 K in 20 MPa of hydrogen. The increase in NIRE closely matches the increase in hydrogen content of the powder, saturating at the same time. (b) The normalized Raman peak intensity as a function of temperature for the N – H stretches of Li₄BN₃H₁₀, Mg(NH₂)₂, and Li₂Mg(NH)₂.

This year we also started utilizing transmission electron microscopy (TEM) to address critical issues of the formation, microstructure and crystallography of hydrides. A systematic TEM study has been carried out to characterize in detail the microstructures of hydrogenated epitaxial yttrium films. The key results and observations are summarized as follows: The phase transformation from Y to YH₂ is associated with the nucleation and growth of two twin variants. Superlattice reflections were observed for the YH₂, and the existence of a long-range order superstoichiometric YH₂+x phase was suggested. The ordering is apparently caused by long-range interactions between H atoms on the octahedral interstitial sites. Formation of microcracks along the twin boundaries of YH₂ accompanies the YH₂-to-YH₃ transformation. No trace of the YH₃ phase was found by TEM; YH₃ is unstable and decomposes back to YH₂ during the sample preparation or TEM observation.

Learn More

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