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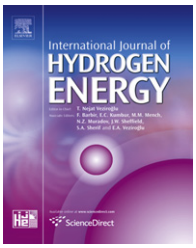

High throughput optical characterization of alloy hydrogenation

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ABSTRACT

Transition from the metallic to the hydride phase is of fundamental importance to achieving hydrogen storage in the solid state. Multi-component metal hydrides belong to one of the promising categories of materials that can potentially offer high hydrogen storage capacity. Despite extensive research on metal hydrides over the past decades, the progress remains limited partly due to the inability of screening a nearly infinite number of possible alloy compositions. High throughput materials fabrication and characterization techniques therefore offer an advantage in studying multi-component alloys and their phase transition to metal hydrides. We fabricated an Mg–Ni–Al and Ca–B–Ti ternary alloy libraries using a continuous combinatorial material synthesis technique, and measured the optical reflectance to examine the formation of metal hydride phase when the alloy library was exposed to hydrogen. The results indicate that mapping the change in reflectance is a viable method to study the kinetics of hydride formation. Monitoring the optical properties provides evidence for the "black state" formed during the transition from α-phase to β-phase. In addition, we found that the fastest reflectance change occurred when the alloy has an Mg to Ni ratio of approximately 2:1, and with low concentration of Al.

1. Introduction

Hydrogen storage is one of the critical challenges in creating a sustainable hydrogen economy. Storing gaseous hydrogen requires high pressures to meet reasonable volume constraints; it also requires heavy, thick-walled containers. Liquid hydrogen storage requires extremely efficient, bulky insulation to maintain temperatures near 20 K. In contrast, metal hydrides offer a promising alternative as a compact, energy efficient storage mechanism, but no simple materials have yet been found that meet all of the requirements such as fast reaction kinetics and high hydrogen storage capacity.

Magnesium-based hydrides have become a model hydrogen storage material system under intensive investigations. Magnesium hydride (MgH_2), with a high theoretical storage capacity of 7.6 weight % coupled with its abundance, low cost, and light weight is a candidate for hydrogen storage. However, the slow kinetics and high heat of formation necessitate the use of catalysts and destabilizing elements to meet requirements for transportation hydrogen storage applications. Nickel (Ni) is a commonly-used catalyst for hydrogen dissociation that can also reduce the enthalpy of formation of the hydride through destabilization. Simply doping Mg with Ni can lead to improved reaction kinetics [1], but the most commonly studied combination of Mg and Ni is the alloy Mg_2Ni, which can be converted to a hydride phase Mg_2NiH_4. The enthalpy of formation has been shown to be 10–15 kJ/mol H_2 lower than MgH_2, leading to a significantly lower desorption temperature [2,3]. Nevertheless, the added weight of the Ni in the alloy decreases the overall theoretical hydrogen storage weight capacity from 7.6%

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to 3.6%. A rapid scanning technique is required to find the optimal Ni concentration for improving kinetics and reducing the hydrogen desorption temperature without drastically limiting the hydrogen storage weight capacity.

The optical properties of metals often change significantly upon the metal–metal hydride transition [4]. In general, metals or alloys have a large reflectance at the infrared wavelengths. During the transition from a metallic phase to the insulating phase of most metal hydrides, the optical reflectance decreases while the transmittance increases [2,6,7]. This is partially due to the opening of an electronic energy band gap when the hydride phase is formed. For example, some of the most favorable materials, MgH_2 and Mg_2NiH_4, have band gaps of 5.6 and 1.75 eV respectively [8]. By monitoring the optical reflectance of a material before, during, and after hydrogenation, it is therefore possible to study the kinetics of metal–metal hydride phase transition. XRD measurements may provide more direct information on the phase of the materials produced, but cannot be performed on the time scale required to obtain true kinetics data. This problem is compounded for a sample of varying composition where measurements would need to be taken at various points across the sample to obtain a valid comparison.

Additionally, it is possible to use well-established optical properties of better known materials to track phase changes in the materials of interest. For example, the Mg_2Ni system is known to exhibit a "black state" during the transition from the α-phase to the β-phase hydride. The α-phase hydride, $Mg_2NiH_{0.3}$, consists of hydrogen dispersed in solid solution in Mg_2Ni, and therefore still exhibits metallic properties. The growth of the β-phase, Mg_2NiH_4, involves the development of a complex hydride, opening up a band gap as described above. When appropriately layered the reflective α-phase and the highly absorbing β-phase lead to a state with low reflectance and transmittance referred to as the "black state" [9]. Using this property of the Mg_2Ni system, it is possible to track potential phase changes during the hydrogenation reaction to determine whether Mg_2NiH_4 is formed or simply MgH_2 with catalytic effects.

Using a continuous combinatorial material synthesis approach, a wide variety of metal hydride systems can be fabricated and analyzed rapidly. By combining three metallic elements, it is possible to study the optimal ratio of metals such as Mg and Ni, while investigating the effect of a third element that may promote the hydrogenation reaction [10]. It has been shown that Al has a destabilizing effect on Mg_2Ni when it is partially substituted for Mg, increasing the equilibrium H_2 pressure although still requiring relatively high temperatures of 473–623 K [11,12]. However, previous studies have only been able to test one or two Mg–Al ratios at a time, and only at high temperatures that are unrealistic for practical storage systems. The method presented here can be used to study a range of material combinations to optimize the destabilizing effects at relatively low temperatures.

2. Experiments

Continuous ternary materials libraries in the form of gradient films were deposited on a quartz substrate by ion-beam sputtering approach. Elemental concentrations were controlled using a synchronized shutter mechanism. By controlling the speed of a moving shutter moving during deposition process, a film with a linear gradient of thickness can be formed [13]. The material library consists of three basic elements, each starting from one corner of a triangle with a thickness of about 20 nm and decreasing to about 0 nm at the opposite edge. Multiple thin layers were deposited alternatively and annealed at least at 425 K to ensure inter-diffusion and alloy formation. All samples were capped with 15 nm of palladium (Pd) to protect them from oxidation as well as enhance hydrogen uptake due to its catalytic property to dissociate hydrogen molecules [1,2,14]. Fig. 1 shows the results of energy dispersive X-ray spectroscopy (EDX) measurements from a Mg–Ni–Al ternary material library sample with continuous composition variation of three elements.

After fabrication, the sample was transferred to a hydrogen gas chamber which has a quartz window for optical access. Optical reflectance measurements were taken using a 1064 nm Nd:YAG laser. The near infrared beam was used since metal hydride systems often show the greatest change in reflectance in this range due to the high infrared reflectivity of metals and the opening of a band gap after transition to a hydride phase [2]. The reflectance was measured through the transparent substrate to eliminate influence from the palladium capping layer. At this wavelength, the absorption coefficients of Al, Mg, and Ni are in the vicinity of 0.06 nm^{-1}, thus the light is 90% attenuated at a depth of approximately 40 nm in the metallic phase. Since the combined layers of the gradient film are at least 40 nm thick at any given point in the film, any light reflected off of the Pd capping layer would travel through 80–120 nm of Mg, Ni and Al and therefore is not expected to contribute to our results.

A beam expander was used to enlarge the laser beam to cover the entire sample surface, and the reflection image was collected using a CCD camera combined with ImageJ software to measure the light intensity. Pictures were taken periodically to track the progression of the metal–metal hydride phase transition. The reflectance at each spot was averaged over an area of approximately 1 mm^2.

3. Results and discussion

Fig. 2 shows the change in reflectance after 1 h at 323 K in 300 psi hydrogen in an Mg–Ni–Al material library sample with two layers of each material with a maximum layer thickness of 20 nm. The regions of interest are identified by a plot of the total change in reflectance in Fig. 2. The time-resolved data show that there is a steady drop in reflectance at the Mg corner. A similar drop is observed along the Mg–Al edge, though the change is smaller. Therefore in this sample we do not see the enhanced kinetics of absorption usually associated with Mg–Al alloys at higher temperatures of 623–673 K [15]. This indicates that under near room temperature reaction conditions, Al does not act to enhance hydrogen absorption of the Mg–Al system and is a less effective additive in the temperature range suitable for practical (near room temperature) hydrogen storage applications.

A point along the Mg–Ni edge shows an initial drop in reflectance, followed by a partial recovery. This is consistent