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Hydrogen storage characteristics of nanograined free-standing magnesium–nickel films

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Abstract Free-standing magnesium–nickel (Mg–Ni) films with extensive nanoscale grain structures were fabricated using a combination of pulsed laser deposition and film delaminating processes. Hydrogen sorption and desorption properties of the films, free from the influence of substrates, were investigated. Oxidation of the material was reduced through the use of a sandwiched free-standing film structure in which the top and bottom layers consist of nanometer-thick Pd layers, which also acted as a catalyst to promote hydrogen uptake and release. Hydrogen storage characteristics were studied at three temperatures, 296, 232, and 180°C, where multiple sorption/desorption cycles were measured gravimetrically. An improvement in hydrogen storage capacity over the bulk Mg–Ni target material was found for the free-standing films. As shown from a Van't Hoff plot, the thermodynamic stability of the nanograined films is similar to that of Mg₂Ni. These results suggest that free-standing films, of which better control of material compositions and microstructures can be realized than is possible for conven-

tional ball-milled powders, represent a useful materials platform for solid-state hydrogen storage research.

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The need for a safe, reliable, and efficient method of hydrogen storage for transportation applications is stronger now than ever before. This need has led to a continuous increase in both the breadth and depth of research in the field of hydrogen storage. Compressed gas, liquid hydrogen, and various chemical and metal hydride approaches have been proposed and studied over the past 20 years [1]. Despite extensive research effort, no definitive best method or best material has been identified. Weaknesses and difficulties for every method and material exist. Examples are the poor volumetric storage of hydrogen as a compressed gas, the boil off of liquid hydrogen, the poor irreversibility of chemical and metal hydrides [2].

Metal hydrides consisting of a high fraction of light-weight elements have attracted much attention. The basic storage mechanisms of hydrogen by physisorption and chemisorption as well as the importance of catalysts have been elucidated [3–5]. More recently, the benefits of using nanometer-sized materials have also been explored [6–8]. Through nanostructuring, improvements in hydrogen uptake and release kinetics at little cost to hydrogen sorption capacities are possible. There are, however, very few material synthesis approaches that can generate a sufficient quantity of nanostructured light-weight metals (which are generally reactive upon exposure toward air and water) for reliable testing of their hydrogen storage properties. The majority of existing studies of metal hydrides are based on the characterization of ball-milled powders. For many materials of

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interest, nevertheless, it is usually difficult to make sub-micron nanoparticles by ball milling process [9]. In this study, we have developed an alternative approach based on free-standing nanograined films and have investigated the hydrogen storage characteristics of such nanostructured free-standing magnesium–nickel films.

Magnesium hydride (MgH_2), with high theoretical storage capacity of 7.6 weight% coupled with its abundance, low cost, and light weight, is an enticing candidate for hydrogen storage. However, the slow kinetics and high heat of formation necessitate the use of catalysts in order to achieve complete utilization so that it may meet the requirements for on-board hydrogen storage applications [10]. Palladium (Pd) and nickel (Ni) are two commonly used catalysts that could enhance for hydrogen dissociation. Ni alloys with Mg to form Mg_2Ni as well as MgNi_2 . While the latter does not react easily with hydrogen, Mg_2Ni can be converted to the ternary hydride Mg_2NiH_4 . This alloy compound is less stable than MgH_2 , therefore releases hydrogen at a somewhat lower temperature. The added weight of the Ni in the alloy decreases the overall theoretical hydrogen storage weight capacity from 7.6 to 3.6%. The use of Pd as a catalyst has also been studied in some detail [11–14]. A reduction in hydrogenation temperature, which is desirable for practical hydrogen storage applications, has been observed for the MgH_2 system in the presence of Pd. In sputtered Mg films [15, 16], the effect of a substrate may drastically affect the hydride nucleation process as has been reported in optical studies [17–19]. To avoid substrate contributions, free-standing films are preferred if the difficulty involved in depositing and delaminating them while avoiding oxidation can be overcome [20–22]. In this study, we report a sandwich configuration for the deposition of such nanograined Mg–Ni films. Thermodynamic and kinetic testings of their hydrogen storage properties free from substrate influences are reported.

Using a pulsed laser deposition approach, Mg–Ni films were deposited on a single-crystal Si (001) substrate under a vacuum of 10^{-6} Torr. Deposition was performed at room temperature, 248 nm laser pulses with a fluence of 4 J/cm^2 were incident alternatively on two targets ($\text{Mg}_{2.8}\text{Ni}$ and Pd) to form the sandwiched structure. The laser was initially focused on the Pd target, then the $\text{Mg}_{2.8}\text{Ni}$ target, and again on the Pd target. This procedure created a capping layer on the top and bottom of the Mg–Ni alloy film, which prevents massive oxidation after film deposition and removal from the substrate. Due to the existence of a strain at the Si–Pd interface, the deposited films were easily lifted from the substrate allowing characterization of their hydrogen storage properties free from the substrate contributions. Rutherford backscattering (RBS) was used to determine the composition and thickness of the sandwiched layers. Scanning electron microscopy (SEM) and energy dispersive X-ray

Fig. 1 Cross-sectional SEM image of a section of free-standing Mg–Ni film

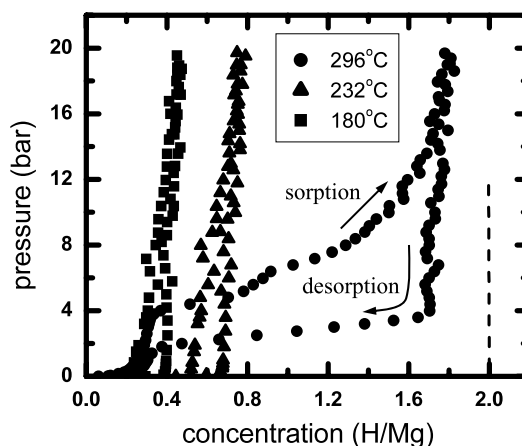
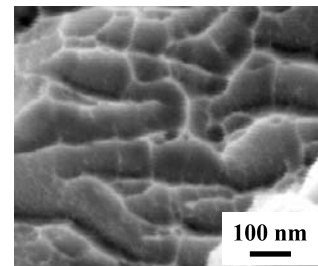


Fig. 2 Pressure–concentration isotherms for a free-standing Mg–Ni film at 180, 232, and 296°C. The dashed line represents the theoretical maximum hydrogen concentration for MgH_2

analysis (EDAX) were used to corroborate the RBS results. The layer thickness and composition were determined to be 3 nm, 1.6 μm , and 17 nm for Pd, $\text{Mg}_{2.8}\text{Ni}$, and Pd, respectively (from top to bottom in Fig. 1). Figure 1 illustrates schematically the morphology of a free-standing film and a cross-sectional SEM image, which shows that the Mg–Ni layer is dense and composed of nanostructured nanosized grains structures. It is known that the diffusivity of hydrogen along the boundaries of grains is much faster than through the bulk; room-temperature pulsed laser deposition thus enables the realization of such desirable nanostructured morphology [23].

Pressure–concentration isotherms were determined gravimetrically using a Hiden microbalance (Intelligent Gravimetric Analyzer) and are plotted in Figs. 2 and 3. At least three cycles were performed at each temperature tested (296, 232, and 180°C), and the hydrogen sorption capacity of the films increased with temperature (Fig. 2). The target material which consisted of a ball-milled mixture of Mg and Ni powders (Alpha Aesar) was tested at 337°C; it took up approximately 1.5 hydrogen atoms per Mg. The nanostructured films absorbed about 1.75 H/Mg even at lower temperature (296°C), closer to the theoretical maximum concentration value of 2 H/Mg for MgH_2 or Mg_2NiH_4 .

An interesting change occurred between the first and the second cycles, as shown from the 296°C pressure–

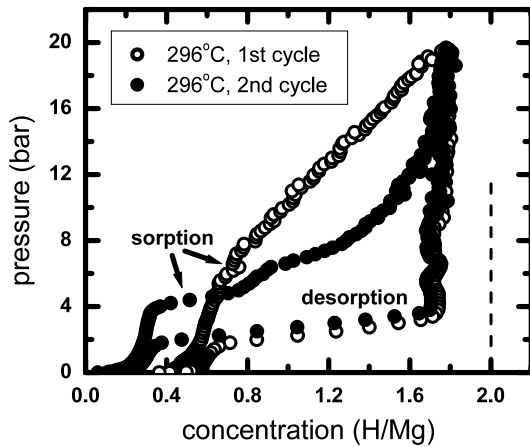


Fig. 3 Pressure–concentration isotherms for the first and the second cycle of a free-standing Mg–Ni film at 296°C. The dashed line represents the theoretical maximum hydrogen concentration for MgH_2

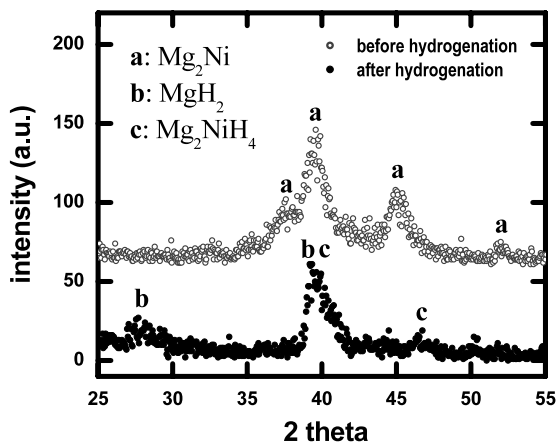


Fig. 4 XRD of the free-standing film before and after hydrogenation. Mg_2Ni peaks that exist after film deposition are replaced by MgH_2 and Mg_2NiH_4 peaks after hydrogenation

concentration curves (Fig. 3). The same concentration of hydrogen was reached during the sorption process, but the route taken to reach this capacity was drastically different for the two cycles. The desorption pressure plateau is longer for the second cycle than it is for the first cycle. The fact that a clear pressure plateau was not apparent in the first sorption cycle suggests the presence of a range of interstitial environments for the hydrogen to occupy. This can be attributed to the lack of order present in the nanostructured films [24, 25]. X-ray diffraction (XRD) scans (Fig. 4) taken before the hydrogenation tests have very broad peaks, indicative of a very small crystallite size according to the Scherrer equation.

The second hydrogenation cycle (Fig. 3) shows the development of a pressure plateau, though it is not as sharp as that of a more crystalline sample. It appears that a range of interstitial environments still exist for the hydrogen, though the sites are more uniform probably due to annealing of the metal phase during the desorption step. The desorption

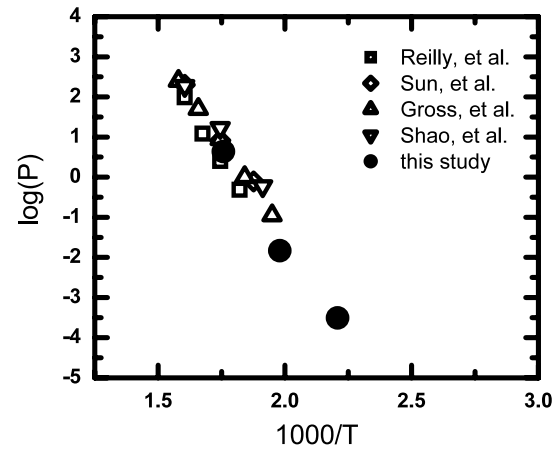


Fig. 5 Van't Hoff plot displaying the thermodynamic stability of the nanograined free-standing film versus published data [28–31]

isotherm shows a sharp transition and pressure plateau. The second cycle desorption isotherm pressure plateau is significantly longer than the one of the first cycle, as indicated by the larger hydrogen concentration change near 2 bar of hydrogen pressure, suggesting a more homogeneous distribution of hydrogen sorption sites with perhaps an increased crystallinity from the first to the second desorption cycle. XRD scans of the sample after hydrogenation show broad metal hydride peaks. These results show that the initially deposited nanograined sample has been partially crystallized by hydrogen cycling at 296°C, but remains nanocrystalline in structure after at least five cycles at 296°C, followed by three cycles at 232°C, and three cycles at 180°C. In addition, the ability of the nanocrystalline films to avoid self-pulverization due to the large volumetric change that occurs during hydrogenation appears to be greatly improved over bulk crystalline samples. A van't Hoff plot of the desorption plateau pressures (Fig. 5) shows the thermodynamic properties of the films are consistent with published data for Mg_2Ni .

Whereas previous attempts to use a film technique [26, 27] for hydrogen storage study suffered from the difficulty of removing the effect of substrates, the free-standing sandwiched films, as demonstrated in this work, provides a more reliable determination of the hydrogen sorption properties as well as the ability to study correlations with film morphology. Pulsed laser deposition followed by an annealing process can produce films ranging from dense crystalline films to porous nanoparticle films through an appropriate process control. By sandwiching the material between Pd layers, oxidation is reduced and loose agglomerations or decrepitating materials are given supporting structures and may be tested. Since the samples are removed from the substrate, substrate-induced nucleation can be ruled out as the origin of the phase change between the metal and hydride state.

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