

Hydrogenography of $Mg_yNi_{1-y}H_x$ gradient thin films: Interplay between the thermodynamics and kinetics of hydrogenation

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Abstract

We monitor the hydrogenation of PTFE/Pd-capped $Mg_yNi_{1-y}H_x$ gradient thin films using the change in optical transmission as a function of time, temperature and hydrogen pressure, to study the relation between kinetics and thermodynamics of hydrogenation of this multiphase hydride system. The interplay between kinetics and thermodynamics is used to extrapolate the hydrogenation equilibrium pressures via the H-absorption rate. Pressure–optical-transmission–isotherms determined independently at different temperatures provide a cross-check for the equilibrium pressure and the enthalpy of H-absorption. We find that the hydrogenation reaction is destabilized with respect to the $Mg_2Ni \rightarrow Mg_2NiH_4$ reaction for Mg fractions close to the Mg_2Ni –Mg eutectic point. From a comparison with calculated enthalpies obtained from density functional theory, we conclude that the experimentally observed destabilization originates from the well-mixed microstructure around the eutectic point.

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1. Introduction

Pure MgH_2 would in principle be an attractive system for hydrogen storage as it contains as much as 7.6 wt.% of hydrogen. However, its large negative enthalpy of formation ($\Delta H = -76 \text{ kJ (mol H}_2\text{)}^{-1}$) implies that high temperatures are needed to desorb hydrogen from MgH_2 at ambient pressure. Furthermore, the diffusion of hydrogen in the MgH_2 phase is very slow, and unless high temperatures are used, a blocking layer of the hydride forms that

prevents further hydrogenation of Mg [1]. Many attempts have been made to destabilize MgH_2 and improve its kinetics by alloying it with transition metals [2–8] or transition metal oxides [9,10]. The complex hydride Mg_2NiH_4 is one of the most promising: it has a hydrogen capacity of 3.6 wt.% and a desorption enthalpy $\Delta H = -64 \text{ kJ (mol H}_2\text{)}^{-1}$ [3]. The existence of the parent metal alloy, Mg_2Ni , helps make the hydrogenation fast and reversible, even at room temperature [11,12]. The reversible change of MgH_2 and Mg_2NiH_4 from a metallic to a transparent state upon hydrogen absorption makes them ideally suited for application as switchable mirrors [11,13,14], hydrogen sensors [15–17], as well as a model system for hydrogen storage research [18,19].

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The dramatic change in the optical properties of metals induced by hydrogen absorption is the basis of hydrogenography, a new technique to screen for suitable hydrogen sorption properties of potential hydrogen storage materials [20–23]. The formation of the hydrides in metallic thin films with a chemical composition gradient is monitored by following the optical transmission averaged over the visible photon-energy range of all compositions simultaneously.

Here, we present hydrogenography results obtained during hydrogenation of Pd-capped $\text{Mg}_y\text{Ni}_{1-y}$ thin films having a gradient in the Mg fraction y . We determine the kinetics of hydrogen absorption of all compositions simultaneously from their change in optical transmission upon a sudden hydrogen pressure step. Additionally, we determine the enthalpy of hydrogenation for the same films and present the compositional dependence of the pressure–optical–transmission–isotherms (PTIs) and Van't Hoff (VTH) plots. We discuss the compositional dependence of the enthalpy values with respect to the peculiar microstructure found around the Mg_2Ni –Mg eutectic composition and compare it to values we obtain from density functional theory (DFT) enthalpy calculations. Finally, we show in our gradient thin film the selective hydrogenation of either MgH_2 or Mg_2NiH_4 by exploiting the differences in hydrogenation kinetics and thermodynamics of these phases.

2. Experimental

$\text{Mg}_y\text{Ni}_{1-y}$ thin films (30–300 nm) were prepared in a 7-gun ultrahigh-vacuum DC/RF magnetron co-sputtering system (base pressure 10^{-7} Pa) at room temperature. A 5–20 nm Pd capping layer was added in situ to protect against oxidation and to promote hydrogen uptake. On samples designed for kinetics experiments, a 50 nm polytetrafluoroethylene (PTFE) top-layer was further deposited on top of the Pd in the same deposition chamber. For electrolytic loading, glass substrates covered with a 180 nm indium-doped tin oxide (ITO) layer were used. The conducting (and transparent) ITO layer was necessary to ensure a homogeneous potential and hence a homogeneous hydrogen uptake over the entire surface area during electrolytic loading. For hydrogenography measurements, $\text{Mg}_y\text{Ni}_{1-y}$ thin films with a compositional and thickness (30–100 nm) gradient were prepared on $70 \times 5 \text{ mm}^2$ quartz substrates. The Mg and Ni targets were placed in tilted off-axis sputtering guns positioned opposite to each other. By adjusting the power applied to each gun the desired compositional region of the binary phase diagram could be obtained. Typical deposition rates were: $1.2\text{--}3.5 \text{ \AA s}^{-1}$ for Mg (120 W RF power), $0.3\text{--}0.7 \text{ \AA s}^{-1}$ for Ni (20 W DC), 1.3 \AA s^{-1} for Pd (50 W DC), and 0.1 \AA s^{-1} for PTFE (50 W RF). The local composition of the gradient films was determined by Rutherford backscattering spectrometry on films grown in the same deposition run on amorphous carbon substrates. For hydrogenography measurements, the metallic films were transferred to an optical cell to monitor their optical transmission during hydroge-

nation [24]. The whole cell was placed in an oven to control temperature up to $300 \text{ }^\circ\text{C}$. The complete thermal equilibration of the setup was checked by comparing the output of two PT100 resistors placed at different locations in the oven, one of them being in contact with the sample holder. A 150 W diffuse white light source illuminated the sample from the substrate side, and a 3-channel (RGB) SONY XC-003 charged-coupled device (CCD) camera continuously monitored the transmitted light as a function of hydrogen pressure. The 3-channel transmission intensities were added, resulting in a 1.1–3.3 eV photon energy bandwidth. The transmission intensity was integrated over the width of the sample as no significant change of composition or thickness occurs across this direction. The gas pressure increase was controlled by a MKS 248/250 forward proportional–integral–differential (PID) system that regulates both inlet and outlet gas flows. We used 0.1–100% hydrogen in argon mixtures to achieve hydrogen (partial) pressures of $10^{-1} < p < 10^6$ Pa. To relax the initial stress due to deposition, thin films were (de)hydrogenated twice before starting the pressure sweep measurements [20]. Hydrogen desorption is performed at 10^5 Pa in a 10% oxygen in argon mixture. For thermodynamic measurements, typical hydrogen pressure sweeps have a duration of 8.6×10^4 s. For kinetics measurements, the sample is kept at low pressure (100 Pa) for 50 s, after which a sudden hydrogen pressure step is applied to the sample. It takes 2–5 s to reach the desired pressure, which corresponds to a maximum measurable hydrogen absorption rate of 0.2 s^{-1} .

3. Theory

First-principles DFT calculations were carried out using a plane wave basis set and the projector augmented wave (PAW) method [25,26], as incorporated in the Vienna Ab initio Simulation Package (VASP) [27–29]. We use the PW91 generalized gradient approximation (GGA) for the exchange correlation function [30]. The cell parameters and the atomic positions were relaxed using a conjugate gradient algorithm. Nonlinear core corrections were applied [31]. The total energies were calculated on a $5 \times 5 \times 5$ Monkhorst–Pack \mathbf{k} -point mesh using a 700 eV kinetic energy cutoff [32].

Since the zero-point energies of MgH_2 (0.40 eV/ H_2 [33]) and Mg_2NiH_4 (0.42 eV/ H_2 [34]) are very close, we estimate that the zero-point energy correction to the hydrogen desorption enthalpies of nonstoichiometric Mg_2NiH_4 will be almost constant (about +0.11 eV/ H_2). We therefore did not calculate these enthalpies explicitly for these structures.

Starting from the experimental positions and lattice parameters [35], we relaxed the crystal structure of Mg_2NiH_4 . All lattice parameters and atomic positions are relaxed, minimizing the total energy of the electron ion system. From the relaxed structure with minimum total energy, we then construct the nonstoichiometric models.

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