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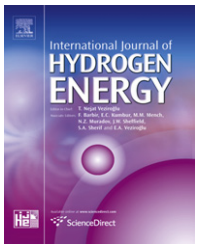

Comparative study on hydrogenation properties of Pd capped Mg and Mg/Al films

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ABSTRACT

Recent emergence of Mg as a promising hydrogen storage material with 7.6 wt% hydrogen encourages study on its thin films to understand physics of storage mechanism. The present study investigates the variations in hydrogen storage properties of Pd sandwiched Mg films upon introduction of Al layer. Multilayered stack of Pd/Mg/Pd and Pd/Al/Mg/Pd were grown on Si substrate using vapor deposition method and further hydrogenated at 150° C under 2 bar H_2 pressure for 2 h. Elastic Recoil Detection Analysis (ERDA) technique with 120 MeV Ag^{9+} ions was used to obtain hydrogen concentration versus incident ion fluence. ERDA study reveals that Pd/Mg/Al/Pd films absorb 6.01×10^{18}hydrogen atoms/cm^2 in comparison to 4×10^{17} atoms/cm^2 absorbed by Pd/Mg/Pd system.

Atomic force Microscopy (AFM) and X-ray Diffraction (XRD) techniques were utilized to analyze the morphological and structural changes in the hydrogenated films. Results indicate that addition of Al to the base system has led to the formation of $Mg(AlH_4)_2$ along with MgH_2 causing an increment in the hydrogen storage capacity and reduction in the oxygen content.

1. Introduction

Hydrogen storage for mobile applications such as fuel cell driven cars has been a very active research area for decades. Magnesium has been considered as a strong candidate for these applications because of its high gravimetric (~ 7.6 wt% for MgH_2) and volumetric (~ 150 kg H_2/m^2 MgH_2) efficiency, light weight, low cost and abundance on earth crust. Unfortunately, the practical application of Mg is limited by its slow hydriding/dehydriding kinetics even at high temperatures. The slow kinetics is attributed to (i) low dissociation rate of hydrogen on Mg surface due to high energy barrier (Ea ~ 72 kJ/mol H_2) [1] and (ii) slow diffusibility of hydrogen atoms in MgH_2 phase (D_H ~ 10^{-16} cm^2/sec) [2]. Additionally, the Mg metal is very sensitive to contamination, which makes it difficult to activate. Various efforts have been made to overcome the thermodynamic and kinetic barriers by alloying Mg with various elements to alter the crystal structure of the hydride [3], reducing the particle and grain size via mechanical milling with e.g nanostructured carbon [4], or by addition of catalytic additives such as Ni, $LaNi_5$ or La–Mg–Ni alloys during milling [5–7].

A possible and better solution would come from the addition of light and cheap elements like Al. Guo and co-workers [8,9], have shown that Al addition to MgH_2 reduces the stability of the hydride leading to an improvement in the dehydrogenation conditions. The heat of formation predicted for the MgH_2+Al system is 28 kJ/mol H_2 [10]. Additionally, it has been found that the thermodynamics and kinetics of Mg–Al as compared to Mg are improved along with resistance

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toward oxygen contamination [11]. Moreover, there is a possibility of formation of complex hydrides, such as alanate compounds, in particular $Mg(AlH_4)_2$, which has a storage capacity of 9.3 wt%.

The best way to understand the reaction mechanism of Mg–Al system is to prepare thin film by sputtering or evaporation method. As in thin film structure, it is easy to control the thickness, composition, interface and structural order. Moreover, the co-operative phenomena and the spill over effects can be induced by synthesis of sandwich structured films, leading to an improved kinetics [12–14]. Ferrer et al. [15] investigated the Mg/Al layer sandwiched between Pd/Fe(Ti) and observed improved storage capacity by the formation of Mg_xAl_y intermetallic. Some authors have reported the formation of $Mg(AlH_4)_2$ from Mg–Al thin films under different conditions [16–18].

This paper mainly focuses on the hydrogenation properties of Mg and Mg/Al thin films sandwiched between Pd layers. The increase in the hydrogen content has been studied by Elastic Recoil Detection Analysis (ERDA). X-ray diffraction and Atomic force microscope have been used to investigate the structural and morphological changes.

2. Experiment

2.1. Thin film preparation technique

The thin film sample of Pd/Mg/Pd was prepared by vapor deposition method at a base pressure of 10^{-7} mbar. The evaporation unit is equipped with 3 KW electron gun, for Pd deposition and two thermal evaporation units used for Mg and Al deposition. 150 nm Mg layer is sandwiched between 20 nm layers of Pd to protect it against oxidation and to promote hydrogen dissociation. The deposition rates of Mg and Pd were kept constant at 0.15 nm/s and 0.1 nm/s respectively. In the second sample 50 nm Mg layer is replaced by 50 nm Al layer deposited by resistive heating at a deposition rate of 0.15 nm/s, to form Pd/Al/Mg/Pd system. Thus, in the present study two systems are being investigated (i) as-deposited (AD1) and hydrogenated (HD1) Pd/Mg/Pd system and (ii) as-deposited (AD2) and hydrogenated (HD2) Pd/Al/Mg/Pd system.

2.2. Thin film hydrogenation technique

Hydrogenation of thin film samples was carried out at 150° C and 2 bar H_2 pressure for 2 h in the system described by Agarwal et al. [19]. Three cycles of hydrogen absorption/desorption were performed to ensure complete hydrogenation of the films.

2.3. Structural characterization using GI-XRD

The structures of the as-deposited and hydrogenated samples were studied by GI-XRD technique using monochromated CuKα radiation of wavelength 1.54060 Å with model Brucker DX 8-Advance.

The spectra were recorded in the 2θ range of 20–50° with scan speed of 0.5°/min and step width of 0.02°. The average crystallite dimension D_P (nm) was calculated using the formula:

$$D_p = \frac{0.9\lambda}{\beta_{1/2}\cos\theta} \quad (1)$$

where λ is the X-ray wavelength, θ is the Bragg Diffraction angle and $\beta_{1/2}$ is the FWHM of the peak after correction for the instrument broadening.

2.4. Morphological characterization using AFM

The surface morphology of all the samples have been investigated by AFM (Nanoscope IIIE model from Digital Instruments, USA), in contact mode at room temperature. The scan area and rate were kept as 5 × 5 μm and 1.526 Hz respectively.

2.5. Hydrogen content measurement using ERDA

Elastic recoil detection analysis (ERDA) measurements for areal concentration of hydrogen (N_H in atoms cm^{-2}) in as-deposited and hydrogenated films of both systems were carried out at Material Science beam line in IUAC, New Delhi. Silver (Ag^{9+}) beam of energy 120 MeV and current 7–9 nA was

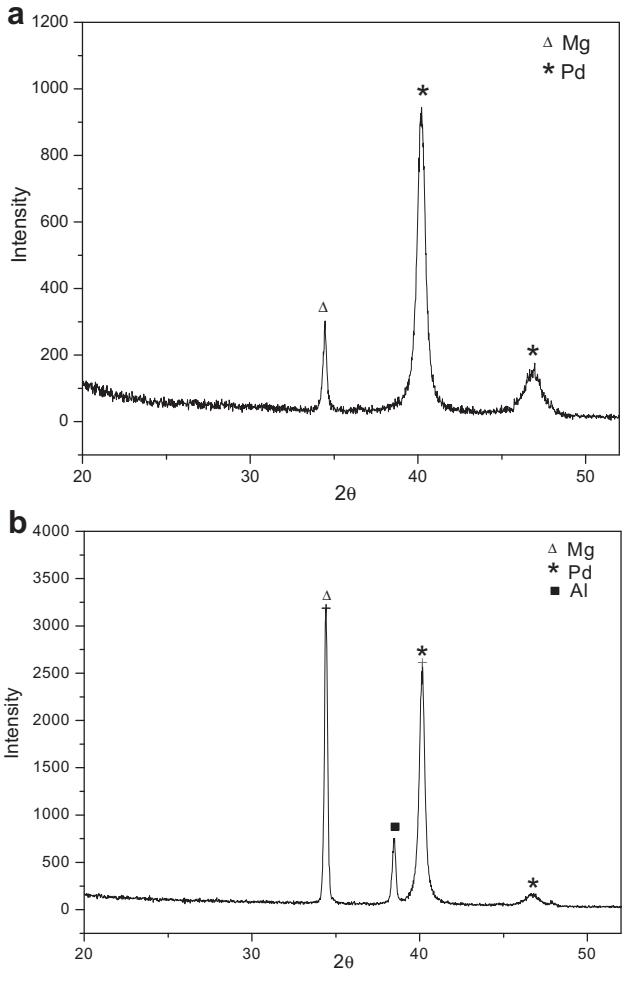

Fig. 1 – XRD spectra of as-deposited (a) Pd/Mg/Pd and (b) Pd/Al/Mg/Pd samples.