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Isochronal hydrogenation of textured Mg/Pd thin films

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ABSTRACT

Magnesium thin films of 350 nm, capped with Pd, were deposited on glass substrates and hydrogenated in two different conditions; namely isochronal and isothermal. As-deposited films were highly textured with Mg (001) parallel to the glass substrate. Experiments have shown that under isothermal conditions starting from 333 K, Mg films can absorb hydrogen producing MgH_2 with a random texture. When the films were heated slowly starting from the room temperature, hydrogenation gives rise to a textured MgH_2, where (110) parallel to the substrate. (101) is also present in this texture as a minor component. Formation of the textured hydride in isochronal loading was discussed within the context of the lattice mismatch in a Mg to MgH_2 transformation.

1. Introduction

With a high gravimetric storage capacity of 7.6 wt.% of hydrogen, magnesium has been the subject of considerable interest. Since Mg does not absorb hydrogen in its bulk form, previous studies have concentrated on means of size reduction, giving large surface area per unit volume. Although mechanical milling is commonly used for this purpose [1], recently thin film processing has emerged as an alternative method for hydrogenation studies, which also produces a large surface-to-volume ratio.

Films as thick as 30 μm [2] have been deposited, but most studies have concentrated on Mg with thicknesses only fractions of a micron. These films were almost always covered by a thin layer of palladium in order to protect the films against oxidation as well as to promote hydrogen dissociation at the surface [3]. Studies [4–9] have shown that such films do absorb and desorp hydrogen at temperatures much lower than those normally achieved with mechanical milling.

Films, in the as-deposited state, could be crystalline with or without a texture or amorphous depending on the conditions of deposition. Singh et al. [10] and Vermeulen et al. [11] have sputter deposited films with a random texture, i.e. all reflections appeared in the X-ray diffraction pattern. Léon et al. [2] and Akyıldız et al. [12] using a thermal evaporation technique have obtained similar structures, i.e. films with a random texture. Upon the hydrogenation of these films, normally carried out under isothermal conditions, Mg was converted into MgH_2 again with a random texture. In the majority of cases in the literature, however, thin films that have been deposited are strongly textured with (001) parallel to the substrate [13–15]. Hydrogenation, under such conditions, leads the formation of a textured MgH_2 with (110) parallel to the substrate.

The nature of Mg to MgH_2 transformation has been the subject of several investigations [16–20]. Westerwaal et al. [16] prepared in-situ MgH_x films through the evaporation of Mg in conjunction with a flux of hydrogen and examined the hydrogenation and dehydrogenation of the resulting films using electrical resistivity and optical techniques. Similarly, Borgschulte et al. [17] have sputter deposited polycrystalline Mg films and studied their hydrogenation by applying a DC potential to the films while exposed to hydrogen atmosphere. Schöber [18] has studied the transformation in high purity magnesium foil, considered to be representative of the bulk, using the transmission electron microscope (TEM). He claimed that Mg is related to MgH_2 with an orientation relation of $(001)\,[110]_{Mg}//(100)\,[001]_{MgH2}$. Bokhonov et al. [19] studying the transformation in single crystals and whiskers reported a different relationship; $(001)_{Mg}//(110)_{MgH2}$. As reported above, this relationship was observed commonly in textured Mg films. Kelekar et al. in a recent study [20], have investigated Mg films which were deposited on glass substrate or grown epitaxially on single crystals of Al_2O_3 and $LiGaO_2$. This yielded the same relationship $(001)_{Mg}//(110)_{MgH2}$ for the glass substrate and for the Al_2O_3 (001). In the case of $LiGaO_2$ (320), however, they report a different relationship, namely $(110)_{Mg}//(200)_{MgH2}$.

In this paper, we report on the hydrogenation behavior of Pd-capped Mg films deposited on a glass substrate with a strong texture. The conversion of these films to MgH_2 was examined under both isochronal and isothermal hydrogenation conditions.

2. Experimental details

Thin film depositions were carried out using a custom-made thermal evaporation unit with a base pressure of 1×10^{-5} Pa. The

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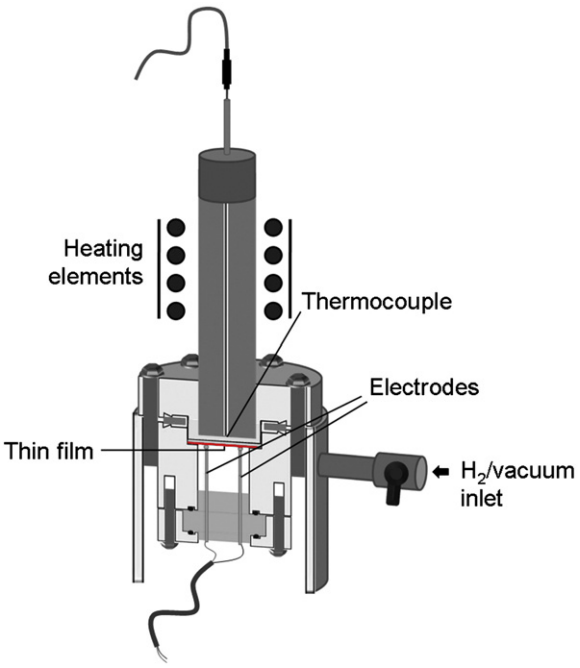

Fig. 1. Schematic drawing of set-up used for hydrogenation of thin films.

unit has four evaporation sources that could be controlled independently with four rotational shutters. Source to substrate distance was typically 350 mm. Films were deposited on glass substrates 0.17 mm thick and 24 mm in diameter. The substrates had a surface roughness (rms) value of 2.0 nm. Films were 350 nm thick, deposited with a rate of typically 1 nm/s as followed by a quartz crystal thickness monitor. They were coated with a thin layer of Pd with various thicknesses (6–48 nm). Materials used were Mg turnings (99.98% pure, −4 mesh) and Pd chips (99.95% pure, 1 mm).

Hydrogen loading experiments were carried out in a custom-made cell, shown schematically in Fig. 1. This is simply a two-part demountable cell, housing the thin film on a base firmly supported on two electrodes, 12 mm apart, used for resistance measurements. The cell has also a heating facility, achieved via an add-in copper rod at the film side of the cell. The rod was heated at a distance using heating coils.

Hydrogenation experiments were carried out under isochronal and isothermal conditions. Isochronal experiments involved heating from room temperature (298 K) to 453 K with a rate of 25 K/h, under constant hydrogen pressure. Isothermal experiments were carried out at temperatures of up to 393 K. This involved heating the cell to a selected temperature and charging it with hydrogen of known pressure.

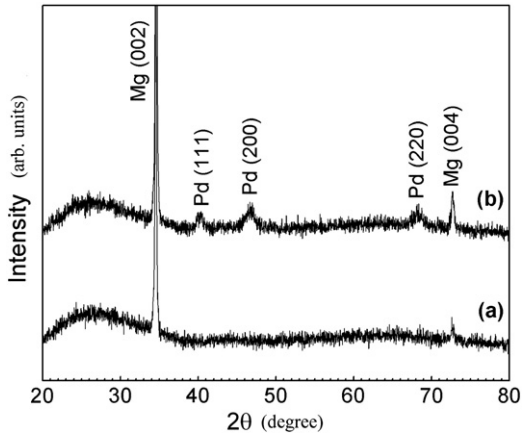

Fig. 2. X-ray diffraction patterns of as-deposited thin films; (a) Mg, (b) Mg/22 nm Pd.

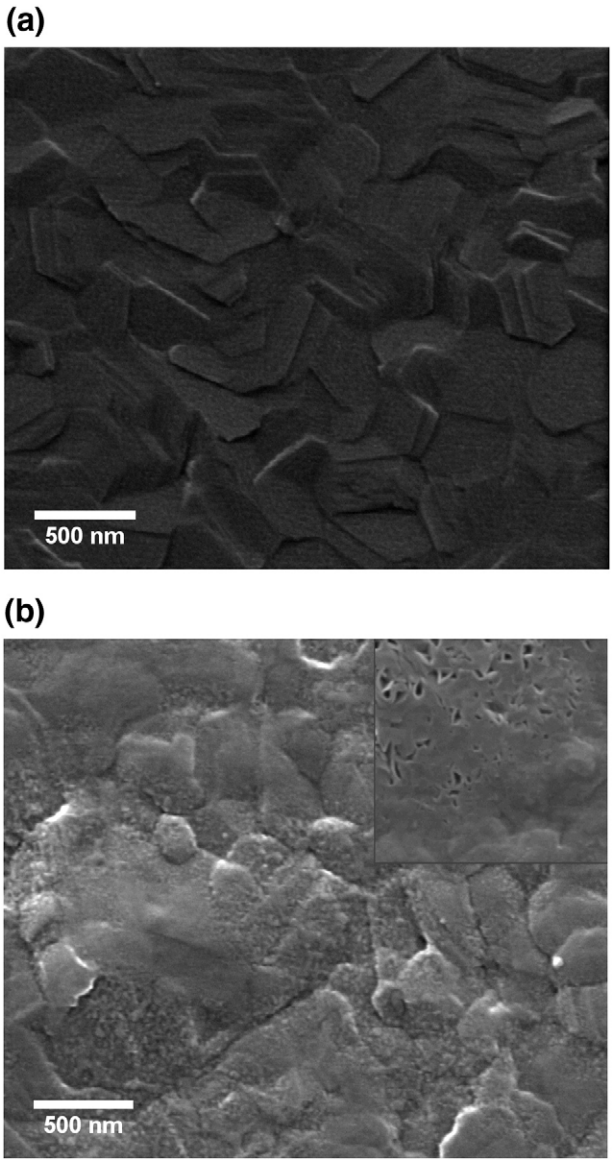

Fig. 3. SEM images of Mg thin films; (a) Mg/22 nm Pd in the as-deposited state, (b) Mg/6 nm Pd hydrogenated (1 bar) isochronally up to 453 K. Inset in (b) shows microcracks in Mg/22 nm Pd thin films hydrogenated (1 bar) isochronally up to 453 K.

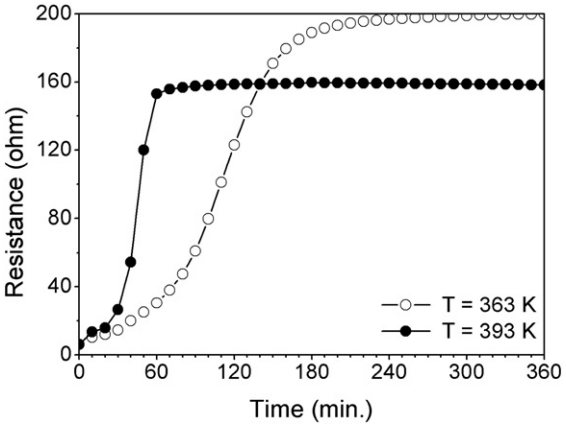

Fig. 4. Resistance vs. time plots for Mg/10 nm Pd thin films hydrogenated under isothermal conditions with a hydrogen pressure of 1 bar.