Deuterium storage in Mg–Nb films

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Abstract

Microcrystalline Mg film samples containing 5 at.% Nb have been prepared by r.f. magnetron sputtering. Structural analysis suggests that Nb is atomically dispersed in the as deposited Mg lattice. When exposed to H_2 or D_2 gas at 10 atm and 600 K the film samples absorb $\sim$7.6 wt.% H_2 indicating a complete h-Mg to β-MgH_2 phase transition. The H_2 desorption from the pure Mg hydride is controlled by the nucleation and growth of the h-Mg phase and occurs with 141 ± 5 kJ mol^{-1} H activation energy and a kinetics order $n \approx 4$. The H_2 desorption kinetics from the Nb doped Mg hydride is of order $n \approx 1$ with activation energy value of 52 ± 5 kJ mol^{-1} H. It is suggested that Nb impurities catalyse the dissociation of the Mg hydride by reducing the thermodynamic stability of the hydride phase.
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1. Introduction

A key point towards the use of hydrogen as an energy vector is the development of efficient and safe systems for the storage of the H_2 gas [1]. Among the hydrides formed by light metals, MgH_2 is probably the most studied owing to its good gravimetric ($\sim$7.6 wt.%) and volumetric efficiency ($\sim$150 kg H_2/m^3). Fast kinetics of the H_2 absorption and desorption process have been obtained by the synthesis of a material with nanocrystalline structure and by the addition of transition metal nanoparticles. The nanostructured materials are, in fact, rich in grain boundaries that favour the hydrogen mobility [2] while the nanoparticles dispersed at the Mg surface increase the reactivity of the H_2 molecules. The nanoparticle catalyst (Nb, $PdFe_3$, Pd), stimulates in fact the H_2 dissociation and facilitates the transfer of the H atoms from the surface of the nanoparticle to the subsurface layers of the Mg matrix.

Among the metallic additives forming low-temperature hydrides, Nb is one of the most studied because the addi-

tion of only 5 at.% reduces the typical sorption times by at least one order of magnitude at 300 °C [3]. The detailed microscopic mechanism, although not completely clarified, is strongly connected to the presence of the catalyst in form of surface nanoparticle on Mg or MgH_2 [4,5]. In this paper we present experimental evidence showing that the catalytic action of Nb may also occur when the metallic additive is dispersed in a MgH_2 matrix having microcrystalline structure: the analysis of the H_2 desorption kinetics suggests that the accelerated desorption process, when compared to that observed with pure Mg, can be explained by the fact that Nb impurities possibly in form of nanoparticles in the β-MgH_2 hydride phase stimulates the nucleation of the metallic h-Mg phase.

2. Experimental

Magnesium–niobium films (Mg:Nb) were deposited by r.f. magnetron sputtering on graphite (g-C) and (1 0 0) oriented Si wafers in a HV system with background pressure in the low 10^{-5} Pa. Samples were grown at 150 W r.f.

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target power by using a 10 cm diameter circular Mg target (99.95 at.% purity) and 0.5 Pa Ar as working gas (99.97 at.% purity). Niobium doping was obtained by inserting small Nb pieces (in form of thin squares, ~3 mm side) over the Mg target material: the Nb content was controlled by adjusting the number of Nb pieces over that part of the target which is preferentially eroded in the magnetron system. The pure Mg and Nb-doped Mg samples (Mg:Nb) were coated with a ~20 nm thick Pd capping layer by rotating the sample holder over a 99.9 at.% purity Pd target. The Pd capping layer avoided the Mg surface oxidation and catalysed the D_2 or H_2 dissociation kinetics during the hydriding process [6] both in the pure and Nb-doped Mg samples: differences in the H_2 kinetics cannot thus be attributed to the Pd surface coating.

After deposition, the film samples deposited on g-C peeled off from the substrates after exposure to air at ambient conditions. The self-supporting samples were thus introduced in a Sievert-type apparatus for the analysis of the hydrogen absorption and desorption kinetics [7]. The activation procedure of the samples consisted of repeated absorption and desorption cycles at 623 K and 0.8 or 0.015 MPa H_2 (or D_2) pressure for absorption and desorption, respectively. The activated samples are then exposed to H_2 (or D_2) gas at ~10 atm and ~600 K: given these thermodynamic conditions, the samples absorb ~7.6 wt.% H_2 (or D_2) indicating a nearly complete transformation of the h-Mg phase to β-MgH_2 phase.

The structural characterization of the Mg film samples was carried out by conventional X-ray Diffraction Spectroscopy (XRD) in Bragg-Brentano ($\theta - 2\theta$) configuration at 40 kV and 40 mA using the Cu Kα radiation and using samples well adherent to the Si substrates. Transmission electron microscopy (TEM) analysis has been carried out by a Philips CM200 microscope at 200 kV. Samples for in plane observations have been mechanically thinned by grinding papers and then polished by diamond pastes. The final thinning was performed by ion beam thinner at 4.5 kV and 0.2 mA. Selected area and convergent beam electron diffraction techniques have been used in order to investigate the crystallographic structure of the samples. The morphologies of the Mg and Pd films was studied by scanning electron microscopy (SEM) while the composition and impurity content was analyzed by energy dispersion spectroscopy (EDS).

3. Results and discussion

The as-deposited Mg and Nb doped Mg film samples on Si substrate present a mirror-like surface and appear very smooth and compact. SEM analysis show that the surface of the as-deposited samples is formed by hexagonal shaped crystals, while the cross section view shows a columnar growth of the deposited layers with column diameter ~1 μm (Fig. 1).

The XRD spectra have been taken from a pure Mg film and a film with ~5 at.% Nb content [8]. The pure Mg film only shows a well defined peak located at $2\theta = 34.46°$ with
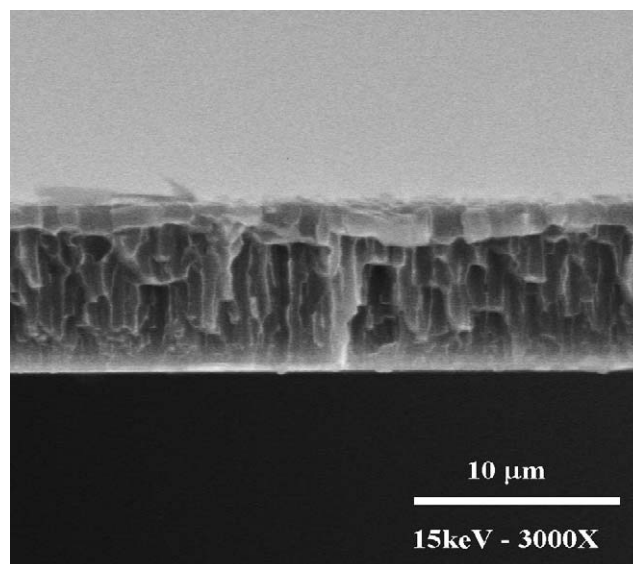

Fig. 1. SEM photographs of the cross section of an as-deposited Mg film sample.

a full width at half maximum (FWHM) $\Delta\theta = 0.156°$ corresponding to the Mg (0 0 2) reflection: the sample thus appears well crystallised with the Mg (0 0 1) planes preferentially oriented parallel to the sample surface (c axis of the hexagonal Mg lattice perpendicular to the substrate). The same XRD reflection is shown also by the spectrum of the Nb doped sample: compared to the pure Mg the peak is weaker, shifted at $2\theta = 35.04°$ and shows a larger FWHM $\Delta\theta = 0.224°$ [8]. The TEM bright field image of the as-deposited Nb doped sample is reported in Fig. 2(a). Large grains with dimensions ranging from 0.5 to 2 μm are clearly visible. Both bright and dark field investigations have never shown secondary phases precipitated inside the grains or on the grain boundaries. A selected area electron diffraction of the sample is reported in Fig. 2(b). This pattern is formed of discontinuous rings indicating a polycrystalline structure. The indexation of this pattern is reported in Table 1: the first column reports the number of the ring starting from the inner one, d_m is the interplanar distance measured from the pattern, d_t the tabulated distance for Mg [9] and (h k l) the corresponding Miller indices. It is worth to note that all the reflections reported in Table 1 are due to Mg planes perpendicular to the $(0\,0\,1)_{Mg}$ plane, suggesting a fibre texture along $[0\,0\,1]_{Mg}$ direction. The bright field image of Fig. 2(a) are evidence of a good crystallization of the Nb doped Mg film sample. The diffraction pattern of Fig. 2(b) has in fact the typical appearance (discontinuous rings) of fibre textured samples with the fibre axis tilted with respect to the surface normal. Moreover, the indexation reported in Table 1 confirms the orientation of the fibre axis along the $[0\,0\,1]_{Mg}$ direction. From the XRD and TEM analysis we can thus conclude that the Nb doped sample is well crystallised and preferentially oriented with the c axis of the hexagonal Mg lattice but tilted with respect to the substrate: preliminary test indicates a tilting angle ~1°.
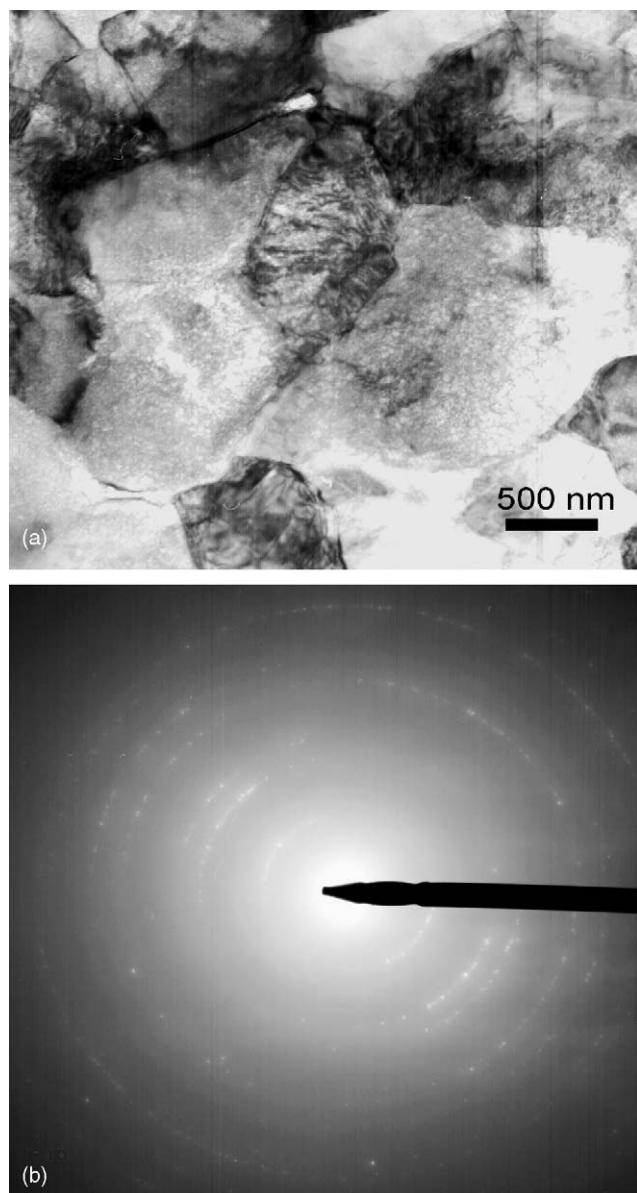
Fig. 2. TEM bright field image (a) and corresponding selected area diffraction pattern (b) of the as deposited Nb doped Mg film sample.

XRD and TEM analysis indicate a decrease of the h-Mg c-axis and an increase of the in-plane lattice parameters in the Nb-doped samples: the observed distorsion of the unit cell can be attributed to the presence of interstitial Nb atoms.

Table 1
The first column reports the ring number starting from the inner one, d_m is the measured interplanar distance, d_t the tabulated distance for Mg and (h k l) the corresponding Miller indices [9]

	d_m (nm)	d_t (nm)	(h k l)
1	0.281	0.2778	100
2	0.161	0.1605	110
3	0.141	0.1390	200
4	0.106	0.1050	210
5	0.094	0.0927	300

To summarize, the relevant points clearly shown by the XRD and the TEM analysis (also in selected area diffraction) of the Mg + 5 at.% Nb film sample are: (a) the microcrystalline structure of the material, (b) the absence of any crystalline compound containing Nb, and (c) the shift of the (0 0 1) reflection to larger 2θ angles as compared to the pure Mg film sample.

Fig. 3 shows the H_2 desorption kinetics, at 623 K, of the pure Mg and of Mg + 5 at.% Nb hydrides after activation, as studied by Sievert analysis: in the figure we plot the reacted fraction α (that is the fraction of Mg hydride that transformed to metal) as function of time. Symbols correspond to experimental data while the solid lines is the result of a numerical fitting based on the Johnson-Mehl-Avrami theory. A strong improvement of the reaction kinetics for the Nb doped Mg hydride sample can be observed: at 623 K temperature, the time required for 50% transformation decreases from 3250 ± 50 s for pure MgH_2 to 110 ± 10 s for the Nb-doped hydride. The present results were analysed in a previous paper [8]: the fitting of the experimental data by the relation

$$\alpha = 1 - \exp[-(kt)^n]$$

where $\alpha(t)$ is the fraction of transformed material given as function of time t, $k = k(T)$ is the temperature dependent kinetic constant and n is the reaction order which is related to the transformation mechanism, resulted in values of n close to 4 for the pure Mg hydride samples and of about 1 for the Nb doped Mg hydride and effective activation energies of the desorption process of the 141 ± 5 kJ/mol^{-1} H for the pure Mg and of 51 ± 5 kJ mol^{-1} H for the Nb-doped Mg hydride. The results were explained by assuming that the evaluated value $n = 4$ of the reaction order was connected with the continuous formation of nucleation centers for the h-Mg phase and a three dimensional growth of the h-Mg grains in the β-MgH$_2$ parent phase. The n value $\sim$1 was attributed to a constant number of h-Mg phase nuclei (instantaneous nucleation) with growth of the h-Mg grains in the parent hydride phase being controlled by a one dimensional atomic diffusion process [10]. The 1D dimensionality of the diffusion process and the low value of the activation energy of the process suggest a preferential motion of the H atoms through interconnected h-Mg grains: the activation energy for H diffusion in α-Mg is 40 kJ mol^{-1}, a value not much different from the present one of 52 kJ mol^{-1} [11]. It is important to also remark that given the microcrystalline structure of the present samples the preferential motion of H atoms through fast diffusivity path such as grain boundaries cannot influence the desorption process kinetics as it is supposed to occur in nanocrystalline samples [2].

The present experimental results indicate a different catalytic role of the Nb additive in the H_2 desorption kinetics as compared to that in the ball-milled samples where Nb nanoparticles promote the transfer of the H atoms from the subsurface layers of the MgH$_2$ matrix and the recombination of the H_2 molecules [4,5]. We tentatively suggest that the
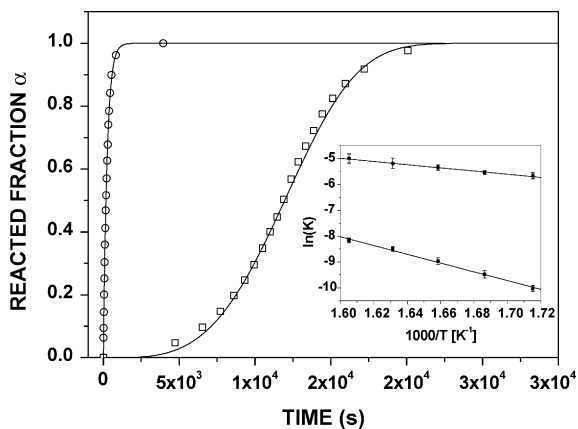
Fig. 3. Hydrogen desorbed fraction vs. time at 623 K of the pure and Nb doped Mg hydride samples (at 0.015 MPa). In the inset we present the Arrhenius plot of the desorption rate constant k of pure (upper data) and Nb doped (lower data) Mg hydrides. The straight line is the least square fit to evaluate the activation energy.

Nb catalytic effect in the present samples is connected to the formation of Nb clusters in the MgH_2 matrix by coalescence of Nb atoms during the H_2 cycling processes. The presence of the Nb clusters would increase the stress level in the MgH_2 matrix thus reducing the hydride stability. To elucidate this point we plan to perform Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) in order to analyse the local arrangement around Nb atoms in the as-deposited Nb doped Mg film samples and after the metal to hydride phase transition.

4. Conclusions

Microcrystalline Mg film samples containing 5 at.% Nb have been prepared by r.f. magnetron sputtering. XRD and the TEM analysis of the as deposited Mg + 5 at.% Nb film

sample indicate the absence of any crystalline compound containing Nb and the shift of the (0 0 1) reflection to larger 2θ angles as compared to the pure Mg film sample. It is suggested that Nb impurities dispersed in the MgH_2 catalyses the dissociation of the hydride phase after the formation of Nb clusters reducing the thermodynamic stability of the hydride phase.

Acknowledgements

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