ELSEVIER

Journal of Alloys and Compounds 356–357 (2003) 530–535

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Hydrogen sorption properties of vanadium- and palladium-implanted magnesium films

A. Léon[a], E.J. Knystautas[a,*], J. Huot[b], S. Lo Russo[c], C.H. Koch[d], R. Schulz[b]

[a]Département de Physique, Université Laval, Québec, Canada G1K 7P4
[b]Institut de Recherche d'Hydro-Québec, Varennes, Québec, Canada J3X 1S1
[c]Unità INFM, Dipartimento di Fisica, Università di Padova, 35131 Padova, Italy
[d]Institute of Materials Science, University of Connecticut, Storrs, CT 06369, USA

Received 3 July 2002; received in revised form 26 August 2002; accepted 6 February 2003

Abstract

Magnesium films prepared by vacuum evaporation were implanted with vanadium and palladium ions in order to study their hydrogenation characteristics. It was found that the hydrogenation kinetics depend on the ion species and on the ion dose implanted. Indeed, the vanadium-implanted magnesium films have faster kinetics than the palladium-implanted ones. However, low vanadium concentration (~0.3 at.%) seems to inhibit the absorption reaction. Among the ion-implanted magnesium films, the fastest kinetics were obtained with the vanadium-implanted film at a dose of 1×10^{16} ions/cm^2: at 623 K and under a hydrogen pressure of 10 bar, a concentration of 6 wt.% of hydrogen was reached in 270 min during the first hydrogenation and in 45 min during the second one.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Magnesium film; Hydrogen storage; Ion implantation; Vanadium; Palladium

1. Introduction

Among the technologies that exist to store hydrogen, metal hydrides, particularly magnesium hydride, appears to be the most attractive one because of its high storage capacity and low cost. Unfortunately, the poor hydrogenation characteristics of magnesium have limited its applications so far. Various attempts have been made to circumvent these disadvantages. One of them is to understand the mechanism of the hydrogenation reaction in order to modify appropriately the properties of the material. Our recent previous work has shown that magnesium film is a convenient form for analyzing the various processes involved in the hydrogenation reaction [1].

In that work, 30-μm thick air-exposed magnesium film absorbed hydrogen at 623 K under a hydrogen pressure of 10 bar and desorbed it at the same temperature under a residual pressure of 0.21 bar [1]. However, the kinetics were slow: 1000 and 200 min were needed to reach 7.5 wt.% during the first absorption and 6 wt.% during the second one, respectively. In the present work, we modified the hydrogenation properties of magnesium film by implanting ions in their near-surface region in order to facilitate hydrogen diffusion.

In previous related work, magnesium films (200 nm) were coated with a palladium layer (25 nm) to limit oxygen contamination and to reduce the activation barrier [2–5]. Unfortunately, the formation of a magnesium hydride layer at the interface blocked further hydrogen uptake [3]. To avoid this interface problem, we used in the present work ion implantation to modify the surface properties of magnesium film. Indeed, this surface modification technique allows the formation of a continuous distribution of ions in the near-surface region instead of the addition of a thin layer. Moreover, this technique has the advantage of introducing vacancies and interstices that occur during the implantation process. To our knowledge, hydrogenation of air-exposed ion-implanted magnesium film has not been attempted so far.

In this paper, we describe the experimental details and present our results on the hydrogenation/dehydrogenation characteristics of 30-μm thick air-exposed magnesium films prepared by vacuum evaporation and subsequently implanted with vanadium and palladium ions. These

*Corresponding author. Tel.: +1-418-656-5569; fax: +1-418-656-2040.
E-mail address: ejknyst@phy.ulaval.ca (E.J. Knystautas).

0925-8388/03/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0925-8388(03)00366-9

elements were selected because palladium is a well-known catalyst of the hydrogenation reaction, whereas vanadium is known to be an element that facilitates hydrogen diffusion even at ambient temperature.

2. Experimental details

Magnesium films were prepared by thermal evaporation. The evaporation system is described in detail elsewhere [1]. Before the evaporation, the working pressure was 3×10^{-6} Torr. During the evaporation, the deposition rate was kept approximately constant, around 50 Å/s, until a final thickness of about 30 μm was reached. After the deposition, the samples were left to cool down before being taken out into ambient atmosphere.

The implantations were done at room temperature. In this process, two parameters are relevant: the ion energy, which determines the penetration depth, and the ion dose, which controls the ion concentration implanted. Numerical simulation was performed using the TRIM Monte Carlo code [6]. This allows us to determine the penetration depth as a function of the ion energy. We used this type of simulation to set up the vanadium and palladium implantation conditions.

In order to compare the effect of the ion species implanted and their concentration, we fixed the average penetration depth at 533 Å for the two species and we varied their concentrations. Using TRIM Monte Carlo calculations, we found that the vanadium and palladium should be implanted at an energy of 42 and 67 keV, respectively. Vanadium was implanted at doses of 1×10^{15}, 5×10^{15} and 1×10^{16} ions/cm^2, whereas palladium was implanted at doses of 8×10^{14}, 4×10^{15} and 8×10^{15} ions/cm^2 which corresponds in both cases to a concentration of 0.3, 3 and 6 at.% of vanadium and palladium, respectively. The range straggling (ΔR_p) calculated for vanadium and palladium was, respectively, 190 and 152 Å.

Morphology, structure and chemical composition of magnesium and hydrogenated magnesium films were characterised by scanning electron microscopy (SEM), using a Jeol JSM 840 A, by X-ray diffraction (XRD) with Cu Kα radiation ($\lambda=1.54056$ Å), using a Siemens D5000 diffractometer and by Rutherford backscattering spectrometry (RBS), using a 7 MV Van de Graaff accelerator.

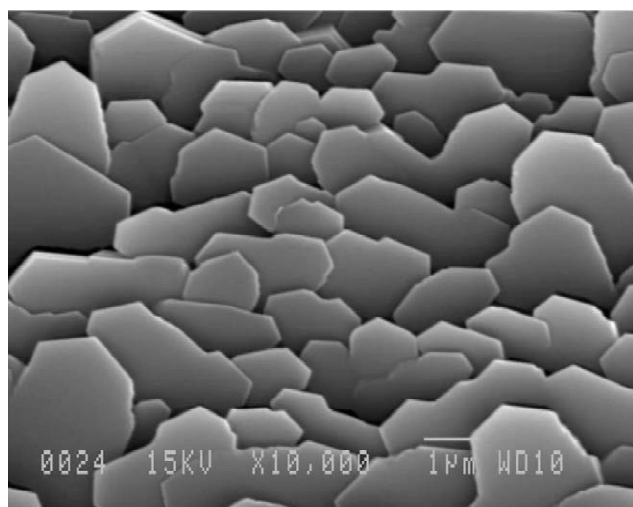
The pressure–composition isotherms and the absorption/desorption kinetics were measured using an automatic gas titration apparatus [7]. The hydrogenation cell used in this work is described elsewhere [1].

3. Results

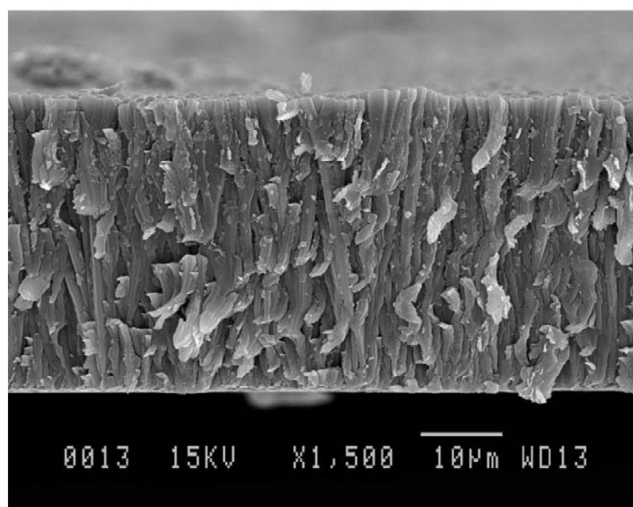
3.1. Characterisation of ion-implanted magnesium film

Fig. 1a,b represents the SEM micrographs of the top surface and the transverse view of a magnesium film implanted with vanadium ions at an ion energy of 42 keV and at an ion dose of 5×10^{15} ions/cm^2. These micrographs show that the hexagonal shaped crystals on the external surface and the columnar structure of magnesium film are conserved once implanted. There is no significant modification of the morphology of magnesium film after ion implantation, except within the first micrometer from the surface.

Rutherford backscattering spectrometry (RBS) using a 40 nA beam of 2.8 MeV He^+ ions in a perpendicular geometry allowed measurement of the vanadium and palladium implanted dose and shows, as an example in Fig. 2, that a magnesium film implanted with vanadium at 42 keV and a dose of 5×10^{15} ions/cm^2 is not contaminated by other elements.



(a)



(b)

Fig. 1. SEM micrographs of the top surface (a) and the transverse view (b) of a magnesium film implanted with vanadium ions. Note that the hexagonal crystals on the external surface and the columnar structure of the magnesium film are conserved after implantation.

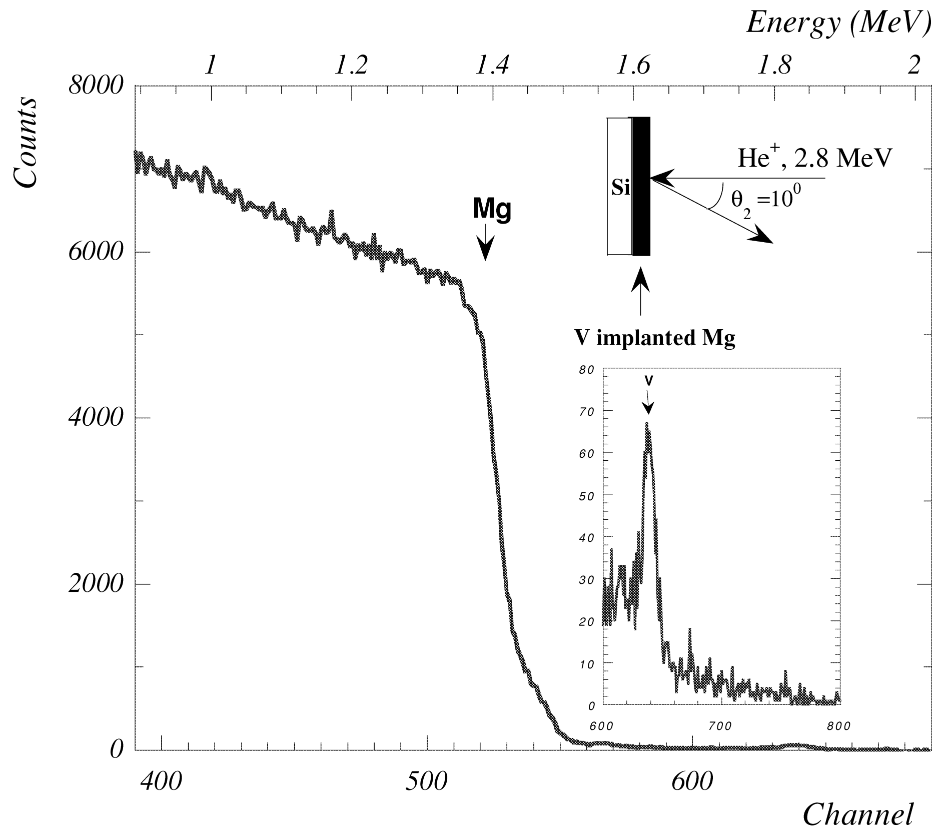


Fig. 2. Rutherford backscattering spectrometry (RBS) using a beam of 2.8 MeV He^+ ions in a perpendicular geometry shows that a magnesium film implanted with vanadium at 42 keV and a dose of 5×10^{15} ions/cm^2 is not contaminated by any other elements.

Neither palladium- nor vanadium-implanted magnesium films undergo any apparent modification in their morphology after ion implantation.

3.2. Hydrogenation characteristics of ion-implanted magnesium film

Fig. 3a,b represents the first-absorption kinetics of vanadium- and palladium-implanted magnesium film. Fig. 3c,d represents their second-hydrogenation kinetics. Both species were implanted at the same penetration depth of 533 Å and at various doses. Fig. 3a,c corresponds to an implanted ion concentration of 0.3 at.%, whereas Fig. 3b,d corresponds to 6 at.%. For comparison, absorption kinetics of pure magnesium, prepared under the same experimental conditions as the magnesium film used for ion implantation, are also presented.

From the first-absorption curves (Fig. 3a,b) one can see that the presence of vanadium or palladium facilitates the absorption of hydrogen compared into pure magnesium, independently of the element implanted or its concentration. However, this effect is much more pronounced for the higher ion concentration. We also note that at a concentration of 6 at.%, the vanadium-implanted magnesium film shows faster kinetics than the palladium one. In fact, Fig. 3b shows that for the magnesium film implanted at 6 at.%, a hydrogen concentration of 6 wt.% is reached in 270, 450 and 600 min for vanadium-implanted, palladium-implanted and pure magnesium film, respectively. Moreover, one can see that the ion concentration influences the nucleation period. At low concentration, the nucleation period is the same irrespective of the element implanted whereas at higher concentration it is shortened by the presence of vanadium or palladium, compared to pure magnesium film.

Considering now the second-absorption kinetics (Fig. 3c,d), one can see that the absorption behaviour is not the same as for the first absorption, as could have been expected. At a concentration of 0.3 at.% (Fig. 3c), pure magnesium film presents faster kinetics than the vanadium or the palladium-implanted magnesium film. Palladium-implanted magnesium film exhibits faster kinetics than the vanadium-implanted one. Vanadium seems to inhibit the absorption reaction. Conversely, for an ion concentration of 6 at.% (Fig. 3d), vanadium-implanted magnesium film presents the fastest kinetics (45 min are needed to absorb 6 wt.% of hydrogen), whereas the presence of palladium at a high concentration seems to totally inhibit the absorption reaction.

3.3. Dehydrogenation characteristics of ion-implanted magnesium film

Fig. 4a,b represents the first-dehydrogenation kinetics of

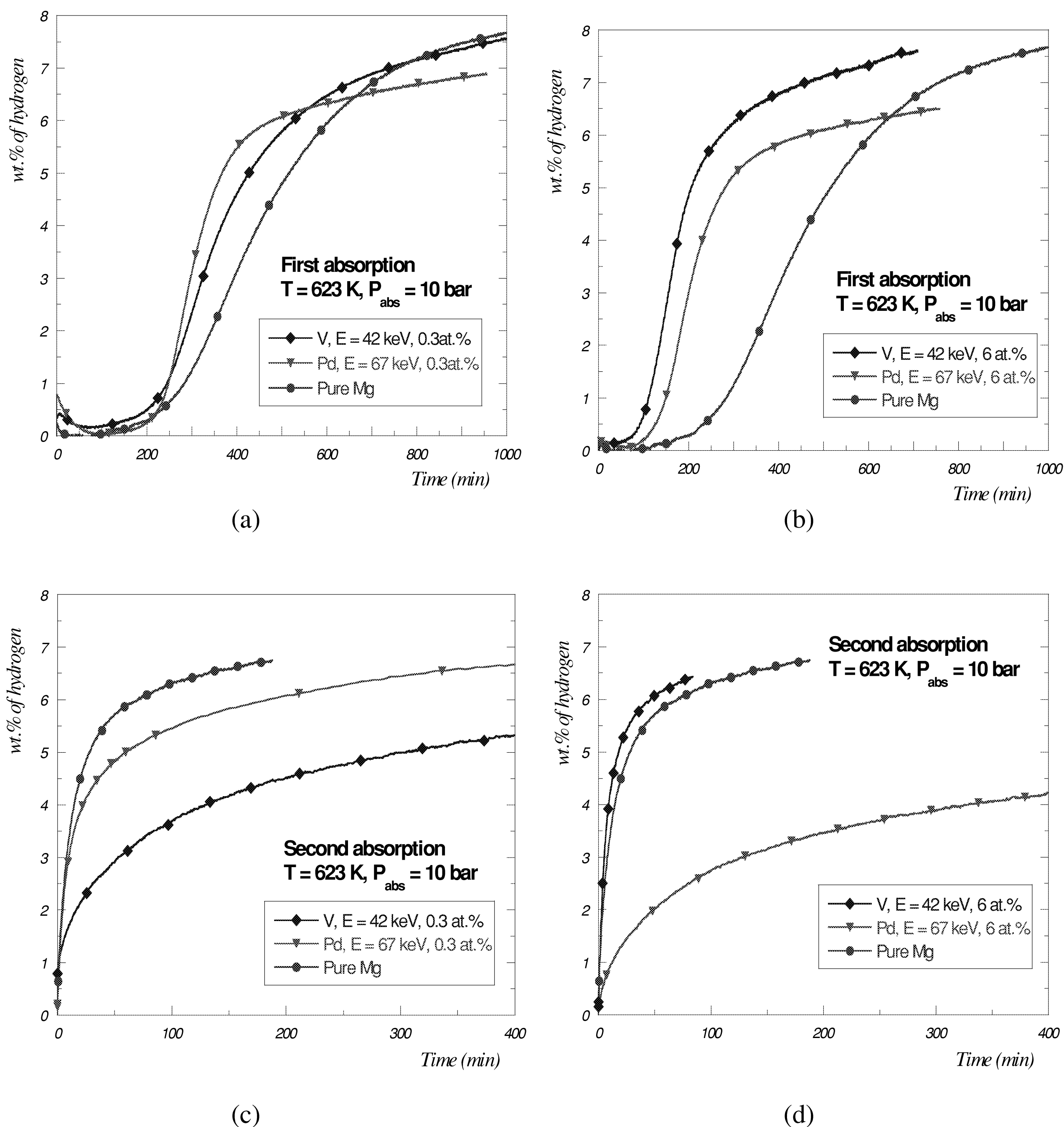


Fig. 3. First-absorption (a,b) and second-hydrogenation (c,d) kinetics of vanadium and palladium-implanted magnesium film. Both species were implanted at the same penetration depth of 533 Å and at various doses (see text). For comparison, absorption kinetics of pure magnesium, prepared under the same experimental conditions as the magnesium film used for ion implantation, are also presented.

vanadium- and palladium-implanted magnesium film under the same conditions as described in Fig. 3. For comparison, desorption kinetics of pure magnesium are also presented. To facilitate the comparison, all the curves were normalised to 7 wt.% for the first desorption.

As was the case for the absorption, one can see that for the first desorption (Fig. 4a,b), the presence of vanadium and palladium ions facilitate the dehydriding reaction, but the desorbed capacity is slightly lower than that for pure magnesium. Moreover, the desorption kinetics depend on the ion concentration: if we consider the vanadium-implanted magnesium films, we can see that 120 and 75 min are needed to desorb 5.5 wt.% of hydrogen by films implanted at an ion concentration of 0.3 and 6 at.%,

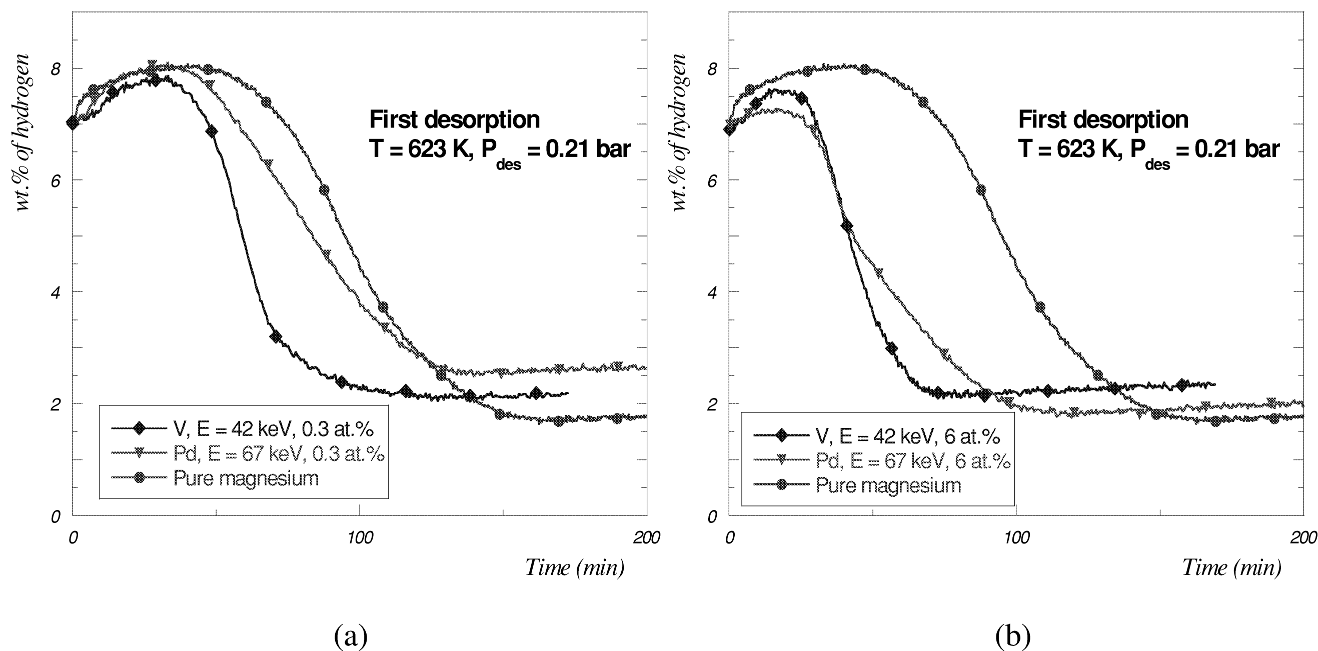


Fig. 4. First-dehydrogenation kinetics of vanadium and palladium-implanted magnesium film under the same conditions as described in Fig. 3. For comparison, desorption kinetics of pure magnesium are also presented. To facilitate the comparison, all the curves were normalised to 7 wt.% for the first desorptions.

respectively. We note, too, that the presence of ions at a high concentration reduces the incubation period.

4. Discussion

We have observed that the absorption/desorption kinetics of magnesium films are influenced by the modification of their near-surface region by ion implantation; the rate of absorption or desorption of hydrogen depends highly on the ion species and on the ion dose implanted.

At an ion concentration of 0.3 at.% the presence of vanadium or palladium ions does not affect significantly the hydrogen sorption kinetics. In contrast, at an ion concentration of 6 at.% the vanadium-implanted magnesium film presents the fastest kinetics, whereas the palladium-implanted film shows very slow kinetics during the second absorption. When vanadium ions are implanted, it appears from these results that a concentration limit exists: below this concentration the hydrogenation kinetics appear to be slowed when vanadium ions are implanted. More experiments at ion concentrations that are intermediate between 0.3 and 6 at.% are needed to confirm this observation. Moreover, experiments at concentrations greater than 6 at.% are also needed to verify whether a higher ion dose will inhibit or accelerate the hydrogenation reaction.

As was stated in Section 1, palladium is a well-known catalyst of the hydrogenation reaction. The results described previously show that the catalytic effect of palladium is inhibited when this element is implanted in the near-surface region of magnesium film.

5. Conclusion

It has been shown that implanted magnesium films conserve the same structure as pure magnesium film. Moreover, no contamination by other elements is introduced during the implantation process.

Faster hydrogen absorption was seen in vanadium-implanted films compared to pure magnesium- and to palladium-implanted films. Hydrogenation/dehydrogenation kinetics depends on the ion dose implanted. For the vanadium-implanted magnesium film, we have shown the existence of a threshold ion dose, above which the kinetics are improved compared to the kinetics of pure magnesium film. The determination of this limit requires measurements at various ion doses between the concentrations 0.3 and 6 at.% studied in the present work.

Acknowledgements

We wish to thank Ing. Moreno Parolin (Laboratori Nazionali di Legnaro, Padova) for some of the ion implantations. S. Lo Russo wishes to thank financial

support by MIUR of Italy through a 'ex 40%' COFIN (PRIN).

References

[1] A. Léon, E.J. Knystautas, J. Huot, R. Schulz, J. Alloys Comp. 342 (2002) 158.
[2] A. Krozer, B. Kasemo, J. Phys.: Condensed Matter 1 (1989) 1533.
[3] J. Ryden, B. Hjörvarsson, T. Ericsson, E. Karlsson, A. Krozer, B. Kasemo, J. Less-Common Met. 152 (1989) 295.
[4] A. Krozer, B. Kasemo, J. Less-Common Met. 160 (1990) 323.
[5] K. Higuchi, H. Kajioka, K. Toiyama, H. Fujii, S. Orimo, Y. Kikuchi, J. Alloys Comp. 295 (1999) 484.
[6] J.F. Ziegler, J.P. Biersack, U. Littmark, SRIM/TRIM (http://www.srim.org/).
[7] R. Schulz, S. Boily, J. Huot, Apparatus for the gas titration and cycling, patent pending, CAN serial number 2207149.