DEVELOPMENT OF HYDROGEN STORAGE ALLOYS USING PHYSICAL VAPOR DEPOSITION TECHNOLOGIES

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Introduction

Due to its low density, one of the main obstacles to the widespread use of hydrogen in the energy sector is an efficient storage technology. Hydrogen densification is required for many applications. Besides conventional storage methods, i.e. high pressure gas cylinders and liquid hydrogen, progress has been made in efforts to advance the room temperature hydrogen gas storage capacity of traditional hydrides.

Numerous hydrides, with metallic bonding (e.g., those represented by $LaNi_5$ and TiFe) have been developed to reversibly store hydrogen at near-ambient temperatures, but they suffer from poor gravimetric capacity (typically less than 2 wt.% H). At the other extreme, there are ionic and covalent bonded hydrides (e.g., Li and Mg bases alloys, respectively) that good gravimetric capacities (5-10 wt.% H), but require high temperatures (> 500 K) to release the stored hydrogen at positive pressure [1].

It becomes clear that the development of new materials for hydrogen storage requires overcoming many thermodynamic and kinetic limitations. Metastable materials are of a great interest. A proper engineering of the alloy composition, surface properties, microstructure, grain size etc. and control of thermodynamic functions that determine the equilibrium state of metal-hydrogen systems are required.

Thin film hydride storage is an emerging area of research [2,3]. Physical vapour deposition technologies activated with plasma/ion beam irradiation allow the formation of thermodynamically non-stable materials, such as amorphous alloys and nanocrystalline metastable phases, although very often exhibiting stable and reproducing behavior in practical applications. These materials contain many grain boundaries, defects, impurities, disorder and strain and theirs hydrogen adsorption/desorption properties can not be fully described by the basic thermodynamic function. The number of available sites for hydrogen in nanocrystalline materials is higher than in the crystalline, and the unrelaxed material is much easier to hydrogenate than the relaxed one.

Although, there are plenty of investigations on hydrogen absorption in thin metal films under equilibrium conditions to be found in literature, a few publications are concerned with the influence of the very surface on the hydriding behavior under non-equilibrium conditions using external irradiation for the modification of properties and structure of surface and near-surface layer. The concentrated beams of photons electrons, protons and ions are used to modify surface properties during adsorption (*in situ*).

Most magnesium alloys exhibit good properties of hydrogen adsorption and storage. Recent studies have shown that magnesium alanate, $Mg(AlH_4)_2$, which contains 9.2 wt.% H, exhibits promising features as hydrogen storage material [4].

In this paper, the physical technologies (physical vapor deposition and plasma immersion hydrogen ion implantation) are used to optimize hydrogenation and dehydrogenation properties of magnesium alloys.

Results and discussions

An *in-situ* system was used for fabrication of 2-5 μm thick MgAl films on silicon and Alloy 600 substrates. Plasma immersion ion implantation (PIII) was employed for hydrogenation [5]. In PIII, the sample is immersed in high density hydrogen plasma and is biased with a series of 0.5 kV negative voltage pulses. Fig. 1 includes XRD patterns of as deposited MgAl film (a) and after PIII in hydrogen plasma (b). Fig. 1 c illustrates the typical diffractogram of PIII hydrogenated MgAl film, which after deposition was exposed to air and covered by 3-5 nm thick layer of the natural Al_2O_3. It is seen that in the as-deposited film the positions of the Bragg peaks typical for Al and intermetallic compound $Al_{12}Mg_{17}$ are registered, in agreement with the MgAl binary diagram [6].

After the hydrogenation, the sample not exposed in air shows that the peaks Al(111) and Al(200) decrease and the dominant phase becomes $Al_{12}Mg_{17}$. Small amount of Al_3Mg_2 can not be excluded. The PIII hydrogenated sample exposed to air indicates the presence of the magnesium alanate in the MgAl film. The color of sample changes to gray.

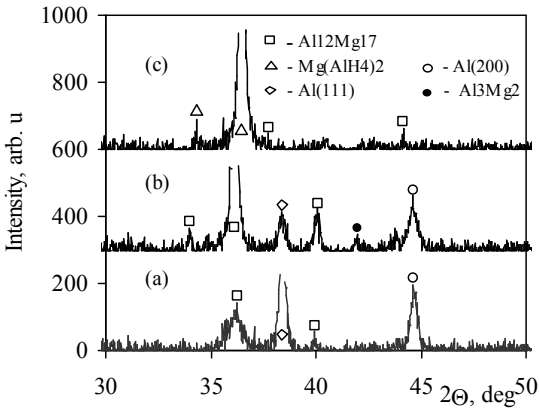

Fig. 1. XRD patterns of MgAl films.

Fig. 2 includes the dependence of hydrogen effusion intensity as a function of sample temperature. It demonstrates the sharp effusion signal from the film centered at about 630 K. The effusion procedure was performed in vacuum for the sample which included magnesium alanate.

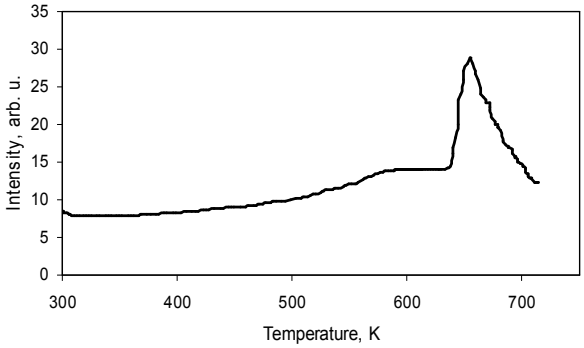

Fig. 2. Hydrogen effusion intensity *vs* temperature.

The SEM surface view (Fig. 3) manifests about the behavior of the released hydrogen after the thermal decomposition of alanate. It has been registered that the magnesium alanate decomposes at temperature around 430 K and releases the bound hydrogen. In the presence of the barrier Al_2O_3 layer on the surface the released hydrogen is accommodated in bubbles.

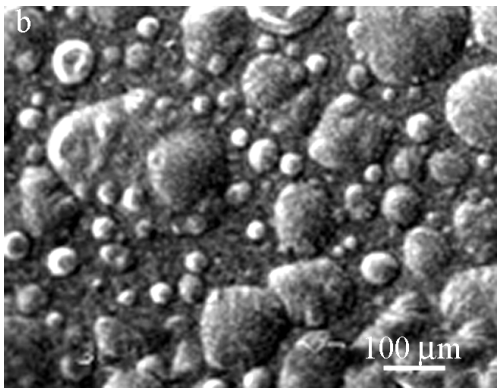

Fig. 3. SEM surface view of MgAl film after dehydrogenation.

Analysis of the effusion peak at about 630 K through the reaction rate theory indicates effusion activation energy of 1.85 eV, which is in very good agreement with the value of 1.9 eV the activation energy for hydrogen diffusion in γ-Al_2O_3 [7].

Conclusions

We have shown that physical technologies give new opportunities in the studies of complex phenomena related to hydrogenation and dehydrogenation processes of magnesium alloys. It is demonstrated the important role of the surface oxide layer on the hydrogenation efficiency and, in particular, it is presented the evidence that this oxide layer controls hydrogenation and H_2 effusion processes.

References

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