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Hydrogen absorption and desorption in rapidly solidified Mg-Al alloys

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Abstract. The addition of Al to Mg has been indicated as a suitable way to destabilise the hydride phase, in order to bring the absorption and desorption reactions close to reasonable temperatures and pressure values for hydrogen storage. Rapid solidification is known to refine the microstructure of Mg-Al alloys and it might improve the H_2 absorption/desorption kinetics. In this paper, the interaction of H_2 with rapidly solidified Mg-Al alloys have been studied for three different composition: $Mg_{38.5}Al_{61.5}$, $Mg_{69}Al_{31}$ and $Mg_{72}Al_{28}$. For $Mg_{72}Al_{28}$, no significant changes in the microstructure have been obtained by rapid solidification. In $Mg_{69}Al_{31}$, a significant grain refinement has been observed, whereas, for $Mg_{38.5}Al_{61.5}$, the formation of a metastable hexagonal phase has been found. In all cases, a disproportionation reaction has been observed after H_2 absorption, leading to MgH_2. After heating up to 430 °C the hydrogenated samples, a main desorption reaction from MgH_2 has been observed, which brings again to the starting phases. Experimental results have been discussed on the basis of a thermodynamic assessment of the Mg-Al-H system.

1. Introduction

Pure Mg can absorb H_2 to form MgH_2 with a H_2 content of 7.6 wt%, but it is too stable for hydrogen storage applications. H_2 desorption thermodynamics and kinetics may be improved to some degree by alloying, the price being a reduced H_2 capacity. Alloying Mg with Al have been reported to improve both thermodynamics [1,2] and kinetics [3] of H_2 absorption/desorption. Microstructural refinement of Mg-Al alloys has been obtained by H_2 treatment [4] and ball milling [3,5,6].

In this paper, the effect of microstructure refinement, obtained by rapid solidification, on the H_2 absorption/desorption processes has been studied in $Mg_{38.5}Al_{61.5}$, $Mg_{69}Al_{31}$ and $Mg_{72}Al_{28}$ alloys, corresponding, respectively, to the β-Mg_2Al_3 compound, eutectic and ipereutectic Mg(Al) + γ-$Mg_{17}Al_{12}$ mixture. The results will be discussed on the basis of the thermodynamic assessment of the Al-Mg-H system, recently obtained by the Calphad approach [7].

2. Experimental

Polycrystalline samples were produced using high-purity elements (99.9% for Mg and 99.98 for Al). $Mg_{38.5}Al_{61.5}$ and $Mg_{69}Al_{31}$ master alloys (MA) were prepared using a levitation induction furnace in a water-cooled copper crucible under a 0.1 MPa protective Ar atmosphere. $Mg_{72}Al_{28}$ MA was obtained with an induction furnace in a stainless steel crucible under 0.05 MPa protective He atmosphere. Rapidly solidified (RS) ribbons, about 0.9 mm wide and 40 μm thick, have been obtained by melt spinning in a He atmosphere on a Cu-Be wheel. In order to increase the surface area exposed to hydrogen, the ribbons have been crushed into powder. The structure of the samples has been checked by X-ray diffraction (XRD), recorded at RT with Cu-K_α radiation. Diffraction patterns have been refined by the Rietveld method using MAUD software. Hydrogenation experiments were performed in a home-made Sievert-type apparatus and in an Hiden IGA microbalance. Thermal programmed desorption (TPD) of the hydrogenated samples were obtained by DSC, equipped with a quadrupole mass spectrometer [8] or with a thermal conductivity H_2 detector, using a heating rate of 5 °C/min.

3. Results and discussion

3.1. Compositional and microstructural characterisation

XRD patterns of the MA and RS samples are shown in fig. 1. $Mg_{38.5}Al_{61.5}$ MA consisted of the high temperature cubic β-phase, with a lattice constant a= 28.285 Å, with no evidence of others phases (fig. 1a). The formation of a hexagonal phase subsequent to rapid solidification and ball milling of the $Mg_{38.5}Al_{61.5}$, has been reported [9,6], although details about the atomic positions in the unary cell were not given. For $Mg_{38.5}Al_{61.5}$ RS sample, diffraction peaks of the hexagonal phase matches reasonably the XRD pattern (fig. 1a), leading to lattice constants a=5.69 Å and c=9.79 Å, in good agreement with ref. [9]. For $Mg_{69}Al_{31}$ (figs. 1b) and $Mg_{72}Al_{28}$ (not shown) MA diffraction peaks are very well matched by cubic γ-$Mg_{17}Al_{12}$ phase and hexagonal Mg(Al) solid solution. XRD patterns of RS samples show broader diffraction peaks (figs. 1b), less pronounced for $Mg_{72}Al_{28}$ with respect to $Mg_{69}Al_{31}$, suggesting a significant refinement of the microstructure. In addition, a significant supersaturation of Al in Mg is verified by a reduction of the lattice constants of the Mg(Al) phase and, simultaneously, by the relative increment of this phase.

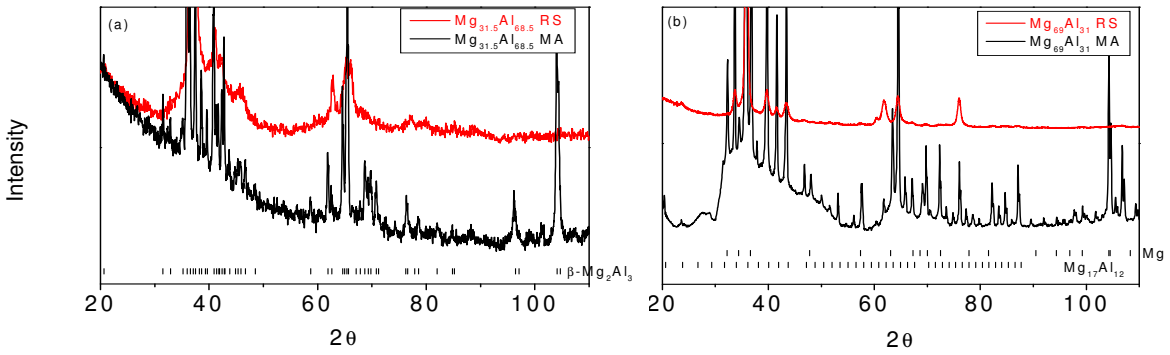

Fig.1. XRD patterns of MA and RS samples for $Mg_{38.5}Al_{61.5}$ (a) and $Mg_{69}Al_{31}$ (b) alloys.

3.2. Hydrogen absorption and desorption experiments

The XRD patterns of hydrogenated RS samples are shown in fig. 2. Fig. 3 shows the H_2 desorption peaks of hydrogenated samples submitted to a thermal treatment up to 430 °C. After H_2 desorption, the samples have been analyzed by XRD and the results are reported in fig. 2.

For $Mg_{38.5}Al_{61.5}$ RS, no evident signal were detected by the Sievert apparatus, suggesting a small amount of H_2 absorption. The XRD pattern of the hydrogenated RS sample shows diffraction peaks of the metastable hexagonal phase, together with narrow peaks related to pure Al phase. Even if the

presence of MgH_2 was not evidenced by XRD, TPD (fig. 3a) reveals a clear desorption peak, starting at about 400 °C, a typical value for H-desorption from MgH_2 [10].

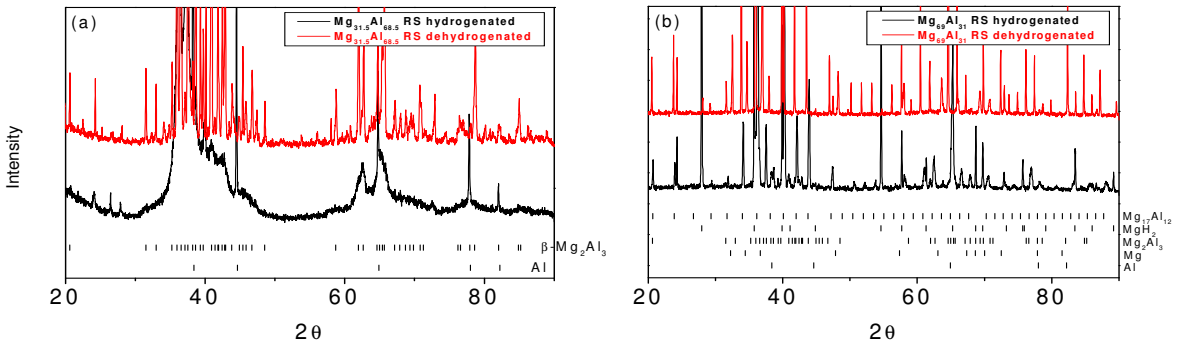

Fig.2. XRD patterns of hydrogenated and dehydrogenated RS samples for $Mg_{38.5}Al_{61.5}$ (a) and $Mg_{69}Al_{31}$ (b) alloys.

Evidence of H_2 absorption in $Mg_{69}Al_{31}$ and $Mg_{72}Al_{28}$ alloys was verified by XRD patterns, where the presence of MgH_2, β-Mg_2Al_3 and γ-$Mg_{17}Al_{12}$ phases was evidenced (fig. 2b). Desorption signals were detected by TPD (figs. 3a and 3b), corresponding to a total amount of absorbed H_2 equal to 4.7 and 4.1 wt% for $Mg_{72}Al_{28}$ MA and RS, respectively, and equal to 1.2 and 3.0 wt% for $Mg_{69}Al_{31}$ MA and RS, respectively. The presence of un-reacted γ-$Mg_{17}Al_{12}$ suggests that H_2 absorption is mainly due to the high fraction of Mg(Al) solid solution, produced by rapid solidification, which becomes unstable and leads to the formation of β-Mg_2Al_3. On the other hand, the significant amount of MgH_2, observed after hydrogenation, suggests that a disproportionation reaction occurred also for $Mg_{17}Al_{12}$ [11].

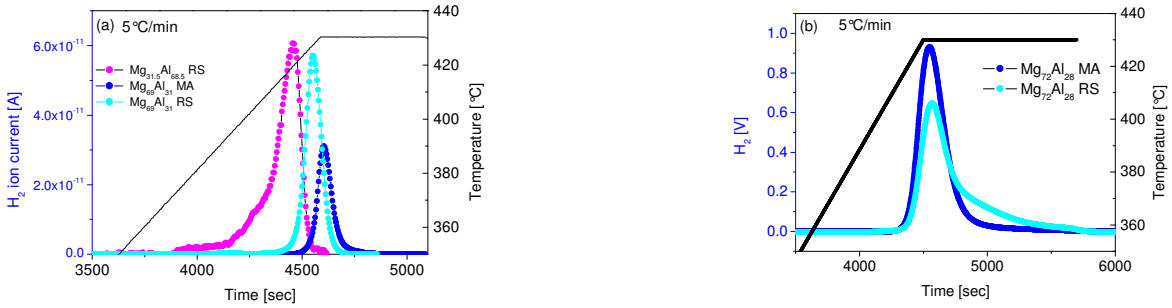

Fig.3. TPD curves for: (a) $Mg_{38.5}Al_{61.5}$ MA and for $Mg_{69}Al_{31}$ MA and RS; (b) $Mg_{72}Al_{28}$ MA and RS.

3.3 Thermodynamic analysis

The CALPHAD approach was employed to evaluate thermodynamically the phase stability in the Mg-Al-H system during the hydrogenation and desorption processes, according to the recent assessment by Palumbo et al. [7]. Three isothermal sections of the ternary Mg-Al-H phase diagram have been calculated and they are reported in fig. 4. For the $Mg_{38.5}Al_{61.5}$ sample, upon addition of H_2 at 200 °C and 40 bar, an equilibrium among β-Mg_2Al_3, f.c.c. Al and MgH_2 phases is achieved in thermodynamic calculations (fig. 4a). Metastable hexagonal phase was not considered in the thermodynamic assessment, but its free energy is likely quite close to that of equilibrium β-Mg_2Al_3 compound. MgH_2 was not detected, likely because of its small quantity, but the presence of Al was verified by XRD (fig. 2a). Both for the $Mg_{69}Al_{31}$ at 400 °C and 30 bar (not shown) and $Mg_{72}Al_{28}$ at 400 °C and 19 bar (fig. 4b), an equilibrium among γ-$Mg_{17}Al_{12}$, MgH_2 and h.c.p. Mg is obtained, from to thermodynamic calculations, in agreement with experimental findings (fig. 2b). The calculated isothermal section in the desorption conditions (T=430 °C, P=0.1 bar) confirms that hydrogenation is a reversible process.

In fact, equilibria between H_2 gas and binary Al-Mg phase(s) is achieved, confirming the occurrence of H_2 release. For example, for $Mg_{69}Al_{31}$, an equilibrium among γ-$Mg_{17}Al_{12}$, Mg(Al) and H_2 gas is obtained (fig. 4c).

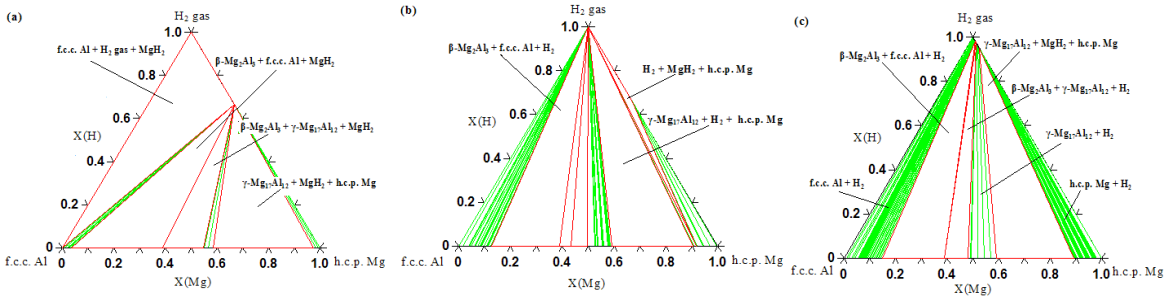

Fig.4. Calculated isothermal sections of the Al-Mg-H ternary phase diagram, according to the thermodynamic assessment in ref [7]: (a) 200 °C, 40 bar; (b) 400 °C, 19 bar; (c) 430 °C, 0.1 bar.

4 Conclusions

In this paper, it has been shown that rapid solidification allowed the formation of a metastable hexagonal phase in $Mg_{38.5}Al_{61.5}$ alloy. Hydrogen absorption has been observed in the hexagonal phase after treatment at 40 bar and 200 °C. MgH_2 and pure Al have been observed as reaction products. Dehydrogenation up to 430 °C brings to the stable β-Mg_2Al_3 phase.

A significant microstructural refinement has been obtained in $Mg_{69}Al_{31}$ eutectic alloy. Hydrogen absorption has been evidenced after treatment at 30 bar and 400 °C. After heating, H_2 desorption is anticipated for RS with respect to MA sample. Moreover, the H_2 absorption capacity is increased from 1.2 wt% for MA to 3.0 wt% for RS sample.

For $Mg_{72}Al_{28}$ alloy a coarse grained microstructure has been found after rapid solidification. After hydrogenation at 19 bar and 400 °C, an H_2 absorption capacity of 4.7 wt% has been observed for MA sample, whereas a value of 4.1 wt% has been obtained for RS sample. In this case, the presence of an higher amount of the Mg(Al) solid solution leads to an higher hydrogen absorption capacity.

For all compositions, the absorption and desorption processes are reversible, as estimated by Calphad and experimentally verified by XRD. However, the refinement of the microstructure, obtained by rapid solidification, disappears after desorption, as evidenced by XRD.

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