HYDROGEN SORPTION IN ORDERED Mg-In ALLOYS

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Abstract

Hydrogen storage (HS) performance of three Mg-*x*In-*y*CB alloys (CB - amorphous carbon, x = 55, 64, 73; y = 10 wt%) was studied. Indium concentration covered an area of ordered β structures. Alloys were prepared by ball-milling in hydrogen atmosphere. Kinetic curves and PCT isotherms were measured in the temperature interval from 200 °C to 325 °C. X-ray diffraction spectroscopy (XRD) was used for structure investigation. Alloy with x = 73 wt% In (β'' structure) showed reversible amorphization during temperature cycling between about 100 °C and 350 °C. Hydrogen sorption experiments were done by the Sieverts method under the hydrogen gas pressure ranging from 0.1 MPa to 2.5 MPa. It was found that hydrogen sorption capacity varied between 0.47 and 1.1 wt% H_2. Hydride formation enthalpy ΔH calculated from desorption PCT experiments was significantly lower than ΔH, known for pure Mg. This invoked an idea that atomic order of Mg-based HS materials might decrease the high thermodynamic stability of hydride phase.

Keywords: Hydrogen storage, Mg alloys, hydride stability, ordering

1. INTRODUCTION

Extensive research efforts have been invested into finding effective energy storage and transport of stored energy. It was found that hydrogen can serve as a secondary fuel that can be used to re-generate "green" energy from conserved source and hence, hydrogen storage (HS) became an issue of primary importance. Many materials for HS were investigated [1,2], but the hydride MgH_2 remains one of most prospective ones [3]. MgH_2 shows attractive features as for example relatively high storage capacity, favorable production costs, abundance of Mg and, last but least, biocompatibility of Mg. However, high thermodynamic stability of MgH_2 together with sluggish hydrogen sorption kinetics in Mg blocks the application of Mg at lower temperatures. Many attempts have been undertaken to destabilize the principal HS phase of these materials, MgH_2, but no significant success was achieved up to now. The aim of the present paper is to test the influence of atomic ordering upon the HS performance of ordered structures of the system Mg-In-C. It could be speculated that attractive forces between Mg and In can weaken Mg-H bonds. Interaction of materials with large-period stacking order (LPSO) structure and hydrogen was investigated, e. g., in papers [4,5]. Possible facilitation of HS in LPSO structures was reported in [6,7], where the authors show that complex several-stage sorption reactions running in HS materials with LPSO seem to lower overall energy budget of the sorption process as a whole. Binary alloy base Mg-In was chosen as a model HS material, which shows atomic ordering in extended composition range persisting up to sufficiently high temperatures [8]. Structure of ordered β phases was investigated in recent papers [9-11], survey of older results on ordered Mg-In alloys can be found in [12].

2. EXPERIMENTAL

Samples were made from pure components by ball milling (BM) in hydrogen atmosphere using Fritsch Pulverisette6 ball-mill. Each alloy contained about 10 wt% of carbon black (CB) that facilitated fine milling.

Using X-ray diffraction analysis, it was proved that CB reacted neither with Mg nor with In and therefore, the experimental materials were considered effectively to behave as quasi-binary Mg-In alloys. The mass ratio of the milling balls to the milled blend was about 60 and the milling cycle - 10 min milling/50 min cooling - was repeated 90 times. All manipulations of the milled blend were done in the glove box in protective Ar atmosphere. The chemical composition of samples is listed in **Table 1**.

Table 1 Composition of experimental alloys. CB - carbon black. c_n - nominal chemical composition, c - chemical composition of binary base Mg-In (wt%).

Alloy	c_n	c
1	27Mg-61In-12CB	31Mg-69In
2	26Mg-64In-10CB	29Mg-71In
3	17Mg-73In-10CB	19Mg-81In

Hydrogen absorption under pressure p = 2.5 MPa and desorption into a fixed volume with hydrogen pressure always well below the $p_{eq}(T)$ was carried out using Sieverts-type gas sorption analyzer PCT-Pro *Setaram Instrumentation* at temperatures T lying between 200 °C and 350 °C.

Phase composition of samples was checked by XRD EMPYREAN device using CoKa radiation and the results were interpreted (Rietveld analysis) with the HighScore Plus SW and ICSD databases. Accuracy of phase composition was about 2 wt%. Average chemical composition was checked by SEM TESCAN LYRA3 equipped with X-max80 EDS in the area approximately 300 × 500 μm containing about 10^2 grains. Accuracy of average concentration of substitution elements was within 1.5 wt%.

3. RESULTS AND DISCUSSION

3.1. Structure

In equilibrium, there are five ordered structures in the system Mg-In [4, 5]: Mg_3In (β1) with LPSO 12R that changes with increasing temperature to 3R (β') and at higher temperatures to disordered β. It is reported in [10] that this structure sequence depends on pressure (above about 2×10^3 MPa). Mg_2In (β2) and Mg_5In_2 (β_3), which decompose into β' and β_2 above 210 °C. Structure of ordered Bertholide phase β" (MgIn) is $L1_0$ - prototype CuAu.

Structure of experimental alloys prepared in the present work by BM was far from being equilibrium. Phase composition obtained by XRD is shown in **Figure 1**, where the first temperature cycle can be seen. It is obvious that Alloys 1 and 2 remain crystalline; however, the phase composition in the first cycle differed from that in all following cycles. The Alloy 3 was crystalline at room temperature but during the temperature increase (at about 200 °C) it amorphized and at the room temperature it crystallized again, but into another phase. All the sorption experiments were conducted at stabilized state (after the first temperature cycle).

3.2. Kinetics of hydrogen sorption

All measured kinetic curves, c_H vs t, showed sigmoid-type, typical for the nucleation-and-growth mechanism [13]. The curves were linearized in co-ordinates $[-\ln(1-\alpha)]^n$ vs t with slope k, where fraction of reacted amount is $\alpha = c_H / c_H^{max}$ (c_H^{max} stands for hydrogen sorption capacity and exponent n lies between ¼ and 4). One example of linearized kinetic curves is plotted in **Figure 2**. Values of n varied from ¾ to 3, which complies well with interval expected in literature (summary, e.g., in [13]) for the nucleation-and-growth mechanism.

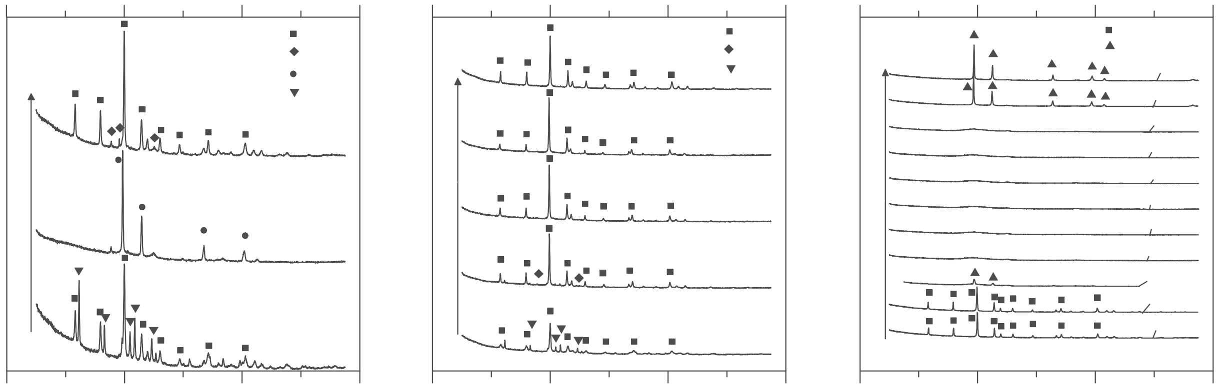

Figure 1 Structure of experimental alloys

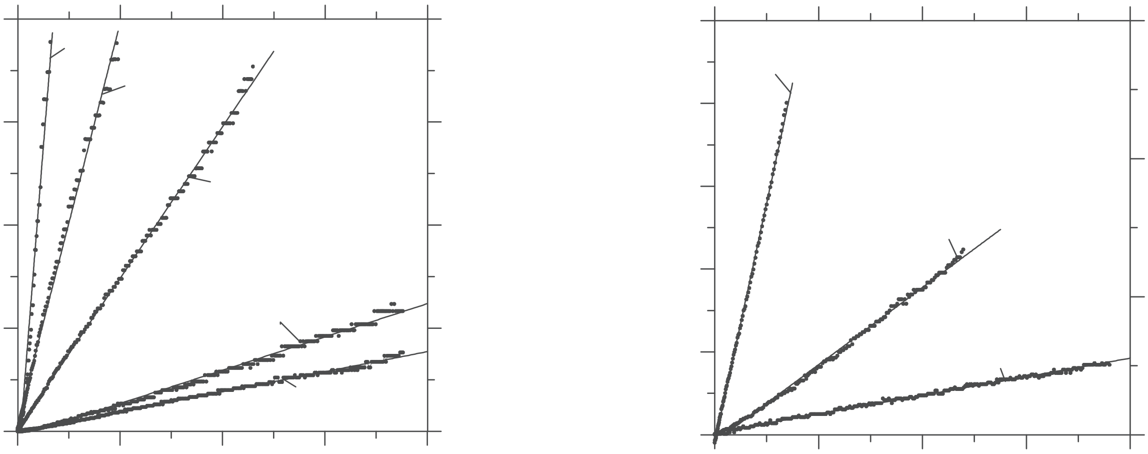

Figure 2 One example of linearized kinetic curves

Activation energy of hydrogen absorption and desorption kinetics, E_a^A and E_a^D, respectively, can be evaluated from the temperature dependence of slope k of the straight lines in **Figure 2** from equation

$$k(T) = k_0 \exp\left(-\frac{E_a^{A,D}}{RT}\right). \quad (1)$$

Temperature dependence of all obtained values of k can be seen in **Figure 3**, fitting results are listed in **Table 2**.

Table 2 Activation energy of hydrogen absorption E_a^A and desorption E_a^D and hydrogen sorption capacity c_H^{max}

Alloy	E_a^A	E_a^D	c_H^{max}
	(kJ/mol H_2)	(kJ/mol H_2)	(wt% H_2)
1	109 ± 16	121 ± 22	1.1 ± 0.2
2	106 ± 10	147 ± 15	0.7 ± 0.2
3	49 ± 15	129 ± 13	0.47 ± 0.09

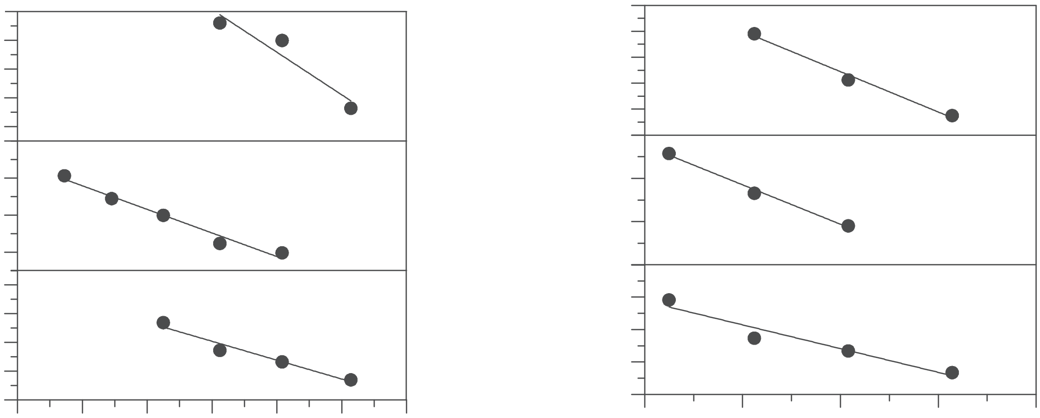

Figure 3 Temperature dependence of rate constants k from **Eq. (1)**. (a) - absorption, b - desorption

It is obvious that the values of activation energies of desorption, E_a^D in Alloy 3, are considerably lower than in Alloys 1 and 2. We propose that this phenomenon may be caused by tendency of Alloy 3 to self-amorphizing - see **Figure 1c**. No evidence of amorphizing in Alloys 1 and 2 was observed (see **Figures 1a, b**).

It should be noted, however, that easier activation of hydrogen sorption in Mg-In alloys was achieved at the cost of lowered hydrogen sorption capacity c_H^{max} - see **Table 2**. The decrease in c_H^{max} with increasing c_{In} can be reasonably explained by decreasing content of Mg in alloys with increasing In concentration.

3.3. Measurement of pressure-concentration isotherms (PCT)

One example of measured PCT curves for hydrogen desorption is shown in **Figure 4**. Only one plateau was observed in all cases that indicates that only one hydride phase - MgH_2 - takes part in the process of hydrogen sorption in Alloys 1-3. The plateaus have shown considerable slope and curvature. It may be due to dependence of p_{eq} on hydrogen concentration, c_H, as proposed in [14]. Dashed lines show approximate position of phase boundaries α/ α+β and α+β/ β. It was found that c_H^{max} decreased with increasing c_{In} (see **Table 2**), and also that the two-phase field α+β tend to close at decreasing temperature with increasing c_{In}. Critical temperature T_c in Alloy 3 was even as low as 250 °C. For construction of Van't Hoff diagram in **Figure 5**, value of p_{eq} *at about middle of respective plateau* [2] was taken- see the intersections of PCT curves and thick gray line in **Figure 4**. Enthalpy and entropy of hydride phase *decomposition* are listed in **Table 3**.

Table 3 Enthalpy Δ*H* and entropy Δ*S* of hydride decomposition. Average literature values of Δ*H* and Δ*S* for Mg are added for comparison

Alloy	**Δ*H***	**Δ*S***	**remark**
	(kJ/mol H_2)	(kJ/mol H_2/K)	
1	57 ± 3	0.117 ± 0.005	This work
2	54 ± 3	0.114 ± 0.006	This work
3	51.5	0.117	This work
Mg	75 ± 2	0.135 ± 0.002	[15-18]
Pd	52	0.117	[1]

It can be seen that all measured values of p_{eq} in temperature interval 473 - 648 K are above the equilibrium hydrogen pressure reported for pure Mg. It means that addition of In decreases the stability of MgH_2. It can also be seen in **Figure 5** that values of p_{eq} measured for Alloy 3 approximately coincide even with the values reported in [1] for Pd (hydride $PdH_{0.6}$).

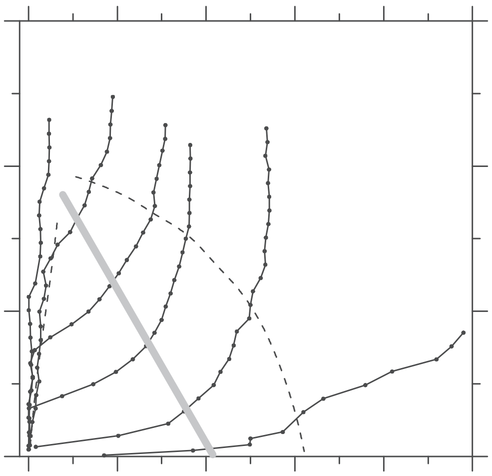

Figure 4 Example of measured PCT isotherms of hydrogen desorption

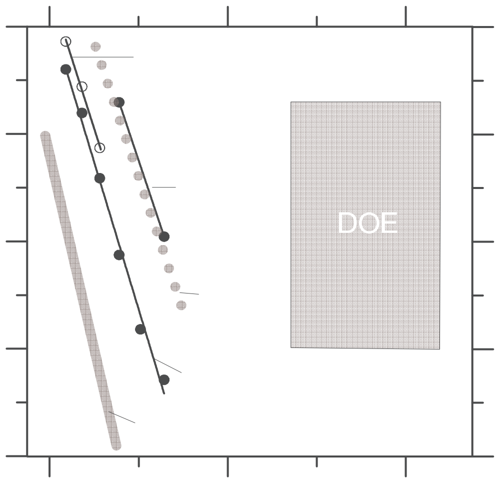

Figure 5 Van't Hoff plot. Numbers count experimental alloys. Gray straight line - average values for Mg from [15-18], gray dotted line - literature values for Pd (hydride $PdH_{0.6}$) [1], DOE - desired area according to US Department of Energy [1]

4. CONCLUSIONS

Addition of indium to Mg decreases the thermodynamic stability of MgH_2 and facilitates the hydrogen sorption kinetics. This effect can be ascribed to atomic order and/or amorphous structure of the studied alloys. Results obtained for Alloy 3, p_{eq}, enthalpy ΔH and entropy ΔS of hydride sorption in Mg-In even coincide with respective values reported in [1] for Pd. The decreased thermodynamic stability of Mg-In alloys was achieved at the expense of hydrogen sorption capacity that decreased down to c_H^{max} = 0.47 ± 0.09 wt% H_2 (for Alloy 3). Even this low sorption capacity, however, is not lower than value 0.52 wt% H_2 known for $PdH_{0.6}$ [1,8]. It is obvious that values of p_{eq} of Alloy 3 approached significantly to area desired for vehicular applications as demanded by US Department of Energy (see DOE rectangle in **Figure 5**: temperature between 25 °C and 100 °C and hydrogen working pressure between 0.1 and 1 MPa). Beneficial effect of ordering upon sorption performance of HS Mg-In alloys seems to be a prospective way how to effectively decrease MgH_2 hydride thermodynamic stability. This conclusion, however, deserves a more detailed study in the future carried out with other Mg-based alloys with ordered structure.

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