

Significant decrease of hydride decomposition enthalpy in ordered Mg-In alloys induced by growing hydrogen concentration

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Abstract

Hydrogen sorption in four ball-milled Mg- x In alloys (with $x = 9, 61, 69,$ and 81 wt.%) was studied. It was found that pressure-concentration isotherms (PCI curves) of hydrogen desorption from disordered alloy (9 wt.% In) showed “ordinary” appearance leading to a constant hydride decomposition enthalpy ΔH close to the value known for pure Mg; however, the plateaus of PCI’s obtained for desorption from ordered alloys ($x > 9$ wt.% In) were significantly upward-curved. Observed values of ΔH in ordered alloys were lower and decreased with increasing x and hydrogen concentration. Results were explained by size effect.

Key words: hydrogen storage, Mg alloys, ordering, hydrides, ball milling

1. Introduction

Extensive research is steadily devoted to searching effective ways on how to store energy [1–3]. According to the current commonly accepted opinion, hydrogen might serve as a fuel that can be used to storing and re-generating “green” energy from a secondary source [4]. Hence, hydrogen storage (HS) became an issue of primary importance in the sense of storage and transport of conserved energy [5–7]. HS in solid-state avoids safety hazards – nowadays commonly tolerated – coupled with usage of containers with compressed or liquefied hydrogen. Astonishingly, both volumetric and gravimetric density of hydrogen stored in solid-state may be higher than that stored in compressed and even that in the liquefied form [8].

Many diverse materials for HS were investigated up to now [9, 10], but the magnesium hydride MgH₂ remains one of the most prospective ones [11–21] due to relatively high storage capacity, favorable production costs, abundance of Mg and, last but not least, to bio-neutral reaction and non-toxicity of Mg.

However, the high thermodynamic stability of MgH₂ together with sluggish hydrogen sorption kinetics in Mg blocks the application of Mg at lower tem-

peratures. There are four main strategies effectual in improving sorption kinetics: alloying [11], nano-sizing [22], nano-confinement [11] and catalysis [9–11, 23]. Moderate success was achieved as for lowering in thermodynamic stability of Mg-based hydride phase up to now [10]. Improvement in MgH₂ destabilization was reported in disordered solid solutions Mg-In [24–26].

Using Mg-based alloys with a tendency to long-period stacking order (LPSO) [27] may be a new way how to decrease the thermodynamic stability of MgH₂ and, at the same time, to preserve other favorable features of Mg-based HS alloys. It was reported that LPSO in complex HS alloys led to nucleation of phases formed during hydrogenation that acted as a very fine distributed catalyst for hydrogen storage [27–32]. Therefore, it is highly eligible to orient future research in this direction.

LPSO structure is, in fact, a derivative of hexagonal close-packed structure that can be generated by stacking of hexagonal basal planes 0001 in a sequence ...ABABAB... . Introduction of a plane C produces a stacking fault (SF) that can be understood as local FCC interlayer (regular FCC structure originates by stacking 111 planes in a sequence ...ABCABC...) [33]. LPSO structures have been investigated in past two

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decades first of all as structural (not functional) materials owing to their low density, high specific strength and specific stiffness and good cast characteristics, which have a high potential to be used in automotive and aerospace industries [34].

Based on recently published results, utilization of LPSO phases seem to be also a novel way, how to improve HS performance. New Mg-based hydrogen storage materials (HSMs) with LPSO were investigated, e.g., in [23, 27–32, 34–36]. Their interaction with hydrogen was studied, e.g., in [22, 29, 30, 32, 37, 38]. Possible facilitation of HS in LPSO structures was reported, e. g., in [30, 31, 37], where the authors showed that complex several-stage sorption reactions running in HSM with LPSO could decrease overall energy budget of the sorption process as a whole. The beneficial effect of LPSO is not straightforward. It was found that the ordered structure was not restored after the first hydrogenation cycle [23, 27–32, 34–36]. Instead, the additive elements segregate to SF's, generate (more or less) stable structures [27] that are approximately regularly distributed [27, 39, 40]. They generate nucleation loci that grow to very finely dispersed particles [31]. These particles act as extraordinary effective intrinsic catalysts for the hydrogenation process. In this sense, LPSO materials, generally, may serve as precursors for HSMs with fine dispersion of effective catalyst, promising for HS applications. Moreover, the fine particles of new phases are located (and persist) in planes along the original SF's that are known to be the paths of rapid hydrogen diffusion. Hence, it can be presumed that these “2D channels” keep their high hydrogen diffusivity due to lattice distortion. This is a further argument that contributes to the attraction of the study of HS in materials prepared from LPSO precursors.

2. Experimental

In the present work, we have chosen – as a model material – binary alloy system Mg-In that, in a concentration range between about 25 and 60 at.% In, forms ordered phases β_1 , β_2 , β' , and β'' [41]: Crystalline

Mg₃In (β_1) phase changes with increasing temperature from 12R to 3R phase β' with FCC interlayers identical with L1₂ – prototype AuCu₃ and at higher temperature finally to disordered β . Mg₂In (β_2) is stable up to about 548 K, and Mg₅In₂ (β_3) decomposes into ordered β' and β_2 above 483 K. LPSO phase MgIn (β'') has FCC interlayers identical with L1₀ (prototype CuAu) [42, 43].

Samples of four alloys were made from pure components Mg (3N8 purity) and In (4N) by ball milling (BM) technique in hydrogen atmosphere using Fritsch Pulverisette 6 ball-mill. The BM was facilitated by an admixture of about 10 wt.% carbon black (CB – 2N purity). Carbon did not enter any phase, and hence, the studied alloys could be effectively treated as binary alloy systems. Its presence, however, may catalyze the hydrogen sorption kinetics.

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. Hydrogen was absorbed under hydrogen gas pressure of $p = 2.5$ MPa, and desorbed into a fixed volume under hydrogen pressure, being always well below the equilibrium hydrogen pressure $p_{\text{eq}}(T)$. The sorption experiments were carried out using Sieverts-type gas sorption analyzer PCT-Pro Setaram Instrumentation at temperatures between 475 and 648 K.

Morphology of milled samples, average chemical composition and chemical maps were observed by SEM TESCAN LYRA3 equipped with X-max80 EDS in the area approximately $300 \mu\text{m} \times 500 \mu\text{m}$ containing about 10^2 grains. The typical grain size was about $30 \mu\text{m}$. Accuracy of the average concentration of substitution elements was within 1.5 wt.%.

All manipulations of the milled blend inclusive the filling the cuvette were done in the glove box in a protective Ar atmosphere. Sample in the cuvette was transported in a small container filled by Ar and inserted into the sorption apparatus.

3. Results and discussion

Nominal chemical composition of ball-milled

Table 1. Experimental alloys. c_{In} – chemical composition and equilibrium phase composition within the interval of sorption temperatures ΔT according to literature sources [42–44]

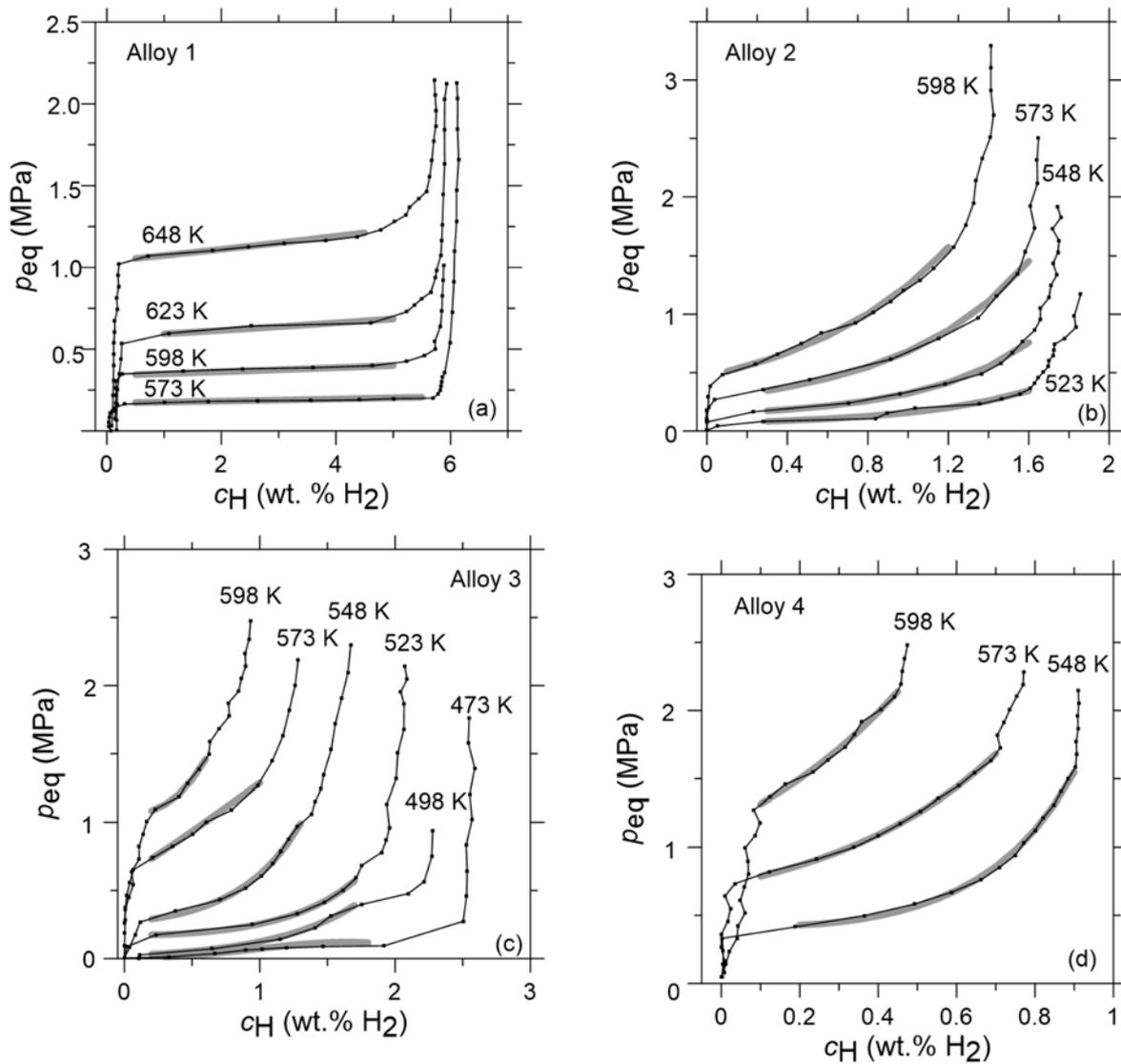
Alloy	c_{In} (wt.%)	ΔT (K)	Phase composition		
			[42]	[44]	[43]*
1	Mg-9In	573–648	(Mg)	(Mg)	(Mg)
2	Mg-61In	523–598	β_1	β'	β_1
3	Mg-69In	473–598	$\beta'^{**}, (\beta' + \beta_2)^{***}$	β'	$\beta'^{**}, (\beta' + \beta_2)^{***}$
4	Mg-81In	473–523	–	β''	–

* taken from [41], ** $T \geq 573$ K, *** $T < 573$ K

Table 2. Phase composition at room temperature. Literature data are only estimated (there are no exact data on phase boundaries at low temperatures); this work – phase composition obtained by XRD

Alloy	Phase composition			
	[42]	[44]	[43]	This work
1	(Mg)*	(Mg)*	(Mg)*	(Mg)*
2	β_1	(Mg) + β'	β_1	β_1
3	$\beta_3 + \beta_2(+\beta'')$	$\beta' + \beta''$	$\beta_3 + \beta_2(+\beta'')$	β''
4	–	–	–	$\beta'' + (\text{In})^{**}$

* solid solution of In in Mg, ** $\beta'' +$ solid solution of Mg in In at $T < 473$ K (amorphous at $T \geq 473$ K)



Figs. 1a–d. PCT desorption curves.

batches (irrespective to CB) and nominal phase composition of equilibrated alloys according to [42–44] are listed in Table 1.

Alloy 1 represented the HS behavior of the disordered solid solution of In in Mg, Alloy 2 was designed

to represent LPSO β_1 structure 12R/3R [42] and Alloys 3 and 4 should behave as ordered structures β' and β'' , respectively.

However, it is difficult to reach an equilibrium state of ordered alloys [41–44]. The structure of both Al-

loys 3 and 4 was found to be β'' at room temperature even after several hydrogen absorption (A)/desorption (D) cycles – compare present results obtained by XRD with estimations from [42–44] in Table 2.

Pressure-composition isotherms (PCT) of desorption are shown in Fig. 1. It can be seen that PCT curves measured with Alloy 1 (disordered solid solution of In in Mg) show distinctly separated segments. At a small concentration of hydrogen, c_H , the first, steep segment is related to the hydrogen solution in a disordered solid solution of hydrogen in Mg. The second part is a slightly sloped, approximately linear plateau, related to a mixture of Mg with solved hydrogen and hydride phase and the last, steep part, originating in the solution of hydrogen in hydride phase. The subdivision of PCT curves obtained with other alloys into the three segments is much less distinct. Moreover, the medium part of PCT isotherms is considerably convex-curved. In the case of Alloy 4, only two isotherms were measured due to low critical temperature limiting the existence of hydride phase (the maximum temperature at which the hydride phase can exist) [9].

To obtain enthalpy of hydride decomposition, ΔH , from the Vant' Hoff diagram, the value of equilibrium hydrogen pressure, p_{eq} , at the middle of the plateau ([9, 10]) is commonly taken.

Systematic expressive curvature of all PCT's measured with all ordered alloys makes the construction of the Vant' Hoff diagram for Alloys 2–4 in this way difficult. Therefore, respecting the observed curvature, the middle part of all PCT's was fitted by polynomials of second order in c_H (thick gray curves in Fig. 1) and enthalpies ΔH were calculated using the fitted values of $p_H(c_H)$ at several values of c_H .

It is evident from Fig. 2 that ΔH does not depend markedly on c_H in disordered Alloy 1, and that it is close to the value $\Delta H = 75 \text{ kJ mol}^{-1} \text{ H}_2$ known for pure Mg [10]. In Alloys 2–4, however, ΔH decreases significantly with growing values of c_H and c_{In} . These trends may be a consequence of the size-effect during the hydride decomposition in studied alloys: It can be found that a partial volume of unit cell of MgH_2 per one Mg atom is $61.6 \text{ \AA}^3/\text{at H}$. In Alloy 1 the partial volume of unit cell makes $46.5 \text{ \AA}^3/\text{at Mg}$ [45] and in phases β_1, β'' and in solid solution (In), the values of volume fraction are 22.6, 23.0, and $26.1 \text{ \AA}^3/\text{at Mg}$, respectively [46]. Hence, it can be concluded that the misfit between the partial volumes falling to one Mg atom in the original hydride phase on one side and hydrogen-free phase on the other one increases with increasing c_{In} . The size effect can also explain upward curvature of plateaus of PCT curves.

Similar curvature of PCT diagrams was also observed in the case of hydrogen sorption in binary alloy system Mg-Cd [47]. The authors explained the curvature by a decrease of the chemical potential (partial

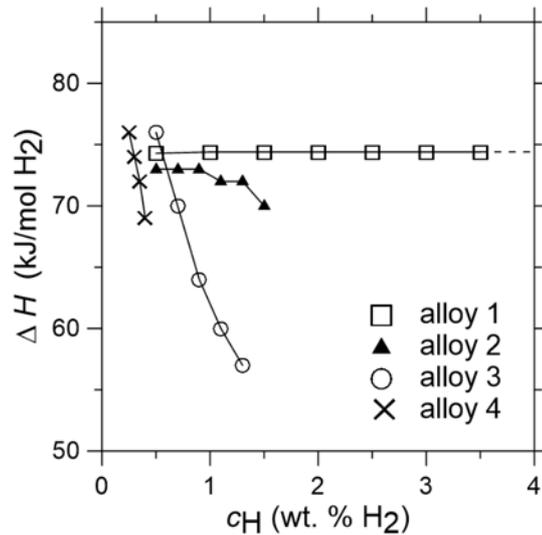


Fig. 2. Hydride decomposition enthalpy ΔH in dependence on hydrogen concentration c_H . Calculated from fitted values obtained from plateaus of desorption PCT isotherms.

molar free enthalpy $\overline{\Delta G_{Mg}}$ of Mg in the Mg-Cd solid solution with increasing Cd content in H-free matrix due to the Cd rejection by the newly formed MgH_2 . Using thermodynamic model proposed in [47], one can easily obtain (with $\Delta S = 0.135 \text{ J/K mol}^{-1} \text{ H}_2$, which is a constant for all HS materials [10]) for Mg_3Cd values $\Delta H = 71.8 \text{ kJ mol}^{-1} \text{ H}_2$ and $61.0 \text{ kJ mol}^{-1} \text{ H}_2$ at $c_H = 0 \text{ wt.}\% \text{ H}_2$ and at $c_H = 3 \text{ wt.}\% \text{ H}_2$, respectively. It can be speculated that a similar mechanism may be at work also in the Mg-In system.

Another factor that can decrease ΔH with increasing c_{In} is easier hydrogen diffusion and mobility in matrix that significantly tends to atomic ordering, since it can be supposed that affinity of one strong hydride-forming element (Mg) of the alloy to hydrogen is lowered by competitive attraction of the element to the other alloy component (In).

Moreover, with increasing c_{In} , the Mg-In alloys show the increasing tendency to a refinement of crystalline grains. Analyzing the width of diffraction peaks in XRD patterns, corresponding to respective majority Mg_xIn_y phase, it was found that the size of crystallites, d (more precisely: the size of diffraction area), decreased with increasing c_{In} . In Alloys 2 and 3, values of d were 478 and 324 Å, respectively. Alloy 4 showed even self-amorphizing behavior: When the temperature increased above approximately $T_a = 473 \text{ K}$, the crystalline ball-milled matrix Mg_xIn_y amorphized, and after the temperature decreased below T_a , the peaks of Mg_xIn_y phase appeared again – see in Fig. 3. This amorphizing behavior of Mg_xIn_y phase was observed repeatedly during temperature cycling.

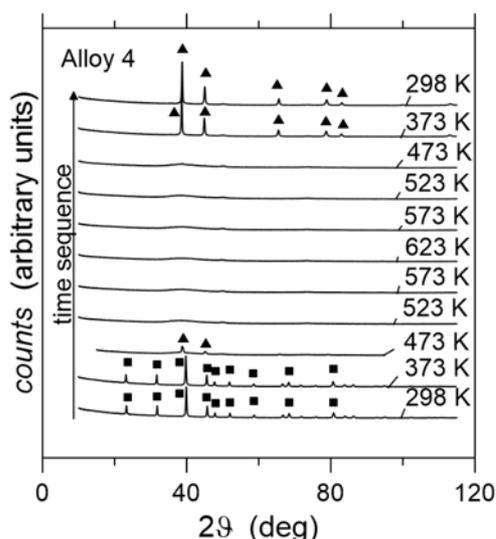


Fig. 3. XRD patterns measured with Alloy 4 at varied temperatures. – MgIn, – Mg_{0.1}In_{0.9}.

4. Summary

It was found in the present paper that Mg-In model alloys that show ordering may serve as prospective precursors for hydrogen storage materials. These materials – due to a high fraction of Mg – may keep relatively high hydrogen storage capacity of Mg and, at the same time, the hydride decomposition enthalpy may be lowered compared to common Mg-based crystalline hydrogen storage alloys. This idea is currently being tested with more complex HS materials in running research.

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