

HYDROGENATION OF CHOSEN Mg_mX_n INTERMETALLICS (X= Al, Ga, In, Si, Sn)

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Abstract

Hydrogen sorption in chosen intermetallics Mg_mX_n ($Mg_{17}Al_{12}$, Mg_2Ga , mixture of β -Mg-In phases, Mg_2Si and Mg_2Sn) formed by magnesium and elements from the 13th (X: Al, Ga, In) and 14th (X: Si, Sn) groups was studied between the room temperature and $T = 350$ °C. Hydrogen pressure p varied from 10^{-3} MPa to 6 MPa. Hydrogen solubility in α phase (solid solution of hydrogen in Mg_mX_n before the hydride phase was nucleated) was close to hydrogen solubility in pure Mg. Concentration c_H of hydrogen solved in Mg_mX_n depended linearly on pressure p ; dependence of c_H on temperature T was relatively weak. MgH_2 was the main hydrogen storage phase in all the compounds Mg_mX_n . Nucleation of MgH_2 at 350 was observed at pressure above approximately 1 MPa in $Mg_{17}Al_{12}$ and above 2 Ma in other compounds. Maximum values of c_H in hydride-containing compounds Mg_mX_n detected at $T = 350$ °C depended on the stability of Mg_mX_n .

Keywords: Hydrogen, hydrogen storage, Mg alloys, hydrogen solubility, MgH_2

1. INTRODUCTION

One of the key technology issues of clean power generation, energy transport and energy storage based on hydrogen is effective storage of hydrogen itself. Magnesium is a prospective candidate base component of hydrogen storage alloys, because its hydride, MgH_2 , contains 7.66 wt. % H_2 . However, poor kinetics of MgH_2 formation during hydrogen storage and reverse decomposition into Mg and hydrogen during hydrogen desorption is a serious obstacle that prevents a wide application of pure Mg as a hydrogen storage material [1-7]. Great effort has been devoted in literature to find ways how to improve the sorption kinetics by catalysis. Particles of catalyzing phase(s) were deposited on the surface of Mg-rich grains that are the main hydrogen reservoir [5, 6]. They acted as entrance gates for hydrogen.

It was reported earlier [8, 9] that light construction Mg-based alloys, exposed to corrosion environment, showed less corrosion damage in the vicinity of $Mg_{17}Al_{12}$ particles. Bearing in mind this fact together with the possible catalytic effect of Al [10, 11], it can be supposed that this phase, harmful in construction materials due to its brittleness, may be beneficial in function materials designed for hydrogen storage. Similar effect can be expected in other elements from the 13th group of periodic table. Beneficial effect upon the hydrogen storage was reported also in Mg alloyed by elements from the 13th and the 14th group [5, 12-15].

In the present work, hydrogen sorption behavior of chosen ball-milled Mg_mX_n intermetallics (X= Al, Ga, In, Si, Sn) was studied with the aim to judge the availability of Mg_mX_n to catalyze the hydrogen sorption in Mg. Acceptable hydrogen solubility and resistance to form hydrides are desirable: high solubility assures good hydrogen throughput and hydride phase is characterized by low hydrogen diffusivity.

2. EXPERIMENTAL

The compounds $Mg_{17}Al_{12}$, Mg_2Ga , β_n -Mg-In (a mixture of phases β_n - mainly Mg_3In), Mg_2Si and Mg_2Sn were prepared by induction melting of pure components (Mg with Al, Ga, In) and by subsequent ball-milling in hydrogen, or by ball-milling only in hydrogen (Mg with Si, Sn). The samples were ball-milled using *Fritsch-*

Pulverisette 6 (450 rpm, 10min milling / 50min cooling - 14 times repeated; mass ratio of the balls to the charge was about 240). Powder samples were taken out of the ball mill jar in the glove box, weighted and sealed into sorption cell - all manipulations were done in Ar protective atmosphere. The mass of powder samples for the sorption experiments was about 150 mg.

Hydrogen sorption characteristics were measured using Sieverts-type gas sorption analyzer *PCT-Pro* Setaram Instrumentation. This equipment enables safe and fully automated repeated sorption measurements. The study was carried out at temperatures between the room temperature and 350°C and under hydrogen pressure from 10⁻³ to 6 MPa. The purity of both hydrogen and helium (calibration gas) was 6N.

The samples were annealed at 360 °C for 2 hours. The hydrogen solubility in Mg_mX_n was estimated first at temperature 250°C and then at temperature 350°C. The onset of hydride nucleation, equilibrium hydrogen pressure of hydride phase and α_H^{\max} were estimated at 350°C. After the measurement at 350 °C, the phase composition of (hydrogenated) samples was performed by XRD phase analysis by *X'Pert Pro MPD* device using CoK_α radiation.

3. RESULTS AND DISCUSSION

Concentration of absorbed hydrogen, α_H , in dependence on hydrogen pressure p is plotted in **Figure 1a-c** and in **Figure 2b, c** for elements from the 13th and 14th group, respectively.

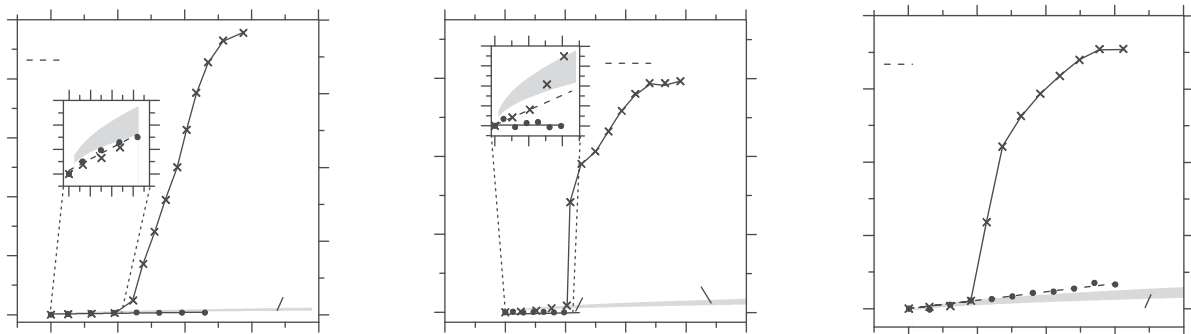


Figure 1 Dependence of hydrogen absorption in Mg_mX_n compounds with X from 13th group

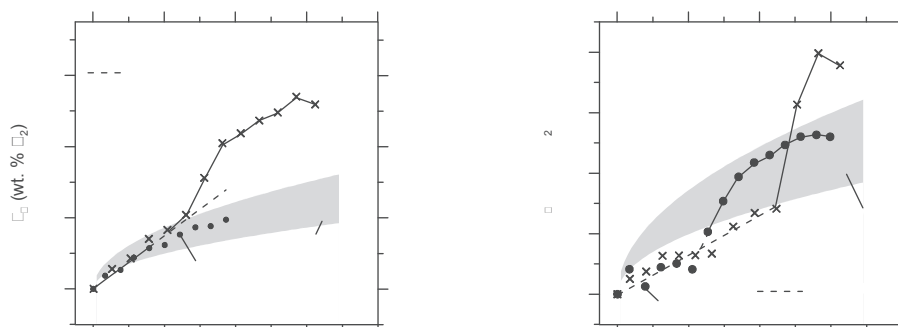


Figure 2 Dependence of hydrogen absorption in Mg_mX_n compounds with X from 14th group

At the temperature of $T = 250$ °C, the hydride nucleation was very slow, therefore measurement was conducted in supersaturated solid solution of hydrogen in Mg_mX_n up to the highest hydrogen pressure. For X=Ga, no measurable hydrogen solubility was obtained. Negligible difference between α_H found at 250°C and 350°C

was observed at low pressure p for $X=Al, In, Si$ and Sn . All measured values of c_H were close to hydrogen solubility known for pure Mg [16] (gray areas in **Figures 1, 2**).

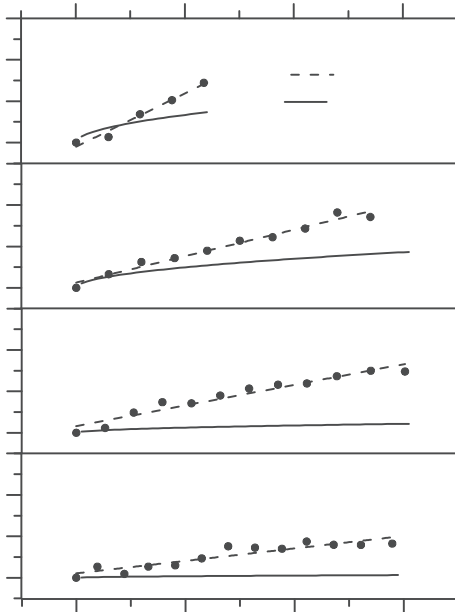


Figure 3 Hydrogen solubility in β_n -Mg-In

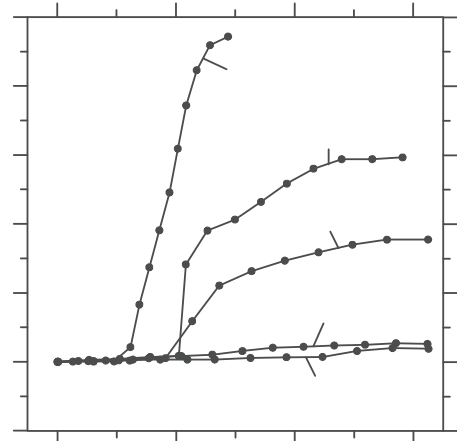


Figure 4 Hydrogen solubility in Mg_2In at 350 °C

Systematically higher hydrogen solubility, c_H , - compared to that in pure Mg - was found only in β_n -Mg-In, where the Henry's constant, k_H ($p = k_H c_H$), significantly depended on the temperature (see in **Figure 3**). Average values of Henry's constants for other Mg_mX_n are listed in **Table 1**.

At temperature $T = 350^\circ C$, the onset of hydride nucleation was detected - see the abrupt increase in c_H - **Figure 4**. The nucleation started for $X=In$ at about $p = 1$ MPa, for other X at about $p = 2$ MPa.

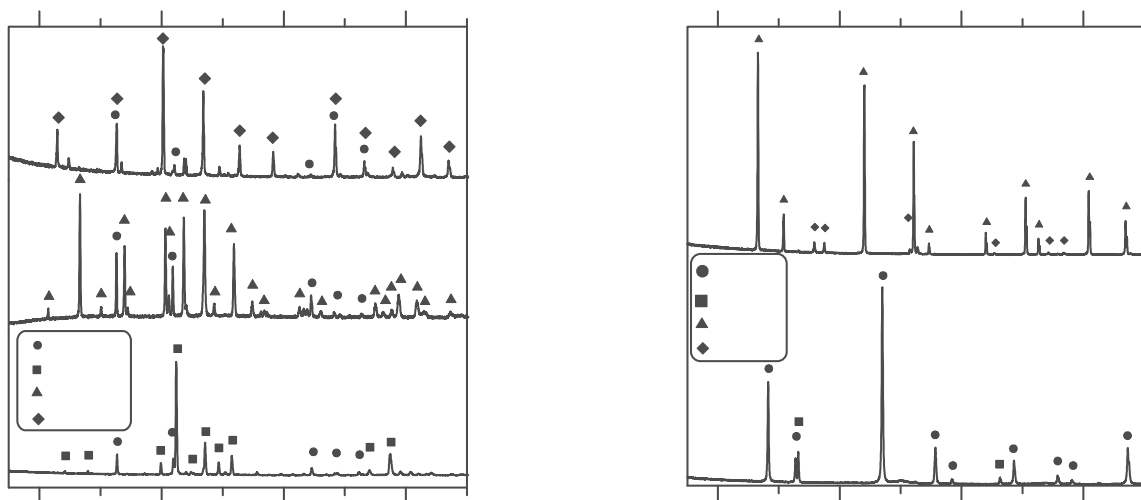


Figure 5 XRD pattern measured with hydrogenated Mg_mX_n . X from the 13th (a) and 14th (b), group respectively

It can be seen in **Figures 1, 2** and in **Figure 4**, where the sorption curves measured at 350°C are plotted for comparison that values of maximum hydrogen content, c_H^{\max} , are negligible for X from the 14th group, where the compounds Mg_mX_n are very stable (measured by the value of critical temperature T_c of respective Mg_mX_n compounds [17] - see in **Table 1**).

The phase composition of samples Mg_mX_n was analyzed after the hydrogen sorption experiment at $T = 350^\circ\text{C}$. XRD patterns are shown in **Figures 5a, b** and results of Rietveld analysis are listed in **Table 1**.

It can be seen that the only hydrogen-containing phase is MgH_2 . This is qualitatively in agreement with the general reaction scheme [18]



According to Eq.(1), hydrogen under elevated pressure dissociates Mg_mX_n compounds into hydride MgH_2 and elemental X. This reaction runs easier if Mg_mX_n is not too stable ([17]), which is evident if the content of MgH_2 obtained for X from group 13 and 14 is compared (**Table 1**).

Table 1 Characteristics of studied materials

group	Mg_mX_n	T_c °C	c_H^{\max} wt. % H ₂	k_H MPa/wt.%H ₂	phases in charged sample (after 350 C) in wt. %				
					Mg_mX_n	Mg	X	MgH_2	MgO
13	$Mg_{17}Al_{12}$	437	1.95	78.1 ± 3.9 ¹⁾	84.1	0	0.7	13.VI	1.VII
	Mg_2Ga	373	1.19	127.5 ± 1.6 ²⁾	73.7	0	0	26.I	0.2
	$\beta_n\text{-Mg-In}^{4)}$	360	0.71	70.1 ± 2.3 ³⁾	80.8 ⁴⁾	1.VI	1.0	13.IV	3.II
14	Mg_2Si	1085	0.09	60.8 ± 1.7 ¹⁾	87.6	0	8.IX	0	3.IV
	Mg_2Sn	771	0.08	149.0 ± 8.1 ¹⁾	94.3	0	5.VII	0	0
¹⁾ average value for temperatures from interval 250 °C - 350 °C ²⁾ for values measured at 350 °C ³⁾ for values measured at 250 °C ⁴⁾ mainly Mg_3In									

It can be speculated that hydrogen can be partly absorbed in Mg_mX_n without formation of hydride (hydrogen sorption in hydrogen supersaturated Mg_mX_n). The hydrogen sorption behavior observed at temperature 250°C can be taken as an evidence for this conclusion: The increase in c_H was observed even at pressures, where the presence of hydride could be expected.

It should be noticed that the weight ratio of MgH_2 and X obtained by XRD (**Table 1**) did not reflect quantitatively the Eq. (1): The ratio of maximum values of c_H^{\max} obtained from sorption experiments (see **Figure 4**, and **Table 1**) does not agree with amount of hydrogen calculated by Rietveld (phase) analysis from amount of MgH_2 (**Table 1**). This quantitative discrepancy originate, most likely, in non-equilibrium conditions of hydrogenation.

4. SUMMARY

Hydrogen sorption was studied in $Mg_{17}Al_{12}$, Mg_2Ga , in a mixture of β phases $\beta_n\text{-Mg-In}$, and in compounds Mg_2Si and Mg_2Sn . Measured dependence of hydrogen concentration c_H on hydrogen pressure p was linear for small values of p and for temperature between 250 °C and 350 °C. It was found that hydrogen solubility in

Mg_mX_n did not depend strongly on the temperature and that it is close to that for pure Mg. The only studied material, where the distinct temperature dependence was observed and where, at the same time, the hydrogen solubility was significantly higher than solubility in Mg was a mixture of β phases β_n -Mg-In.

In the temperature interval 250 °C - 350 °C, none of the studied compounds showed the hydride formation below the pressure 1 MPa. This is important from the point of view of application of Mg_mX_n in the field of hydrogen storage, since the rate of hydrogen diffusion in hydride can be expected slower than in the lattice without hydride phase.

5. CONCLUSION

Comparing the hydrating behavior of studied materials, it can be concluded that the mixture of β phases β_n -Mg-In is the material that shows the highest hydrogen solubility in α phase of Mg_mX_n. Its resistance to form hydride phase is sufficient for the application as catalyst phase in hydrogen storage alloys.

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