

## HYDROGEN SORPTION BEHAVIOR OF CHOSEN BINARY MAGNESIUM-CONTAINING INTERMETALLICS

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### Abstract

Hydrogen absorption in chosen binary Mg-X (X-Al, Ga, In, Si and Sn) intermetallics was studied. These compounds are prospective as additives in other Mg-based hydrogen storage materials. From this point of view it is desirable to know the hydrogen solubility in Mg-X and their resistivity against hydride formation. The present study was carried out at temperatures up to 623 K.

**Keywords:** Hydrogen storage, magnesium alloys, Mg-based intermetallics

### 1. INTRODUCTION

Conservation and transport of energy are key issues of future technologies. It seems that promising solution could be the energy storing in hydrogen that can serve as a clean fuel. Solid magnesium is potentially very high capacity hydrogen storage (HS) material [1] that can absorb up to 7.7 wt.% H<sub>2</sub> in the form of MgH<sub>2</sub> hydride. However, there are two main reasons that cause that Mg cannot be applied for HS in a pure form: (i) high thermodynamic stability of MgH<sub>2</sub> which implies that sorption temperatures  $T_s$  must be high ( $T_s$  above approximately 280 °C) and (ii) lazy sorption kinetics caused by slow hydrogen diffusion in hydride that is by about three orders of magnitude slower compared to pure Mg [2]. There are numerous studies devoted to the elimination of these two drawbacks. The main ideas can be summarized as follows: nanosizing /nanostructuring, alloying with other elements and catalysis. The first idea led to an elimination of the influence of slow hydrogen diffusion in hydride phase by reducing the diffusion length. The second one - the alloying - has brought only negligible improvement in kinetics and almost no effect in dynamics [1]. The high thermodynamic stability of MgH<sub>2</sub> causes that formation of the hydride during the H-charging expels the alloying elements from the alloy, which means that they become non-effective [1]. The catalysis was also thoroughly examined up to now, but it still remains an area that is under intensive investigation of many research groups. Catalysis of sorption process in Mg-based HS alloys (HSA) by particles of other phases was investigated in a series of studies. The best results were achieved by addition of particles of Nb<sub>2</sub>O<sub>5</sub> oxide [3]. The authors demonstrated that the catalytic effect of Nb<sub>2</sub>O<sub>5</sub> was superior by absorption as well by desorption.

In the present paper, we examine the sorption characteristics of several chosen Mg-X intermetallics that may be interesting as catalyst of the hydrogen sorption in Mg-based HSA.

### 2. THE CHOICE OF EXPERIMENTAL MATERIALS

Chosen intermetallic compounds Mg<sub>m</sub>X<sub>n</sub> formed by magnesium and elements X from the 13<sup>th</sup> and 14<sup>th</sup> group of the periodic table were investigated. The elements X and Mg<sub>m</sub>X<sub>n</sub> compounds are listed in **Table 1**. In the case of X = In, the mixture of phases  $\beta_n$  was used with prevailing Mg<sub>3</sub>In phase.

**Table 1** Formation enthalpy  $\Delta H_f$  (kJ/mol of formula unit) of  $Mg_mX_n$ , higher temperature of the sorption experiment (623 K) normalized to critical temperature  $T_c$  of  $Mg_mX_n$  ( $T_H = 623/T_c$ ), most stable oxides of X and their free enthalpy of formation  $\Delta G_f$  (kJ/mol of  $O_2$ ) and phases detected by XRD in  $Mg_mX_n$  samples after the H-charging at 573 K in wt. %  $H_2$ .

group	$Mg_mX_n$	$-\Delta H_f$	$T_H$	oxide	$-\Delta G_f$ <sup>4)</sup>	phases detected in H-charged $Mg_mX_n$ sample				
		kJ/mol fu			kJ/mol $O_2$	$Mg_mX_n$	Mg	X	$MgH_2$	MgO
13	$Mg_{17}Al_{12}$	31.61 <sup>6)</sup>	0.88	$Al_2O_3$	996 <sup>2)</sup>	84.1	0	0.7	13.6	1.7
	$Mg_2Ga$	38 <sup>8)</sup>	0.96	$Ga_2O_3$	603 <sup>3)</sup>	73.7	0	0	26.1	0.2
	$\beta_n - Mg-In$ <sup>1)</sup>	29 - 35 <sup>5)</sup>	0.98	$In_2O_3$	502 <sup>3)</sup>	80.8	1.6	1.0	13.4	3.2
14	$Mg_2Si$	79.1 <sup>6)</sup>	0.46	$SiO_2$	812 <sup>3)</sup>	87.6	0	8.9	0	3.4
	$Mg_2Sn$	80.8 <sup>7)</sup>	0.60	$SnO_2$	649 <sup>3)</sup>	94.3	0	5.7	0	0
	$MgH_2$	74.5 <sup>9)</sup>		MgO	1080 <sup>3)</sup>					
<sup>1)</sup> mainly $Mg_3In$ , <sup>2)</sup> [4], <sup>3)</sup> [5], <sup>4)</sup> at 573 K, <sup>5)</sup> [6], <sup>6)</sup> [7], <sup>7)</sup> [8], <sup>8)</sup> [9], <sup>9)</sup> [10]										

The choice of X was guided by following demands that would assure that  $Mg_mX_n$  particles can act as effective hydrogen gates to particles of HSA: (i) elements X itself should not form stable hydrides, (ii) X - as addition elements in solid solution with Mg - should improve the hydrogen sorption kinetics, (iii) the catalyst particles of  $Mg_mX_n$  must be able dissociate effectively the hydrogen molecule, but they must not form complex hydrides (where the hydrogen diffusion is very slow), (iv)  $Mg_mX_n$  must well solve hydrogen, (v) they have to be resistant to oxidation [4, 5] and (vi) the hydrogen diffusivity in  $Mg_mX_n$  must be sufficiently high. At present, it is impossible to judge the convenience of chosen compounds  $Mg_mX_n$  with respect to all the above mentioned demands (i through vi) due to lack of experimental data. The present paper contributes to investigation of hydrogen solubility in  $Mg_mX_n$  and to finding the conditions when their hydride(s) start to form only. In the following paragraphs, the synopsis of known sorption behavior of X and/or  $Mg_mX_n$  is summarized.

Al additions to Mg alloys led to an improved corrosion resistance: It was observed [11, 12] that the phase  $Mg_{17}Al_{12}$  improves local corrosion resistance of light Mg alloys and a very thin  $Mg_{17}Al_{12}$  shell of 2-5 nm on Mg suppresses significantly the formation of MgO [1]. Interesting feature of hydrogen sorption in  $Mg_{17}Al_{12}$  is *fully reversible* disproportionation [13]. The sorption occurs in two - individually reversible - steps that can be described by two equations



There is little knowledge on influence of Ga upon the corrosion resistance in Mg alloys in general. In light alloys Al-9Mg, however, it was reported [14] that the presence of Ga in the solid solution deteriorates slightly the resistance to stress corrosion cracking. It was reported that Ga improves hydrogen sorption in Mg [15]. In a mixture of  $MgH_2$  with  $Mg_5Ga_2$ , fully reversible hydrogen sorption was observed [16]. First  $Mg_5Ga_2$  reacted with  $MgH_2$



and then the rest of Mg hydride decomposed

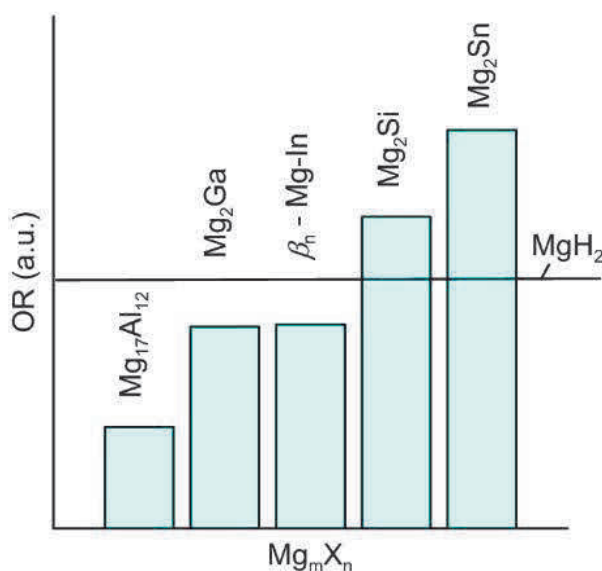


Addition of In improves resistance to oxidation, increases dehydrogenation rate, decreases the desorption temperature and the activation enthalpy of hydrogen desorption [17]. Detailed phase analysis reported in [18] revealed that the hydrogen sorption in Mg-In alloy occurs along different pathways via several intermediate  $Mg_mIn_n$  compounds and/or Mg(In) solid solution depending on the sorption temperature. The authors concluded that the re-hydrogenation may not be fully reversible.

Vajo et al. [19] found that Mg reacts with Si forming a very stable compound  $Mg_2Si$ , which helps to reduce the enthalpy of dehydrogenation. The solubility of Si in Mg is considered very small. The hydrogen desorption reaction is considered reversible, but the yield (hydride phase) is extremely low and kinetics is lazy. To improve the kinetics, high hydrogen pressure and very small particles of HSA (~ 10 nm) must be applied [20]. No significant hydrogen up-take was observed in  $Mg_mSn_n$  compound [20].

Thermodynamic stability of  $Mg_mX_n$  can be assessed simply by the critical temperature  $T_c$  of respective compound, or using its formation enthalpy  $\Delta H_f$  [6-10] (**Table 1**). It can be seen that the compounds formed by elements from the 14<sup>th</sup> group are much more stable than those from the 13<sup>th</sup> group. The  $\Delta H_f$  values for X from the 13<sup>th</sup> group are lower and  $\Delta H_f$  values for X from the 14<sup>th</sup> group are greater than  $\Delta H_f$  for Mg hydride. It means that compounds  $Mg_mX_n$  formed by X from the 14<sup>th</sup> group can be well used as catalyst.

The oxidation resistance of  $Mg_mX_n$  can be assessed only indirectly. Qualitative comparison of the  $\Delta H_f$  and free enthalpy of oxide formation  $\Delta G_f$  from Ellingham diagrams [4, 5] may serve as an appropriate guide. In **Table 1**, the values of  $\Delta G_f$  are listed for the temperature of  $T = 573$  K, but since formation entropies  $\Delta S_f$  of oxide formation is almost the same for the majority of oxides, the relative comparison made by using these values of  $\Delta G_f$  are valid within a relative wide temperature interval. If one *ad hoc* defines the relative oxidation resistivity of  $Mg_mX_n$ , OR, as a ratio  $OR = \Delta H_f / \Delta G_f$ , he obtains results shown in **Figure 1**, where the ratio OR is compared with the ratio of formation enthalpy of  $MgH_2$  and free formation enthalpy of MgO oxide.



**Figure 1** Oxidation resistance of  $Mg_mX_n$

### 3. EXPERIMENTAL

The compounds  $Mg_{17}Al_{12}$ ,  $Mg_2Ga$ ,  $\beta_n$ -Mg-In and  $Mg_2Sn$  were prepared by induction melting of pure components (Mg with Al, Ga, In and Sn) and by subsequent ball-milling in hydrogen, or by ball-milling only in hydrogen (Mg with Si). The samples were ball-milled using *Fritsch- Pulverisette 6* (450 rpm, 10 min milling / 50 min cooling - 14 times repeated; mass ratio of the balls to the charge was about 240). Powder samples

were taken out of the ball-mill 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. The study was carried out at temperatures between the room temperature and 623 K and under hydrogen pressure from  $10^{-3}$  to 6 MPa. The purity of both hydrogen and helium (calibration gas) was 6N. All manipulations of the milled powder was done in the glove box in protective Ar atmosphere.

The samples were annealed at 633 K for 2 hours. The measurement of hydrogen solubility in  $Mg_mX_n$  and PCT isotherms was carried out first at temperature 523 K and then at temperature 623 K. After the measurement at 623 K, the phase composition of (hydrogenated) samples was performed by XRD phase analysis by *X'Pert Pro MPD* device using  $CoK_{\alpha}$  radiation.

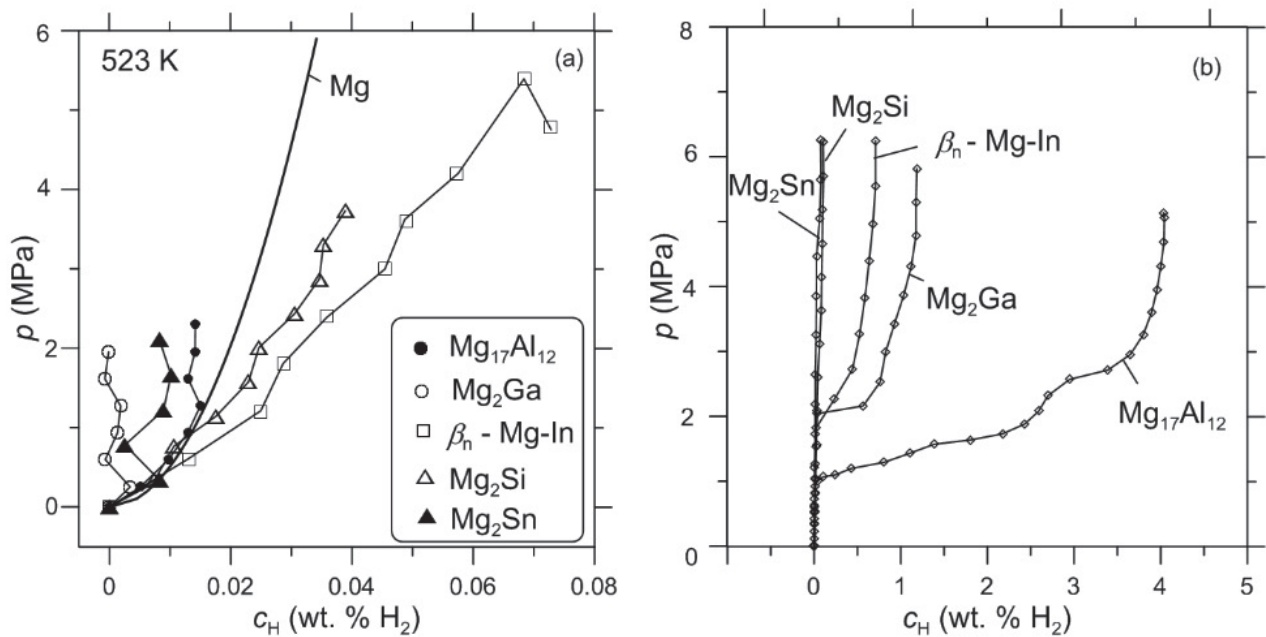
#### 4. RESULTS AND DISCUSSION

Dependence of hydrogen equilibrium pressure  $p$  on hydrogen concentration  $c_H$  in  $Mg_mX_n$  was measured at temperatures 523 K and 623 K. Results are summarized in **Figure 2**.

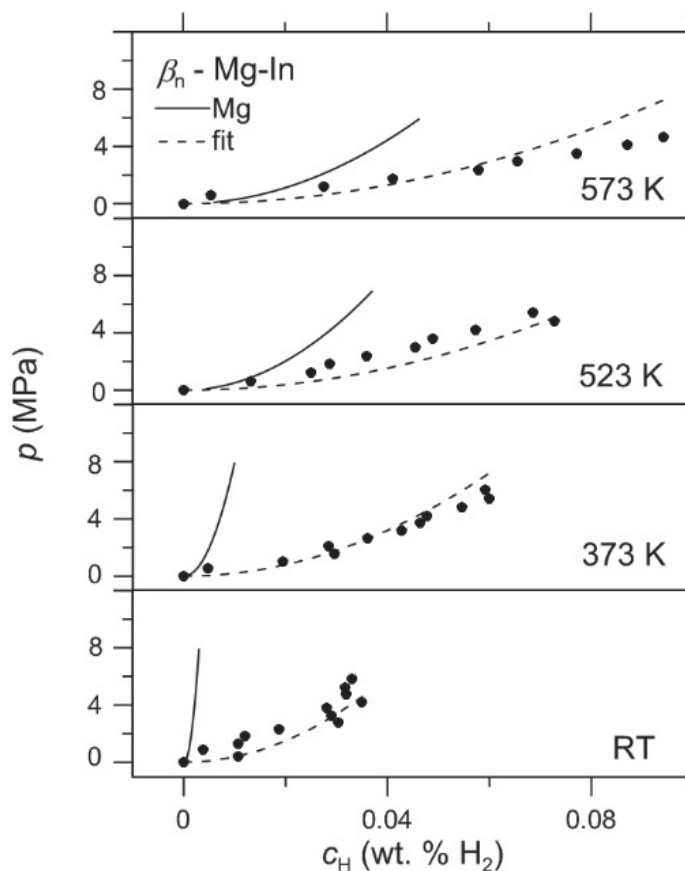
It was found that the hydrogen solubility in  $\beta_n$ -Mg-In and in  $Mg_2Si$  at the lower temperature exceeds the hydrogen solubility in Mg [21], whereas in other  $Mg_mX_n$  compounds the solubility is lower than in Mg. The solubility in  $Mg_2Ga$  was negligible. The curves for  $\beta_n$ -Mg-In, which shows the maximum solubility, were measured also at room temperature (RT), 373, 523 and at 573 K. The solid and dashed curves in the **Figure 3** show the hydrogen solubility in Mg and function [21]

$$\log p = 2 \left[ \log c_H + a + \frac{b}{T} \right], \quad (5)$$

fitted to the data, respectively. The fitting constants for  $\beta_n$ -Mg-In are  $a = (1.09 \pm 0.06)$ ,  $b = (208 \pm 20)$  K, and for  $Mg_2Si$  (data obtained at 250°C and 350°C were fitted only)  $a = -(0.42 \pm 0.14)$ ,  $b = (1113 \pm 83)$  K. It is obvious from **Figure 2b** that - after the  $\alpha$ -phase is saturated with hydrogen - the hydride phase is nucleated.



**Figure 2** Equilibrium pressure  $p$  in  $Mg_mX_n$  at 523 K (a) and 623 K (b)



**Figure 3** Equilibrium pressure  $p$  in  $\beta_n$ -Mg-In at 250°C. Fit - Eq. (5)

This occurs in  $Mg_{17}Al_{12}$  at about 1 MPa, in other compounds at about 2 MPa (refers to the temperature of 623 K). The PCT curves in **Figure 2b** are measured in absorption mode to estimate the high limit of applicability of the  $Mg_mX_n$  compounds as catalysts without hydride phase.

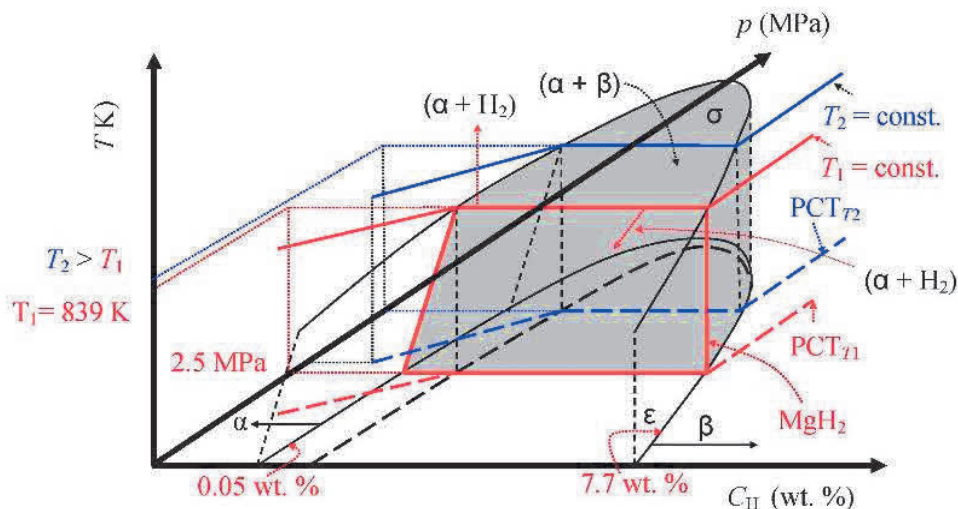
Two significant plateaux on the  $Mg_{14}Al_{12}$  curve and a short plateau and an inflexion that can be identified on the  $Mg_2Ga$  curve reflect the disproportionation reactions described by **Eqs. 1-4**.

Positive sign of fitting parameter  $b$  in **Eq. (5)** agrees with the increasing hydrogen solubility with increasing temperature (see in **Figure 3**). This can be verified using a composition-pressure-temperature 3D phase diagram in **Figure 4** (schematically for the Mg-H system [22]). The two-phase area  $\alpha+\beta$  is limited by the plane  $\sigma$  and by lateral surface intersecting the plane  $p$ - $c_H$  in the boundary  $\alpha/\alpha+\beta/\beta$  in PCT diagram.

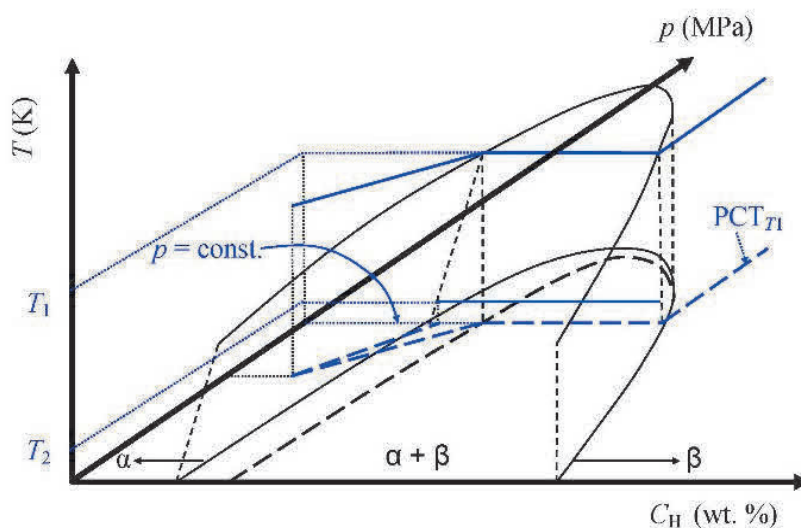
The thick red trapeze encloses the  $\alpha+\beta$  area in equilibrium phase diagram of Mg-H binary system for  $p = 2.5$  MPa [22]. Two PCT isotherms for  $T_1 < T_2$  are schematically shown in the plane  $p$ - $c_H$ . Construction of another solubility curve (dashed blue curve in  $\alpha$  region for  $T_2 = \text{const.} < T_1$  is shown in **Figure 5**. The qualitative agreement ( $b > 0$ ) with measured data in **Figure 3** is obvious.

## 5. CONCLUSION

Compounds  $Mg_2Si$  and  $\beta_n$ -Mg-In show the potential for catalysis of HS in Mg-based HSA due to relatively high hydrogen solubility, OR index and to sufficient resistivity to form hydride phase.



**Figure 4** Composition-pressure-temperature 3D phase diagram (schematically for the Mg-H system)



**Figure 5** Composition-pressure-temperature 3D phase diagram. Construction of solubility curve at  $T_2 < T_1$

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