HYDROGEN STORAGE IN Mg-In-C ALLOYS: EFFECT OF COMPOSITION AND AGEING

ČERMÁK Jiří [1,2], KRÁL Lubomír [1]

[1] IPM AS CR, v.v.i., Brno, Czech Republic, EU
[2] CEITEC-IPM, Brno, Czech Republic, EU, cermak@ipm.cz, lkral@ipm.cz

Abstract

Hydrogen storage in two Mg-In-C alloys with different indium concentration c_{In} was studied in the temperature range from 250 °C to 350 °C after five-years-ageing at room temperature. The both alloys show acceptable cycling stability, however, the storage capacity of the alloys decreased from about 5 wt.% H_2 to about 2.5 and 3.1 wt.% H_2 by higher c_{In} and lower c_{In} concentration, respectively after 5 years. The sorption kinetics degraded much more by high c_{In} than by lower c_{In}. PCT isotherms, TPS and DSC patterns were measured for both materials. It was found that the hydrides responsible for hydrogen storage in alloy with higher c_{In} were slightly more stable.

Keywords: Hydrogen, hydrogen storage, magnesium alloys

1. INTRODUCTION

In our previous papers [1-4] we studied hydrogen sorption in chosen Mg-based alloys that are perspective for hydrogen-storage (HS) [5]. Our interest was focused especially to ball-milled alloys composed mainly from Mg that contained Ni as catalyzing element, C as an element that assures fine milling (anti-sticking agent) and the third additive X. Elements X were chosen from the 13th and the 14th group of the periodic table and we tested, first of all, their effect on hydrogen sorption capacity, desorption kinetics and on the resistance of HS alloys against the detrimental effect of air residuals in absorbed hydrogen.

Samples (see [4]) were ball-milled from pure components (splinters of Mg, Ni, X and powder of C) using *Fritsch-Pulverisette6* (450 rpm, 10 min milling / 50 min cooling - 20 times repeated; mass ratio of the balls to the charge was about 60). Powder was compacted at room temperature into pellets and annealed at 360 °C / 20 h / Ar. Before annealing, the samples were composed exclusively from Mg and Ni, after the thermal treatment, phases Mg and Mg_2Ni were observed by XRD.

Hydrogen sorption experiment in [1-4] was of the type *one-charging-and-one-desorption*, i.e., the ball-milled, compacted and annealed samples were charged by gaseous hydrogen at 345 °C / 20 h / 3 MPa in a pressure vessel and desorbed into large volume of about 5 l in a Sieverts-type apparatus [6]. The previous experiments led to a conclusion that indium improves substantially hydrogen sorption characteristics of a single absorption / desorption (A/D) cycle and the composition of HS alloy that was found as an optimum became a subject of the Czech patent [7].

It was shown that sorption characteristics depend on time τ elapsed from the charging. In [2] we investigated the behavior of HS alloys after times τ up to about on month. In the present work, we tested the same samples after extended time of 5 years. In contrast with the previous work, we also conducted measurements in absorption regime, studied of A/D cycling stability and dynamic measurements (measurement of activation enthalpy and entropy of hydrogen sorption).

2. EXPERIMENTAL

Measurements in the present paper were carried out with samples of two alloys that differ in content of indium: Mg-16.1Ni-5.2In-9.9C (Alloy 1) and Mg-15.2Ni-9.7In-9.4C (Alloy 2) - all in wt.%. Ratio of Mg/Ni binary base

was chosen slightly below the eutectic point in Mg-Ni binary alloy system and the ratio Mg/C was about 7. Samples of both alloys were stored in dry air for about 5 years.

Hydrogen sorption characteristics were measured using Sieverts-type gas sorption analyzer *PCT-pro Setaram Instrumentation*. This equipment enables safe and fully automated measurement in both absorption and desorption regimes. The present studies were carried out at temperatures between 250°C and 350°C and under hydrogen pressure from 10 Pa to 2 MPa. All *desorption* experiments were done in region where the all related hydrides were *unstable* (below the PCT isotherm), *absorption* experiments were run always *above* the PCT isotherm. These conditions were fulfilled also during the A/D cycling. Measurement of DSC pattern was done using differential scanning calorimeter *Netsch DSC 204 F1*.

3. RESULTS AND DISCUSSION

3.1. Cycling stability

Maximum number *n* of A/D cycles in each cycling experiment was 10 because it was proved that this was a sufficient number for stabilizing the alloy sorption behavior in all cases. Example of cycling pattern measured with Alloy 1 cycled at 295 °C between the initial hydrogen pressures of 2 MPa (absorption above the PCT isotherm - positive values of hydrogen concentration c_H) and 10 Pa (desorption below the PCT isotherm - negative c_H) is shown in **Fig. 1**. It is illustrated that A/D behavior of Alloy 1 was well stable starting from the second A/D cycle.
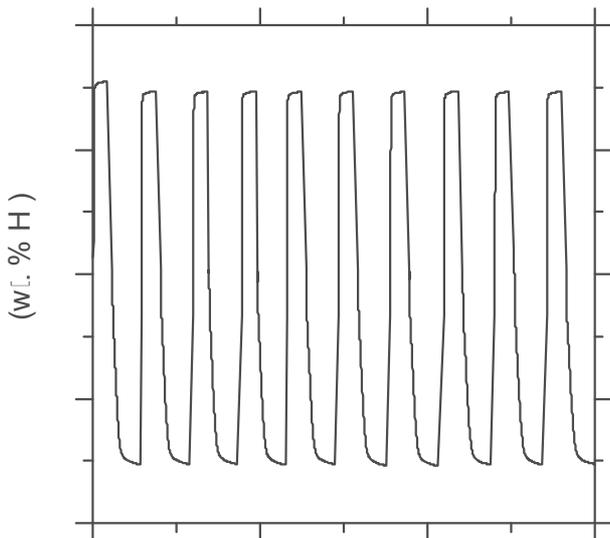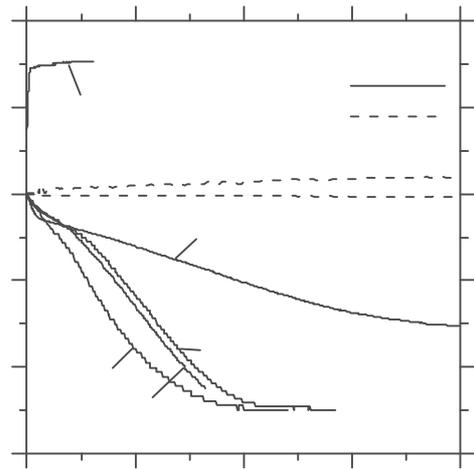

Fig. 1 Cycling stability
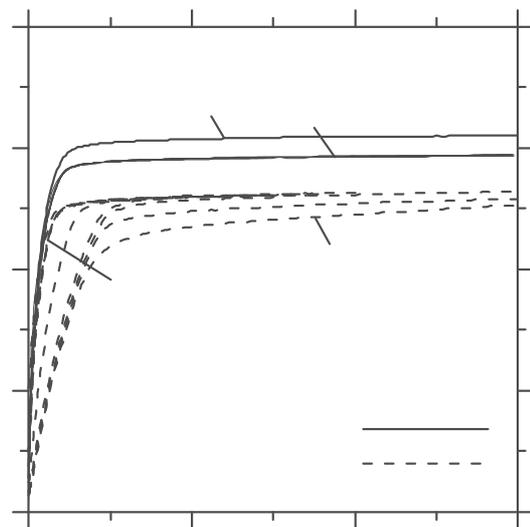
Fig. 2a Absorption kinetics

Hydrogen sorption kinetics obtained with Alloy 2, on the other hand, showed significant dependence of sorption rate on number *n*: the stable behavior was reached after first 4 cycles. Comparison of both alloys is shown in **Figs. 2a, 2b** ($\Delta t = t - t_s$; t_s - start of sorption). It is obvious that Alloy 2 with higher In concentration needed more cycles to reach the stable A/D operation. This alloy also showed slower hydrogen desorption kinetics and lower hydrogen sorption capacity.
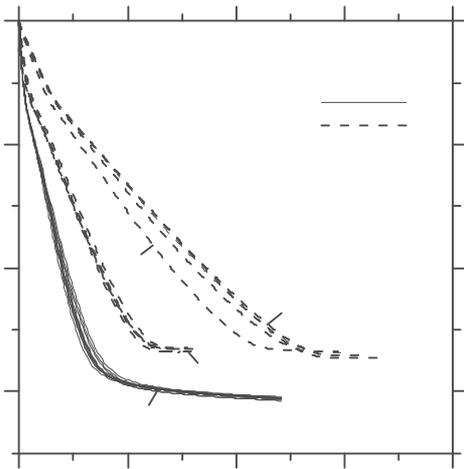
Fig. 2b Desorption kinetics   **Fig. 3** Influence of ageing

3.2.   Influence of ageing - A/D cycling

In our paper [2], we observed influence of time τ elapsed from hydrogen charging (ageing time) upon the hydrogen desorption kinetics. Improvement in desorption rate with increasing τ was explained by gradual change of interface between the Mg-rich grains and small Mg_2NiH_4 particles due to diffusion redistribution of alloying elements. In another paper [4], however, we studied the phase composition in HS alloys with In and C and came to a conclusion that by alloys, containing carbon above certain concentration, a partial decomposition of phases might occur. It could be supposed that such decomposition decreased the efficiency of hydrogen storage and affects also the rate of sorption. Therefore, it seemed as highly interesting to repeat the sorption experiments after a long period τ that might accentuate the undesired phase decomposition. This test was carried out in the present paper and its results are shown in **Fig. 3**.

Desorption curves in **Fig. 3** obtained in the previous measurement with Alloy 1 clearly illustrate that increase in τ improved the desorption kinetics (absorption kinetics was not studied in [1-4]). The present measurement conducted with the same alloy after 5 years, however, showed that this trend could be seen only at the very early stages of desorption, whereas at longer times, the desorption rate decreased, most likely due to decomposition of phases that were effective for HS. The XRD studies with aged samples that might support this conclusion are running at present.

Difference in sorption behavior of the two aged alloys was expressive especially at low temperatures. Comparison shown in **Fig. 3** is convincing: the hydrogen sorption of Alloy 2 at 250 °C was almost negligible within the first hour.

3.3.   Influence of ageing - PCT isotherms

Measurement of equilibrium hydrogen pressure p_{eq} was carried out with both aged alloys. It should be noticed that all the PCT curves (dependence of p_{eq} on hydrogen concentration c_H at constant temperature) were measured in the absorption regime in the present paper. In **Fig. 4**, one can see a comparison of two PCT isotherms obtained at 250 °C with Alloy 2 after different treatment. It can be clearly seen that the isotherm for pre-annealed sample has two plateaus - the MgH_2 is responsible for the lower one, the short upper plateau reflects the presence of Mg_2NiH_4-In hydride (squares). This was confirmed by experiment with Alloy 2 without only pre-annealing 360 °C / 2 h - i.e. without Mg_2NiH_4-In phase [8] - which led to a PCT curve with lower plateau (diamonds). Catalyzing effect of Mg_2NiH_4 phase can be documented, e.g., by DSC measurement. It is clear

from **Fig. 5** that non-alloyed alloy (without Mg$_2$NiH$_4$-In phase) decomposed at temperature that was about 25 °C higher than the annealed Alloy, and that it showed no decomposition peak of Mg$_2$NiH$_4$-In.
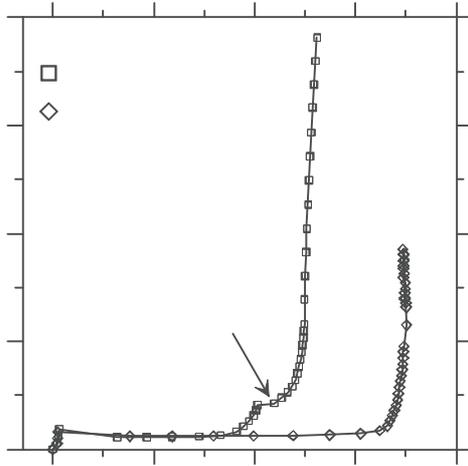

**Fig. 4** PCT: Influence of Mg$_2$NiH$_4$-In phase
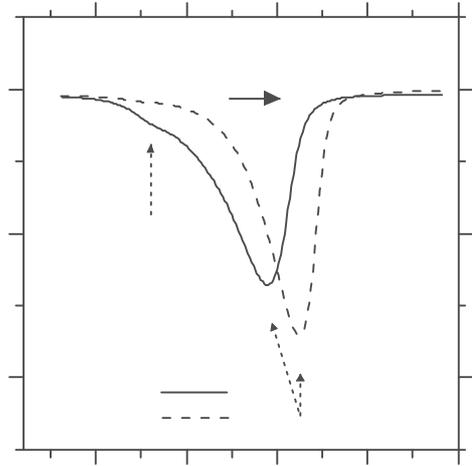
Fig. 5 DSC - desorption peaks

Comparing PCT curves for both alloys (**Fig. 6**), it could be also concluded that the nucleation of hydride (phase β) was much easier in Alloy 1 compared to Alloy 2, because edge of both plateaus were sharper in Alloy 2. At lower temperatures, it could be even observed that the plateau decreased with increasing c_H behind the edge. This fact might be a consequence of lower catalytic efficiency of Ni-containing phase and corresponded with the poor hydrogen sorption kinetics in aged Alloy 2 (**Fig. 3**).
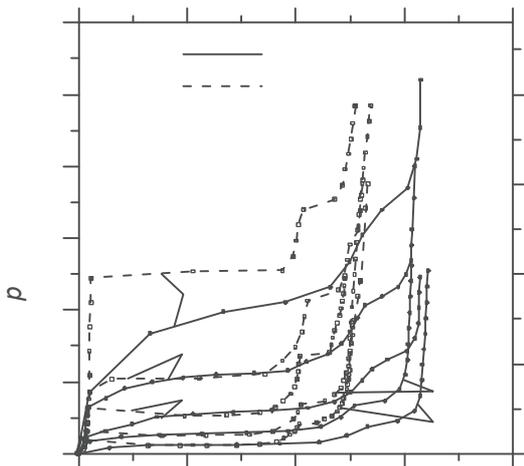
Fig. 6 PCT curves
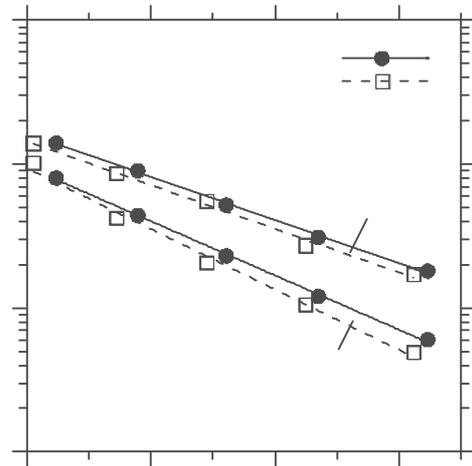
Fig. 7 Van't Hoff diagram

Plotting the values of p_{eq} in dependence on inverse temperature averaged during each isothermal experiment, van't Hoff's diagram was obtained (**Fig. 7**) and the activation entropy ΔS and enthalpy ΔH could be evaluated from the intercept and slope of the diagram, respectively. Obtained value of ΔH (see **Table 1**) for MgH$_2$-In was slightly higher and that for Mg$_2$NiH$_4$-In was slightly lower than respective values for pure MgH$_2$ and Mg$_2$NiH$_4$ [9]. This was due to the effect of In.

Table 1 Activation parameters of hydrogen sorption

		ΔS [kJ/(K ·mol H$_2$)]	ΔH [kJ/mol H$_2$]	**Remark**
Alloy 1	Mg$_2$NiH$_4$-In	0.115 ± 0.002	57.6 ± 1.3	This work
	MgH$_2$-In	0.114 ± 0.002	72.2 ± 1.3	This work
Alloy 2	Mg$_2$NiH$_4$-In	0.115 ± 0.004	58.1 ± 2.5	This work
	MgH$_2$-In	0.147 ± 0.007	80.4 ± 4.2	This work
	Mg$_2$NiH$_4$	0.134	74.2	[9]
	MgH$_2$	0.130	70.8	[9]

Values of p_{eq} in Alloy 1 and Alloy 2 were close to one another, but for Alloy 1 they were systematically higher than values for Alloy 2. This means that hydrides in Alloy 1 (and/or dehydrogenated phases alloyed by lower concentration of In) are slightly more stable, which may be the origin of better resistance of Alloy 1 to long-term ageing.

3.4. Differential scanning calorimetry and Temperature programmed sorption

Equilibrium hydrogen pressure p_{eq} was measured also by differential scanning calorimetry (DSC), and/or by measurement pressure of hydrogen released into fixed volume during absorption/desorption at variable temperature $T(t)$ (temperature programmed sorption - TPS). Examples of results obtained by DSC and TPS are plotted in **Figs. 5, 8**. It is illustrated in **Fig. 9** that TPS in regime *desorption* (**Fig. 8b**) could be used to relatively reliable extension of PCT measurements to low temperatures, where the measurement of PCT was difficult and DSC measurement offers reasonably reliable results that were, however, scattered over wide interval of pressures. TPS at high pressures and temperatures (regime *absorption* - see **Fig. 8a**) suffered from limited reliability, which was due most likely to strongly non-equilibrium conditions.
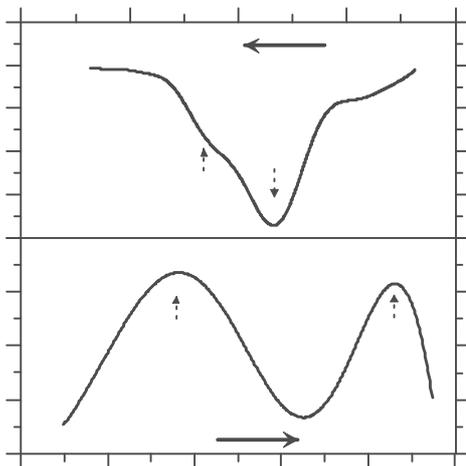
Fig. 8 TPS pattern (0.7 °C / min)
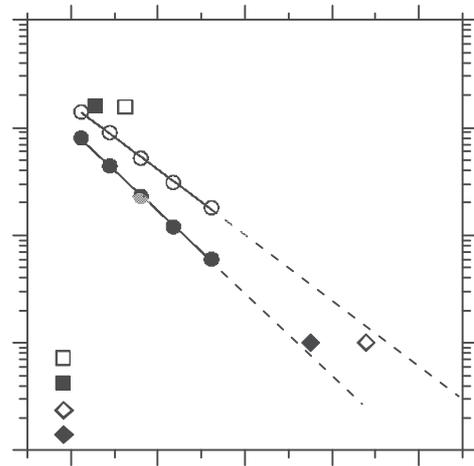
Fig. 9 Van't Hoff diagram with TPS and DSC

4. CONCLUSION

Hydrogen sorption characteristics of two alloys Mg-Ni-In-C that differed in indium concentration (Alloy 1 with lower and Alloy 2 with higher In concentration) were studied. It was found that the original hydrogen sorption capacity (about 5 wt.% H$_2$) decreased after 5 years down to about 3 wt.% H$_2$. Alloy 1 showed very good cycling stability, and stable sorption kinetics starting from the second A/D cycle, higher hydrogen sorption capacity and slightly lower activation enthalpy ΔH of hydrogen sorption. The difference in hydrogen sorption

characteristics between both alloys grew more significant with decreasing sorption temperature. At 250 °C, the Alloy 2 absorbed and desorbed almost no hydrogen during the first hour, whereas Alloy 1 absorbed and desorbed 90 % of maximum capacity within about 100 s and 1 h, respectively.

ACKNOWLEDGEMENTS

REFERENCES

[1]   CERMAK J., KRAL L. Improvement of hydrogen storage characteristics of Mg/Mg2Ni by alloying: Beneficial effect of In. Journal of Power Sources, Vol. 214, 2012, pp. 208-215.

[2]   CERMAK J., KRAL L. Ageing of MgeNieH hydrogen storage alloys. International Journal of Hydrogen Energy, Vol. 27, 2012, pp. 14257-14264.

[3]   CERMAK J., KRAL L. Alloying of Mg/Mg2Ni eutectic by chosen non-hydride forming elements: Relation between segregation of the third element and hydride storage capacity. Journal of Power Sources, Vol. 197, 2012, pp. 116-120.

[4]   CERMAK J., KRAL L. Beneficial effect of carbon on hydrogen desorption kinetics from Mg-Ni-In alloy. Journal of Alloys and Compounds, Vol. 546, 2013, pp. 129-137.

[5]   HIRSCHER M. (Ed.) Handbook of Hydrogen Storage. Wiley-VCH Verlag: Weinheim, 2010.

[6]   CERMAK J., KRAL L. Hydrogen diffusion in Mg-H and Mg-Ni-H alloys. Acta Materialia, Vol. 56, 2008, pp. 2677-2686.

[7]   CERMAK J., KRAL L., DAVID B. Porézní materiál pro skladování vodíku a způsob jeho přípravy (The porous material for hydrogen storage and method of his preparation) [patent CZ, 302464, B6] 2011).

[8]   CERMAK J., DAVID B. Catalytic effect of Ni, Mg_2Ni and Mg_2NiH_4 upon hydrogen desorption from MgH_2. International Journal of Hydrogen Energy, Vol. 36, 2011, pp. 13614-13620.

[9]   SCHWARZ R.B. Hydrogen storage in magnesium-based alloys. MRS Bulletin, Vol. 24, 1999, pp. 40-44.