IMPROVEMENT OF HYDROGEN DESORPTION CHARACTERISTICS OF EUTECTIC
Mg/Mg$_2$NiH$_4$ AND Mg$_2$NiH$_4$ BY In ADDITION

J. Cermak$^a$, L. Kral$^b$

$^a$ IPM AS CR, v.v.i., Žižkova 22, CEITEC IPM, 616 62 Brno, Czech Republic, cermak@ipm.cz

$^b$ IPM AS CR, v.v.i., Žižkova 22, 616 62 Brno, Czech Republic, lkral@ipm.cz

Abstract
The paper is devoted to study of the influence of alloying the eutectic Mg/Mg$_2$Ni with elements from the 13th and 14th group and alloying the intermetallic Mg$_2$Ni with In upon the hydrogen storage characteristics. It was found that In increases considerably hydrogen desorption rate from Mg$_2$NiH$_4$. Addition of In to eutectic Mg/Mg$_2$Ni alloy improves hydrogen storage capacity and preserves relative good resistance against poisoning by air.

Keywords: Hydrogen storage; Magnesium hydride; Dehydrogenation; Intermetallic compounds

1. INTRODUCTION

Mg-xNi alloys are known as perspective hydrogen storage materials [1,2]. Hydrogen storage capacity and hydrogen desorption rate of binary alloys Mg-Ni are, however, still unsatisfactory and therefore, improvements are sought, e.g., by introduction of a proper catalyst [3]. As candidate elements, transition metals [4] are often used that attract bonding valence electrons and, hence, destabilize the hydrides. However, also elements with weaker bond to H than that of Mg, or even non-hydride forming elements show a beneficial effect upon the hydrogen desorption rate [5,6].

The present investigation continues our previous work [7,8]. Here we investigate the resistance of eutectic Mg/Mg$_2$Ni against the poisoning by residual air and possible ways how to improve the hydrogen desorption kinetics of Mg$_2$NiH$_4$ by doping. As dopants, elements of the 13th and the 14th group were tested that do not form stable hydrides.

2. EXPERIMENTAL

Binary alloy with the average composition Mg-11.3 at.% Ni and seven ternary alloys of Mg–8.5 at. % Ni–2.8 at. % X (X = Al, Ga, In, Si, Ge, Sn, and Pb) were prepared from pure materials. Purity of elements X was better than 99.99 %, purity of Mg and Ni was 99.98 % and 99.96 %, respectively. Ball-milling was performed in Fritsch-Pulverisette6. Ball to charge ratio was about 60, rotation speed was 450 rpm and powders were prepared in 20 cycles: 10 min milling/50 min cooling. The milled powder blend was compacted at room temperature into pellets (diameter 20 mm, height 4 mm) and annealed in Ar at 620 K for 20 h.

Hydrating of the samples was done at 620 K/30 bar of H$_2$ for 20 h. Phase composition was checked by XRD after the hydrating. It revealed that two main phases (prevailing volume content) MgH$_2$ and Mg$_2$NiH$_4$ were present in the samples. Hydrogen storage capacity, $c_{\text{max}}$, was measured by precise weighing of samples before and after the hydrogen charging.

To assess the influence of rest air during the hydrogen charging upon the hydrogen storage characteristics, hydrating of samples was done in two ways: (i) Pressure vessel of the hydrating furnace with samples was filled by hydrogen and pressurized to total pressure of 30 bars. Hence, the samples were hydrogen charged in a mixture of air/hydrogen = 1/30. This way of hydrating is referenced as “charging with air” hereafter. (ii) Pressure vessel was three times evacuated to total pressure $10^{-1}$ mbar and pressurized up to 10 bars.
Finally, it was pressurized to total pressure of 30 bar of H\textsubscript{2} and then annealed. This way of hydrating is referenced as "charging in H\textsubscript{2}" hereafter.

Desorption curves, \( p(t) \) (\( p \), \( t \) – pressure of desorbed H\textsubscript{2} and time of desorption, respectively), were measured at three temperatures \( T = 501, 517 \) and 535 K. It was assured that \( p \) after total desorption of each sample was lower than equilibrium plateau pressure of MgH\textsubscript{2} and Mg\textsubscript{2}NiH\textsubscript{4} respectively [9]. Desorption apparatus and further experimental details are described elsewhere [10].

3. RESULTS AND DISCUSSION

3.1. Poisoning resistance of modified eutectic alloys (Mg/Mg\textsubscript{2}Ni)-X

Results obtained with eutectic samples (Mg/Mg\textsubscript{2}Ni)-X are listed in Tab. 1. Alloying elements X and air residuals in hydrogen change the charge density and, hence, binding of H-atoms with lattice atoms [4-6]. It can be seen that (i) alloys with In show the highest hydrogen storage capacity and (ii) the presence of air lowers significantly the hydrogen storage capacity of all experimental alloys. It suggests itself to introduce an index of corrosion resistance, \( ICR = 1 - \frac{c_{\text{max}}^{\text{H}_2}}{c_{\text{max}}^{\text{air}}} \), that scales the sensitivity of the respective hydrogen storage alloy to the presence of air during the hydrogen charging. It is obvious in Tab. 1 that In shows the optimal results: Compared to non-alloyed material, it increases \( c_{\text{max}}^{\text{H}_2} \) and keeps relative high poisoning resistance.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{group} & X & c_{\text{max}}^{\text{H}_2} & c_{\text{max}}^{\text{air}} & ICR \\
\hline
13 & Al & 0.76 & 5.2 & 0.15 \\
 & Ga & 0.68 & 4.6 & 0.15 \\
 & In & 2.3 & 5.3 & 0.43 \\
14 & Si & 0.55 & 2.9 & 0.19 \\
 & Ge & 0.45 & 3.6 & 0.13 \\
 & Sn & 1.4 & 4.6 & 0.30 \\
 & Pb & 0.70 & 4.0 & 0.18 \\
\hline
\text{non-alloyed} & 2.7 & 5.0 & 0.54 \\
\hline
\end{array}
\]

3.2. Hydrogen desorption from Mg\textsubscript{2}NiH\textsubscript{4}

It was reported in [8] that Mg\textsubscript{2}NiH\textsubscript{4} is an effective catalyst of the hydrogen de-charging and that In concentrates preferentially in Mg\textsubscript{2}NiH\textsubscript{4}. In the light of these facts, it seems as useful to elucidate, how the In influences the rate of hydrogen desorption from Mg\textsubscript{2}NiH\textsubscript{4}.

It is known [11, 12] that there is a cubic high-temperature phase (HT) of Mg\textsubscript{2}NiH\textsubscript{4} and two monoclinic low-temperature phases (LT). The phase transition between the HT and the LT was reported in the literature close to \( T_{\text{tr}}=510 \) K. Difference between the two LT’s is subtle only: one of them (LT1) contains no micro-twins whereas the other (LT2) is micro-twinned. Nevertheless, the both LT modifications behave as fully distinguished phases with their own peaks in XRD pattern and differ also in hydrogen diffusivity [10], catalyst ability [8] and some other characteristics [13].

Various types of desorption curves can be obtained (see, e.g., [14]) with hydrogen storage Mg-Ni alloys prepared under different conditions (hydrogenation temperature and pressure) and moreover, different
desorption behavior was observed even for the same hydrogen charged material in dependence on ageing time at room temperature. Differences in desorption behaviour can be rationalized by differences of phase topology and by different nucleation rate. It can be expected that both LT phases of Mg$_2$NiH$_4$ can be present either in continual form (i.e., macroscopically long path can be found in respective phase) or in dispersion form (i.e., in form of small particles) – see Fig.1. In dependence on fraction LT1/LT2, structure subtype A or B can prevail (prevailing phase tends to be in a continual form). The fraction LT1/LT2 can be controlled, e.g., by the H$_2$ pressure during hydrogen charging – the higher is the H$_2$ pressure the higher is the fraction of LT1/LT2.

![Fig. 1. Model of phase topology of low-temperature Mg$_2$NiH$_4$ — schematically. Upper type – the general structure, A, B and C – limiting structure subtypes.](image)

In Fig. 2, simulated desorption curves for all three limiting structure subtypes, A, B and C, are shown for the fraction LT1/LT2 = 3/2. The curves are plotted in coordinates fraction of released H$_2$ vs. time of desorption, $t$.

![Fig. 2. Desorption curves simulated for structure subtypes A, B and C with LT1/LT2 = 3/2 and hydrogen diffusivity in LT1 higher than in LT2.](image)
Fraction of released $H_2$ is a ratio of hydrogen pressure in time $t$ and ultimate hydrogen pressure in the desorption chamber obtained after the complete hydrogen desorption from the sample, $p(t)/p_{\text{max}}$. It is illustrated that the onset of desorption from the dispersed phase is delayed due to the incubation needed for its coalescence into more or less continual form. Incubation period depends also on hydrogen diffusivity [10].

Differences in desorption behavior of the same hydrogen-charged material were observed in dependence on ageing time elapsed from the hydrogen charging. The samples were aged at room temperature. It was observed that incubation period of the hydrogen desorption from LT1 shortens significantly (about 2 orders of magnitude) in the course of several days after the charging. This can be explained by finite time needed to form nucleation centers of hydrogen de-charged phase. The difference between the nucleation rate in LT (nucleation rate in LT1 is much less than in LT2) contributes to the observed ageing effect. It was found that (i) the ageing does not change substantially the phase ratio LT1/LT2 and (ii) after several days, the desorption curves reach their almost stationary shape, which does not change after eventual further ageing. The latter feature can be explained by the fact that after a certain ageing time, nucleation is no more the exclusive controlling process of desorption (in LT1, number of nucleation centres is close to its equilibrium whereas in LT2, still almost no nucleation runs) and the phase topology starts to play an exclusive controlling role.

3.3. Influence of In upon hydrogen desorption kinetics from $\text{Mg}_2\text{NiH}_4$

In was tested as a unique element, since the other elements $X$ did not led to satisfactory results in corrosion resistance tests. To assess the influence of In, desorption curves were measured at three temperatures close to expected transition temperature $T_{\text{tr}}$. The curves plotted in Fig. 3 were measured in approximately equal stage of ageing (several days after the hydrogen charging) with $\text{Mg}_2\text{Ni}$ charged under the $H_2$ pressure

![Fig. 3. Desorption curves measured with $\text{Mg}_2\text{NiH}_4$. Dashed line – without In, solid line – with In.](image-url)
of 30 bars. It can be seen that the measured desorption curves are similar to those simulated for structure subtype C.

This could be expected, since the amount of both LT phases is about the same (sufficient amount of both LT phases is in a continuous form) and the measurement was carried out with aged material (almost stationary density of nuclei in LT1 was available). It is obvious that In does not change the phase ratio LT1/LT2, since the break point between the two branches keeps its coordinate LT1/LT2 = 0.5 – 0.6 approximately constant.

It can be also seen in Fig. 3 that desorption curves with two branches were observed – similarly as in [10] – both below and above equilibrium transition temperature \( T_\text{tr} = 510 \text{ K} \) and that an expressive accelerating effect of In was detected for both phases LT at all three desorption temperatures. Acceleration of the hydrogen desorption from LT1 and LT2 caused by the presence of In is due, most likely to an increase in nucleation rate in In-doped material.

4. SUMMARY

It can be summarized that In acts as a beneficial additive in hydrogen storage eutectic Mg/Mg\(_2\)Ni. It accelerates significantly the hydrogen desorption rate from the hydride Mg\(_2\)NiH\(_4\), which acts as gate for hydrogen in eutectic alloy Mg/Mg\(_2\)Ni [15], slightly increases the hydrogen storage capacity in eutectic Mg/Mg\(_2\)Ni and preserves its resistance against the poisoning by residual air in hydrogen.

ACKNOWLEDGEMENTS

The present work was supported by Czech scientific foundation – grant No. GACR P108/11/0148, GACR 106/09/0814, by project of the Academy of Sciences of the Czech Republic - project No. AV0Z20410507 and by CEITEC CZ.1.05/1.1.00/02.0068.

REFERENCES


