Influence of long-term ageing upon the capacity of hydrogen storage in two novel Mg-Ni-In-C alloys

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Abstract

We have shown previously that the addition of In and C enhances the hydrogen desorption capacity and considerably improves the kinetics of hydrogen desorption from Mg-Ni based alloys, important from the perspective of hydrogen storage. In this paper, we present the results of tests of the long-term stability of the sorption behaviour of these materials. We studied how the capacity and sorption kinetics changed 5 years from the preparation of two chosen Mg-Ni-In alloys differing in indium concentration. Kinetic curves and PCT isotherms were measured at temperatures of 250–350 °C. It was found that long-term storage of the hydrogen-charged samples led to no significant downgrade in hydrogen sorption kinetics. However, the absorption capacity somewhat decreased from about 5 wt.% H2 to about 3 wt.% H2 due to partial phase decomposition. Relatively intensive tentative oxidation during preparation, which had a slightly beneficial effect on the desorption rate of freshly-prepared samples, caused almost total blocking of hydrogen sorption in the aged samples.

Key words: hydrogen, hydrogen storage, magnesium alloys, indium

1. Introduction

Magnesium and its alloys have frequently been studied as light-weight materials for applications where the mechanical strength, creep, fatigue resistance [1, 2], structure, corrosion, and biodegradability [3, 4] were of prime importance. The materials have also been under investigation for hydrogen storage [5, 6] since hydrogen is a very prospective fuel both for direct combustion and in electrochemical batteries and fuel cells.

The remarkable hydrogen storage capacity of Mg (theoretically 7.7 wt.%) and its low cost still keep Mg-based hydrogen storage materials (HSMs) in the focus of interest, in spite of the relatively high hydrogen sorption temperature and poor sorption kinetics of pure Mg [7]. Series of studies have been devoted to the further improvement of hydrogen sorption kinetics in binary ball-milled Mg-based hydrogen storage (HS) alloys [8–16]. Recently, great attention has been paid to preparation methods and the effect of the size of the Mg particles (see e.g. [17]). Tuning the kinetic properties by catalyst additions [18] is also one of the possible ways to improve the application potential. A high beneficial effect was reported for Ni [19, 20] and some other elements, e.g. Ti [21, 22], Al [23, 24], Nb [25], and Li-containing compositions [26, 27].

In our previous studies [28–32], it was observed that additions of carbon and indium to a Mg-based alloy improved its hydrogen desorption behaviour. It was also shown that the alloy undergoes some ageing/ripening after the initial hydrogen charging [29], which induced a substantial improvement in hydrogen desorption kinetics. A similar beneficial effect of the storage time of Mg-based HSM on the hydrogen sorption characteristics was also reported in [33].

The combined effect of Ni and elements X from the 13th and 14th group was investigated in [30]. It was found that the best results could be achieved when In is introduced into the Mg-Ni base. This was in agreement with the expectation generated by the results reported earlier in [34] for pure Mg. The distribution

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of X over the phases present in HSM is not uniform. Additive elements X prefer rather the $\text{Mg}_2\text{Ni}$ phase than the Mg phase and the segregation of X is especially strong in the hydrated phase $\text{Mg}_2\text{Ni}(X)\alpha\text{H}_4$, as was reported in \[30\]. This means that the overall effect of X is mediated by its influence on phase $\text{Mg}_2\text{Ni}$.

The beneficial effect of indium on hydrogen desorption was observed first by Mintz et al. \[34\], where the kinetics of magnesium hydride formation from pure activated magnesium and from some indium-containing magnesium alloys was studied. Improvement in sorption characteristics was recently confirmed in In-containing alloys $\text{Mg}-\text{Ag}$ \[35\], $\text{Mg}-\text{In}-\text{Ni}$ \[36\] as well, and in an experimental survey \[14\].

In \[31\], the effect of carbon upon hydrogen desorption in $\text{Mg}-\text{Ni}-\text{In}$ was investigated. The results of that study led to the conclusion that C, ball-milled together with other components, substantially improved the desorption kinetics of the $\text{Mg}-\text{Ni}-\text{In}$ base alloy. However, when the carbon concentration exceeded a certain limit, the phase $\text{Mg}_2\text{Ni}(\text{In},\text{C})$ decomposed during desorption: in desorbed samples, the $\text{In}$, $\text{Ni}$, and $\text{Mg}_2\text{In}$ phases were identified by XRD analysis. These products of decomposition are – with respect to hydrogen desorption – less effective. Hence, the sorption cycle (repeated hydrogen charging and desorption) became (partly) irreversible.

It follows that Mg-based alloys containing $\text{Ni}$, $\text{In}$, and $\text{C}$ are promising candidates for effective HSMs. In the present work, we tested the HS behaviour of two chosen Mg-Ni-In-C alloys differing in content of $\text{In}$, $c_{\text{In}}$, and with a carbon concentration that was below the limit found in \[31\] as critical for intensive phase decomposition. The aim of the present study was to assess the influence of $c_{\text{In}}$ variation and the influence of long-term ageing upon HS characteristics. We conducted measurements in the sorption regime and studied the stability of A/D cycles. Also, dynamic measurements of formation enthalpy and entropy were carried out.

2. Experimental

Measurements in the present paper were carried out with samples of two alloys that differed in content of indium (wt. %): $\text{Mg}_{16.1}\text{Ni}_{5.2}\text{In}_{9.9}$ referred to as Alloy 1 hereafter, and $\text{Mg}_{15.2}\text{Ni}_{9.7}\text{In}_{9.4}$ referred to as Alloy 2. The ratio of the $\text{Mg}/\text{Ni}$ binary base was chosen below the eutectic point in the Mg-Ni binary alloy system, and the ratio $\text{Mg}/\text{C}$ was about 7. Samples were ball-milled from pure components (splinters of $3\text{N}8$ $\text{Mg}$, $3\text{N}6$ $\text{Ni}$, $5\text{N}$ $\text{In}$; spectroscopic pure $\text{C}$ powder – all purchased from SIGMA-ALDRICH) using the ball-mill $\text{Fritsch-Pulversette}6$ (450 rpm, 10 min milling/50 min cooling – repeated 20 times; the mass ratio of the balls to the charge was about 60). The powder was compacted at room temperature into pellets that were annealed at $360^\circ\text{C}/20\text{h}/\text{Ar}$ (Treatment 1) or $360^\circ\text{C}/20\text{h}/\text{Ar}$ in air (Treatment 2). Treatment 2 simulated the kind of harsh handling that might occasionally occur while the HS alloy under examination was in service. Alloys subjected to Treatment 2 are labelled Alloy 2-Air. Ball-milled, compacted and annealed samples were charged by gaseous hydrogen at $345^\circ\text{C}/20\text{h}/30\text{bar}$ in a pressure vessel. Other details of the sample preparation and measurement arrangement have been described elsewhere \[31\]. Charged samples of both alloys were stored at room temperature in a well-defined atmosphere of dry air for about 5 years. This storage simulated a long-term service period of HS material.

Hydrogen sorption characteristics were measured using the Sieverts-type gas sorption analyser $\text{PCT-Pro Setaram Instrumentation}$ in the present work. This equipment enables safe and fully-automated repeated measurements in both absorption and desorption regimes. The study was carried out at temperatures between 250 and $350^\circ\text{C}$ and under hydrogen pressure from 0.001 mbar to 20 bars. The purity of both the hydrogen and helium (calibration gas) was 6N. The hydrogen was dosed using calibrated volumes corrected to dead volumes at each individual test temperature.

X-ray powder diffraction (XRD) was performed using Cu $K_{\alpha1,2}$ radiation. HighScore Plus software and JCPDS PDF-4 were used for qualitative analysis and Rietveld refinements using external LaB$_6$ standard and structural models based on the ICSD database for quantitative analysis.

3. Results and discussion

3.1. Sample characterization

After ball-milling, samples consisted exclusively of pure milled Mg and Ni, mechanically alloyed with In. During the annealing (Treatments 1 and 2), Mg and Ni formed a mixture $\text{Mg(In)} + \text{Mg}_2\text{Ni(In)}$. XRD phase analysis of charged samples carried out after the ageing led to the conclusion that the Ni-rich phase $\text{Mg}_2\text{Ni(In)}\alpha\text{H}_4$ partially decomposed into Ni, $\text{In}_2\text{Ni}_y$, and $\text{In}_x\text{Mg}_y$. This process was more intensive in Alloy 2, with a higher In concentration: the comparison of XRD patterns in Fig. 1 clearly shows the smaller content of $\text{Mg}_2\text{Ni(In)}\alpha\text{H}_4$ in Alloy 2. The phase composition of hydrogen-charged Alloy 1 and Alloy 2, obtained by Rietveld analysis of XRD patterns, is listed in Table 1.

The structure of alloys was observed by SEM. Typical results are illustrated in Fig. 2, where the structure of Alloy 2 is shown both in SEI (secondary electrons – Fig. 2a) and in BSE (back scattered elec-
Table 1. Phase composition of hydrogen charged materials obtained by XRD in wt.%; alloys after Treatment 1

<table>
<thead>
<tr>
<th>Phase</th>
<th>Freshly-prepared</th>
<th>Aged, before measurement</th>
<th>Aged, after measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alloy 2*</td>
<td>Alloy 1</td>
<td>Alloy 2</td>
</tr>
<tr>
<td>Mg(In)H₂</td>
<td>61.7</td>
<td>71.1</td>
<td>69.2</td>
</tr>
<tr>
<td>Mg₂Ni(In)H₄</td>
<td>28.2</td>
<td>15.0</td>
<td>26.1</td>
</tr>
<tr>
<td>Mg₂Ni(In)H₀.₃</td>
<td>10.1</td>
<td>7.6</td>
<td>20.3</td>
</tr>
<tr>
<td>Ni</td>
<td>5.0</td>
<td>14.4</td>
<td>4.3</td>
</tr>
<tr>
<td>In</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>In₃Mg</td>
<td>10.1</td>
<td>7.6</td>
<td>4.7</td>
</tr>
<tr>
<td>InMg₄</td>
<td>0.7</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td>InNi₃</td>
<td>0.2</td>
<td>0.3</td>
<td>0.9</td>
</tr>
</tbody>
</table>

*Phase composition of freshly-prepared Alloy 2 taken from previous studies [28–32]; XRD analysis of freshly prepared Alloy 1 was not done.

Fig. 1. XRD patterns of Alloy 1 and Alloy 2 after long-term storing.

Fig. 2. Typical structure of studied HSMs. SEM image of Alloy 2: (a) SE, (b) BSE. Light particles – Mg₂Ni(In)H₄ phase.

3.2. Kinetic measurements

Cycling measurements of kinetic curves were done at temperatures between 250 and 295°C with a starting pressure of 20 bars (for absorption) and 0.001 bars (for desorption). The instantaneous hydrogen pressure \( p \) in the sample chamber was always well above the equilibrium pressure \( p_{eq}(T) \) of the respective hydrides and below the \( p_{eq}(T) \) during absorption and desorption, respectively. The maximum number \( n \) of A/D cycles in cycling experiments was 10 because it was...
proved that this was a sufficient number for stabilizing alloy sorption behaviour in all cases.

In both alloys, the sorption capacity reached approximately 3 wt.% H\textsubscript{2} at 295°C, and the cycles were regular. In Alloy 2-Air, the sorption capacity was only about 2.5 wt.% H\textsubscript{2}; the sorption kinetics was slower and more (about 6) cycles were needed to reach a stable state.

Comparison of sorption curves at both temperatures measured in a well-stabilized state (in the 10th cycle) is shown in Fig. 4. It can be seen that the rate of hydrogen desorption is slightly higher in Alloy 2 compared to Alloy 1, which agrees with the results obtained 5 years ago – see Fig. 5a. It is also obvious that the hydrogen sorption capacity in aged Alloy 2 is higher than that of Alloy 1 at a higher temperature (Fig. 4a).

Comparing the time needed for desorption of 90 % of the stored hydrogen (at a test temperature of 250°C used both in the previous and the present studies), one can easily conclude that the hydrogen desorption kinetics remained approximately unchanged after long-term storage of the alloys. However, the hydrogen storage capacity decreased from about 5 wt.% H\textsubscript{2} down to
approximately 3 wt.% H$_2$. Such a decrease in capacity can be explained – at least qualitatively – with reference to the lower fraction of hydrogen storing phases (see Table 1): whereas immediately after the first hydrogen charging, only phases effective for hydrogen storage were present (Mg(In)H$_2$, Mg$_2$Ni(In)H$_6$, and Mg$_2$Ni(In)H$_{0.3}$), Ni-containing phases partially decomposed after the ageing. It can also be seen that the decay products (Ni, In, In$_x$Mg$_{1-x}$, and InNi$_3$) partly reformed into Mg$_2$Ni(In)H$_4$ and Mg$_2$Ni(In)H$_{0.3}$ after cycling measurements with Alloy 1. This means that the degradation of the hydrogen storage capacity originates in the partial decomposition of phases able to store hydrogen during long-term storage.

The XRD study resulted in interesting conclusions about the influence of oxidation upon hydrogen absorption (Fig. 4) and desorption (Fig. 5) characteristics: the relatively intensive exposure of Alloy 2 to the air (Treatment 2) caused the formation of MgO, which was kept at a relatively low level by the presence of In. The first desorption tests of Alloy 2-Air led to even better desorption kinetics as can be seen in Fig. 5. However, the later sorption tests of Alloy 2-Air at 295 °C, carried out in the present work after 5 years, showed considerably reduced hydrogen storage capacity and poor sorption kinetics (Fig. 4a). At a lower temperature, 250 °C, the hydrogen sorption in Alloy 2-Air was even almost blocked (Fig. 4b). The beneficial effect of In upon oxidation resistance even after long-term storing can be documented by the XRD patterns in Fig. 1.

The difference between the relatively rapid hydrogen sorption and poor kinetics of hydrogen desorption (Alloy 1, Alloy 2 – Fig. 4) is caused, most likely, by different driving forces: the difference in hydrogen...
Fig. 6. PCT curves (measured only in an absorption mode).

pressure between the hydrogen reservoir and sample chamber is +20 bars for absorption and −1 bar only for desorption.

The worse sorption kinetics in Alloy 2-Air is most likely caused by the oxide phase nucleation during Treatment 2, which acted rather as a sorption catalyst in the freshly-prepared samples (Fig. 5b). These oxide particles, once formed, grew relatively easily and formed an oxide layer that could later effectively inhibit hydrogen sorption (Fig. 4b). Reliable evaluation of the amount of oxide phase both in freshly prepared and in aged samples was below the detection limit of XRD.

3.3. PCT isotherms

In Fig. 6, PCT isotherms (dependence of hydrogen equilibrium pressure above the respective hydride, \( p_{\text{eq}} \), on hydrogen concentration in solid, \( c_H \), at constant temperature) are compared. All the curves were measured in the absorption regime (some hysteresis can be expected [37], but the absorption mode was chosen as sufficient for relative comparison of the long-term hydrogen behaviour of Alloy 1 and Alloy 2).

The curves show two plateaus – the phase Mg(In)H\(_2\) is responsible for the lower one, the short upper plateau reflects the presence of Mg\(_2\)Ni(In)H\(_4\) hydride [37]. The upper plateau observed in Alloy 2 is less evident, but temperature-programmed desorption carried out with charged samples proved that both phases were also formed in this HS alloy.

The dependence of dissociation pressure \( p_{\text{eq}} \) on the reciprocal temperature of the sample is plotted in Fig. 7. The values of \( p_{\text{eq}} \) were determined at \( c_H = 1.5 \text{ wt.}\% \text{H}_2 \) for the Mg-rich phase, at \( c_H = 2.2 \text{ wt.}\% \text{H}_2 \) for the Ni-containing phase in Alloy 2-Air, and at \( c_H = 2.9 \text{ wt.}\% \text{H}_2 \) for the same phase in Alloy 1 and Alloy 2. Formation enthalpies \( \Delta H \) and formation entropies \( \Delta S \) are listed in Table 2. It is known that formation entropies of hydride formation \( \Delta S \) do not vary too much for different hydrides. The present values of \( \Delta S \) are close to the typical value of \( \Delta S \approx 0.13 \text{ kJ mol}^{-1} \text{H}_2/\text{K} \) [38].

It can be seen that the addition of In very slightly increases \( \Delta H \) and \( \Delta S \) in Mg(In)H\(_2\) and markedly decreases both Arrhenius parameters in Mg\(_2\)Ni(In)H\(_4\). This is, most likely, the cause of the partial decay of Mg\(_2\)Ni(In)H\(_4\) (followed by the decomposition of Mg\(_2\)Ni(In)H\(_4\) into Ni, In, and In\(_x\)(Mg,Ni)\(_y\)) during long-term storage and its relatively easy restoration during cycling (see Table 1).

To decide whether the observed concentration dependence of the Arrhenius parameters is due to ageing or rather to In addition, Alloy 2 was once more freshly prepared and annealed according to Treatment 1. Arrhenius parameters obtained in the repeated experiment agreed very well with their counterparts measured with aged Alloy 2 (Table 2). This means that the Arrhenius parameters in the alloys studied are determined by the alloying with In and remain unchanged during long-term ageing.
The HS characteristics of two prospective HS alloys Mg-Ni-In-C with different In concentration were measured after long-term storage. After 5 years, elapsed from the last hydrogen charging, the A/D cycling tests were performed to assess the behaviour of the material during real service. It was found that:

(i) The beneficial effect of In upon the hydrogen storage characteristics of the alloys studied persisted even after ageing: a higher value of $c_{In}$ leads to better sorption kinetics.

(ii) The formation enthalpy $\Delta H_f$ of Mg(In)H$_2$ measured with aged alloys seems to be independent on $c_{In}$, whereas the value $\Delta H_f$ of Mg$_2$Ni(In)H$_4$ decreased significantly in alloys with higher content of In. When comparing the values $\Delta H_f$ for the aged and freshly prepared Alloy 2, it follows that the decrease in $\Delta H_f$ observed in Alloy 2 is due rather to In than to ageing.

(iii) Hydrogen storage capacity decreased from about 5 wt.% H$_2$ in a freshly prepared state down to about 3 wt.% H$_2$ after ageing.

(iv) A decrease in hydrogen storage capacity was caused by partial phase decomposition of Mg$_2$NiH(In)H$_4$. The Ni-containing phase was partially re-formed during the sorption cycles.

(v) The hydrogen sorption in samples that were thermally treated in an oxidizing atmosphere (Treatment 2) showed a slight improvement in desorption kinetics in the freshly-prepared state. However, hydrogen desorption was almost blocked after their long-term ageing.

(vi) The results of the present paper suggest that the relatively high hydrogen storage capacity of perspective Mg-Ni-In-C alloys could be kept even after long-term ageing if the phase decomposition of Mg$_2$Ni(In)H$_4$ into In$_x$Ni and In$_y$Mg$_z$ is suppressed. How to reach this goal is a subject of further research.

**4. Conclusions**

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**References**


