Aluminium – Hydrogen – Magnesium

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Literature Data

The solubility of hydrogen in Al-Mg alloys was measured for different temperatures and composition ranges using a range of different experimental techniques. [1973Hua] used a modified Sieverts apparatus for determination of solubility of hydrogen in pure magnesium and its alloys including Al-Mg system. It was shown that alloying of magnesium with 10 at.% Al lowered the solubility of hydrogen at 700°C and \( p_{\text{H}_2} = 10^5 \) Pa from 50 cm\(^3\) H\(_2\)/100 g to =40 cm\(^3\) H\(_2\)/100 g (hydrogen volumes measured at 273 K under 101325 Pa). These values are very close to the values calculated by [1965Bur]. [1974And] studied the solubility of hydrogen in (Al) solid solution with 0.45 and 4.75 at.% Mg at 500°C using saturation and vacuum extraction and showed that alloying with Mg raised the hydrogen solubility from 0.012 cm\(^3\) H\(_2\)/100 g (for pure Al) to 0.04 ± 0.01 (for 4.5 at.% Mg) and to 0.06 cm\(^3\) H\(_2\)/100 g (for 4.75 at.% Mg). These results are significantly lower than those presented by [1976Wat]. [1974Gab] studied the solubility of hydrogen in \( \beta \) phase (Mg\(_2\)Al\(_3\)) in temperature interval from 380 to 560°C using high pressure Sieverts apparatus and high temperature vacuum extraction. Under crystallization the hydrogen solubility in Mg\(_2\)Al\(_3\) dropped from 5.9 cm\(^3\) H\(_2\)/100 g to 1.45 cm\(^3\) H\(_2\)/100 g. [1976Lev] studied the porosity of Al-Mg alloys which is caused by hydrogen. [1977Che] investigated permeability, diffusivity and solubility of hydrogen at temperatures from 650 to 800°C in liquid Al-Mg alloys containing up to 16 mass% Al. [1981Tuc] studied the hydrogen saturation of Al-Mg alloys exposed to water-vapor saturated air at elevated temperature.

Reversible hydrogen storage in magnesium alloys was reviewed by [1978Gui]. They reported that \( \gamma \) phase (Mg\(_{17}\)Al\(_{12}\), sometimes designated as Mg\(_5\)Al\(_3\)) did not hydride at 350°C under hydrogen pressure from 3 to 5 MPa. These results are in contradiction with those presented by [1980Min, 1981Gav], who studied the reactions of hydrogen with Mg\(_2\)Al\(_3\) and Mg\(_{17}\)Al\(_{12}\) and reported their main features: hydrogenation of the intermetallic Al-Mg compounds resulting in disproportionation; namely, for Mg\(_{17}\)Al\(_{12}\) the reaction may be written as: Mg\(_2\)Al\(_3\)+2H\(_2\)=2MgH\(_2\)+3Al; while for Mg\(_3\)Al\(_2\), the reaction may be written: Mg\(_{17}\)Al\(_{12}\)+9H\(_2\)=9MgH\(_2\)+4Mg\(_2\)Al\(_3\) [1983Sem] pointed that Al-Mg alloys dissolved only a very small quantity of hydrogen due to very low rate of process.

Differential scanning calorimetry and gas chromatography were used to investigate and quantify the reactions occurring when Al-5Mg (mass%) alloy, previously exposed to water-vapor saturated air, were heated from ambient temperature to 600°C. [1984Lue] measured the equilibrium hydrogen pressure at 142 and 170°C of the three phase fields MgH\(_2\)+(Mg)+, MgH\(_2\)+MgH\(_2\)+\( \beta \) and MgH\(_2\)+\( \beta \)+Al. The H was introduced into Al-Mg alloys by electrolysis in an organometallic melt, NaAlEt\(_4\), containing dissolved Na\(^+\)H\(^-\) as electrolyte. [1985Lue1, 1985Lue2] discussed the results thermodynamically.

[1978Cla1] prepared a ternary hydride Mg(AlH\(_4\))\(_2\) by reaction of NaAlH\(_4\) with MgCl\(_2\) dissolved in tetrahydrofurane and measured its heat capacity at room temperature, to be 136 J/(mol·K)\(^1\). Since [1985Lue1, 1985Lue2] did not find this ternary hydride, it may possibly be stable only under high hydrogen pressure, an assumption supported by the method of sample preparation.

A new theoretical method of describing and investigating metal hydrides has been developed by [1987Lue]. It involves thermodynamics and interprets the hydrogenation reaction by ternary phase diagrams.

[1987Lue] showed that intermetallic compounds formed by elements of the boron group with magnesium form two phase regions with MgH\(_2\) in the ternary phase diagrams. Thus the hydrogen pressures of the resulting three phase equilibria will be higher than or equal to the value of Mg/MgH\(_2\) equilibrium. In these systems, including Al-H-Mg, ternary hydrides are not taken into account.

The solubility of hydrogen in molten aluminium alloys containing magnesium has been calculated from the solubility of hydrogen in pure metals and binary metal-metal interaction parameters by [1989Lin].
The structure and hydrogen absorption properties of Al-Mg alloys prepared by high-energy ball milling were studied over the whole composition range in their as milled and Al-leached forms by [2000Bou]. The latter were obtained from the milled materials by leaching out of Al in a 1N NaOH solution. Their results on the interaction of intermetallic phases with hydrogen are in good agreement with those of [1980Min, 1981Gav].

[2002Her] used Miedema’s model to predict the hydrogen content and the enthalpy of formation of hypothetical ternary hydrides in the Al-H-Mg system.

Binary Systems

The binary systems Al-H [2002Per], Al-Mg [2003Luc] and H-Mg [2001Per] are accepted to present the best boundary systems for the Al-H-Mg ternary system.

Solid Phases

One ternary phase has been reported, Mg(AlH4)2, which is stable under high hydrogen pressure. The phase AlH3 is known to have two polymorphic modifications which are both metastable [1978Cla1, 1978Cla2, 1979Cla]. Chemically AlH3 is stable at room temperature and decomposes when heated at 110°C [1980Her]. Under high hydrogen pressures (2 GPa at 300°C and 6 GPa at 600°C), it is possible to synthesize AlH3 reversibly [1992Kon]. All solid phases are listed in Table 1.

Isothermal Sections

Figure 1 shows the isothermal section between 140 and 170°C [1984Lue, 1985Lue1, 1985Lue2]. The section is corrected to the accepted homogeneity ranges of the Al-Mg phases: (αAl), (Mg), β and γ. Figure 1 shows that MgH2 is in equilibrium with α, β, γ, and (Mg) phases. Mg(AlH4)2 and AlH3 hydrides are stable phases at these temperatures under hydrogen pressure higher than 100 kPa.

Figure 2 shows the solubility of hydrogen in liquid Al-Mg alloys at 500, 700 and 800°C. It is taken from [1976Wat, 1989Lin] with small corrections to match the solubility in Al given in the Al-H system by [2002Per]. From the activity coefficients of hydrogen in molten Al-Mg alloys at 827°C [1989Lin], the interaction coefficient of Mg upon H in liquid Al may be assessed: \( \epsilon_{H}^{(Mg)} = (\frac{dlna_{H}}{dx_{Mg}}) = -8.12 \) at 827°C. This negative value means that Mg in liquid Al increases the solubility of H.

Al-Mg alloys show liquid-solid two-phase fields at 500°C. There, the hydrogen solubility must be represented by a straight line. The pressure-composition isotherms of the Mg2Al3-H system for temperature interval from 335 to 410°C are presented in Fig. 3 [1980Min]. These isotherms are in fair agreement with the measurements of [2000Bou] at 350°C which observed a plateau towards 0.8 MPa for Mg75Al25, corresponding to the Mg-MgH2 equilibrium and a plateau towards 1 MPa for Mg58Al42, corresponding to the equilibrium \( \frac{Mg_{2}Al_{3}}{MgH_{2}} + MgH_{2} \).

Figure 3 shows that under 5 MPa H2, the global composition of the hydride is Mg2Al3H7. The corresponding point lies inside the (Al)-MgH2-MgAl2H6 triangle in Fig. 1, which confirms the formation of the ternary phase under high hydrogen pressures.

Thermodynamics

The dependence of the equilibrium pressure on temperature for the disproportionation reaction

\[
\frac{1}{2}Mg_{2}Al_{3} + H_{2} = MgH_{2} + 3/2Al
\]

was reported by [1980Min, 1981Gav] as \( \log_{10}(p/Pa) = -3306/T + 11.47. \)

Hydrogen activity and Gibbs energy changes for the three-phase reactions in the Al-H-Mg system, as measured electrochemically at 142°C were presented by [1985Lue1, 1985Lue2, 1987Lue], as

- \( Mg_{17}Al_{12} - Mg - MgH_{2} \)
  - \( a_{H2} = 2.7 \cdot 10^{-3} \)
  - \( \Delta G = -20080 J/(mol H_{2})^{-1} \)

- \( Mg_{2}Al_{3} - Mg_{17}Al_{12} - MgH_{2} \)
  - \( a_{H2} = 1.1 \cdot 10^{-2} \)
  - \( \Delta G = -15481 J/(mol H_{2})^{-1} \)

- \( Al - Mg_{2}Al_{3} - MgH_{2} \)
  - \( a_{H2} = 2.3 \cdot 10^{-2} \)
  - \( \Delta G = -12970 J/(mol H_{2})^{-1} \).

These values are about 1.5 kJ lower than the accepted values. For instance, the first figure (\( \Delta G = -20080 J/(mol H_{2})^{-1} \)) which corresponds to the Mg/MgH2 equilibrium has to be compared with the value (-18833 \( J/(mol H_{2})^{-1} \)) accepted by [2001Per] at 142°C. The last value (\( \Delta G = -12970 J/(mol H_{2})^{-1} \)) has to be
compared with \( \Delta G = -11870 \text{ J}(\text{mol } \text{H}_2)^{-1} \) calculated from the expression of [1980Min, 1981Gav] given above.

[2002Her] predicted the enthalpy of formation of some virtual hydrides as

- \( \text{Mg}_17\text{Al}_{12}\text{H}_x \quad x = 29.64 \quad \Delta H_{\text{calc}}(x_{\text{calc}}) = -65000 \text{ J}(\text{mol f.u.})^{-1} \)
- \( \text{Mg}_2\text{Al}_3\text{H}_x \quad x = 5.83 \quad \Delta H_{\text{calc}}(x_{\text{calc}}) = -47000 \text{ J}(\text{mol f.u.})^{-1} \)
- \( \text{MgAl}_2\text{H}_x \quad x = 3.37 \quad \Delta H_{\text{calc}}(x_{\text{calc}}) = -43000 \text{ J}(\text{mol f.u.})^{-1} \)

The molar heat capacity of the hydride \( \text{Mg(AlH}_4)_2 \) has been measured at 25°C by means of a Calvet microcalorimeter as \( C_p = 136 \text{ Jmol}^{-1}\text{K}^{-1} \).

Notes on Materials Properties and Applications

The Al-Mg system is of great importance for developing many of the Al based and Mg based multicomponent light alloys used in avionic and space industry. The Al-Mg alloys are also of potential interest as materials for hydrogen storage.

Miscellaneous

The alloying of Al with Mg dramatically raises the absorption capacity of Al [1976Lev]. [1981Tuc] showed evidence for the formation of MgH\(_2\) on the grain boundaries of Al-Mg alloys when exposed to water-vapor saturated air at 70°C and for about 50 days. These authors suggest that its presence plays a prominent role in the pre-exposure embrittlement and stress-corrosion cracking of Al-Mg alloys.

The diffusion of hydrogen in liquid Al-Mg alloys at temperatures from 650 to 800°C is slowly changed by raising Al contents up to 5.5 mass% Al [1977Che]. The faster rise of \( D_H \) was observed in concentration interval of 5.5 to 12 mass% Al; after that \( D_H \) raised slowly up to 16 mass% Al. For pure magnesium \( D_H(650°C) = 1.5 \times 10^{-6} \text{ m}^2\text{s}^{-1} \) and activation energy is \( E_D = 31380 \pm 1670 \text{ Jmol}^{-1} \). For Al-Mg alloys:

- \( D_H(5.5 \text{ mass}\% \text{ Al}, 650°C) = 1.7 \times 10^{-8} \text{ m}^2\text{s}^{-1} \) and \( E_D(5.5 \text{ mass}\% \text{ Al}) = 34730 \pm 1670 \text{ Jmol}^{-1} \);
- \( D_H(12 \text{ mass}\% \text{ Al}, 650°C) = 8 \times 10^{-8} \text{ m}^2\text{s}^{-1} \) and \( E_D(12 \text{ mass}\% \text{ Al}) = 33470 \pm 1670 \text{ Jmol}^{-1} \);
- \( D_H(16 \text{ mass}\% \text{ Al}, 650°C) = 1 \times 10^{-7} \text{ m}^2\text{s}^{-1} \) and \( E_D(16 \text{ mass}\% \text{ Al}) = 33470 \pm 1670 \text{ Jmol}^{-1} \). But at 7.5 mass% the Al activation energy has a maximum at \( E_D(7.5 \text{ mass}\% \text{ Al}) = 50210 \pm 1670 \text{ Jmol}^{-1} \).

[2000Bou] showed that the measured hydrogen capacity of the as milled material decreases with Al content, from H/M = 1.74 for pure un-milled Mg, to 1.38 for Mg/Al = 90/10, and then to 1.05 for Mg/Al = 75/25. In each case, there is a further 10-15% decline of the hydrogen absorption capacity after leaching. In the case of Mg/Al = 58/42, which basically contains a nanocrystalline Mg\(_{17}\text{Al}_{12}\) intermetallic phase, only hydriding leads to the formation of MgH\(_2\) and Al. This reaction is totally reversible and Mg\(_{17}\text{Al}_{12}\) is recovered upon dehydriding. In each case, there is an increase in the kinetics of hydrogen absorption and desorption following leaching. This change in the sorption kinetics is thought to arise as a consequence of the presence of Al solutes in the hexagonal structure of Mg, rather than to be due to purely geometric effects, such as the increase of the surface area.

References


\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Phase/ Temperature Range [°C] & Pearson Symbol/ Space Group/ Prototype & Lattice Parameters [pm] & Comments/References \\
\hline
(\textit{β}Al) & \textit{hP} & \textit{P6}_3/mmc & at 25°C, 20.5 GPa [Mas2] \\
< 660.452 & \textit{P6}_3/mmc & \textit{Mg} & \textit{a} = 269.3, \textit{c} = 439.8 \\
\hline
(\textit{α}Al) & \textit{cF4} & \textit{Fm\overline{3}m} & at 25°C [Mas2] \\
< 650 & \textit{Fm\overline{3}m} & \textit{Cu} & \textit{a} = 404.96 \\
\hline
(Mg) & \textit{hP2} & \textit{P6}_3/mmc & at 25°C [Mas2] \\
< 650 & \textit{P6}_3/mmc & \textit{Mg} & \textit{a} = 320.94, \textit{c} = 521.07 \\
\hline
\gamma, Mg_{17}Al_{12} & \textit{cF8} & \textit{I\overline{4}3m} & at 25°C [Mas2] \\
\leq 458 & \textit{I\overline{4}3m} & \textit{\alpha Mn} & \textit{a} = 1054.38 \\
\hline
\end{tabular}
\caption{Crystallographic Data of Solid Phases}
\end{table}
### Phase/Temperature Range

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space Group</th>
<th>Pearson Symbol</th>
<th>Lattice Parameters [pm]</th>
<th>Comments/References</th>
</tr>
</thead>
<tbody>
<tr>
<td>β, Mg_{2}Al_{3} ≤ 452</td>
<td>Fd$ar{3}$m</td>
<td>cF1168</td>
<td>$a = 2816$ to $2824$</td>
<td>60-62 at.% Al [2003Luk] 1168 atoms on 1704 sites per unit cell [2003Luk]</td>
</tr>
<tr>
<td>ε, Mg_{23}Al_{30} 410 - 250</td>
<td>R$ar{3}$</td>
<td>hR159</td>
<td>$a = 1282.54$</td>
<td>54.5-56.5 at.% Al [2003Luk] Structure: 159 atoms refer to hexagonal unit cell [2003Luk]</td>
</tr>
<tr>
<td>αAlH$_3$ &lt; 110</td>
<td>R$ar{3}$c</td>
<td>hR24</td>
<td>$a = 445.6$</td>
<td>1183 [1992San], metastable</td>
</tr>
<tr>
<td>βAlH$_3$ &lt; 80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Metastable “Aluminum hydrogenoaluminate” Al(AlH$_4$)$_3$ [1978Cla2]</td>
</tr>
<tr>
<td>MgH$_2$</td>
<td>P4$_{2}$/mm</td>
<td>tP6</td>
<td>$a = 451.68$</td>
<td>302.05 [P]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
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<td></td>
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</tr>
</tbody>
</table>

* Mg(AlH$_4$)$_2$ - - [1978Cla1], stable above 5 MPa H$_2$ at 410°C [1980Min]*

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**Fig. 1:** Al-H-Mg.

Isothermal section at temperatures between 140 and 170°C
Fig. 2: Al–H–Mg.
Hydrogen solubility in liquid Al–Mg alloys under 1 bar at 500, 700 and 800°C

Fig. 3: Al–H–Mg.
Pressure-composition isotherms of the Mg₂Al–H system