ABSORPTION OF HYDROGEN BY MAGNESIUM BASED ALLOYS

Vítězslav KNOTEK, Dalibor VOJTĚCH

Department of Metals and Corrosion Engineering, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic, knotekv@vscht.cz

Abstract

The main task for using hydrogen as energy carrier is its storage. The reversible hydrogen storage in solid state in a form of magnesium hydride seems to be very prospective. Usually, hydriding of Mg alloys is carried out by gaseous hydrogen high pressure and high temperatures. It means this method is technologically and economically demanding.

Simpler method of hydriding, namely electrochemical hydriding of Mg alloys in aqueous solution, was tested in this work. This method requires neither gaseous hydrogen, nor high temperature. In the presented work, electrochemical hydriding of selected binary and ternary Mg-Ni-Mm-based alloys (Mm - mishmetal = mixture of Ce, La, Nd and Pr) was performed. The influence of structure and temperature of electrolyte on ability to absorb hydrogen by tested alloys was determined. It is shown that addition of Ni and Mm and elevated temperature of electrolyte positively influence the amount of absorbed hydrogen by magnesium-based alloys.

Keywords: hydrogen storage, Mg-based alloys, electrochemical hydriding

1. INTRODUCTION

Recently, hydrogen has been considered to be a promising energy carrier especially for vehicles. There can serve as an ideal fuel, because after burning of hydrogen or converting the chemical energy of hydrogen in the fuel cell, no harmful emissions are released.

Despite of necessity to solve the economical production of hydrogen without releasing CO₂, hydrogen storage represent the key problem for exploiting the hydrogen economy. It is necessary to find save, effective and affordable method of hydrogen storage.

Today three basic methods of hydrogen storage are considered [1]: (1) gas-state storage, (2) liquid-state storage and (3) solid-stage storage. The first method requires high pressure and volumetric density is very low in addition. The second approach requires very low temperature to liquefy the hydrogen. This process consumes significant portion of the total energy obtainable from the stored hydrogen. The last storage method can be divided into two types. One is based on adsorption in materials having a very high specific surface, i.e. nanotubes and polymer nanocomposites [2]. However some inconvenient conditions (low temperature, high pressure) are required to store hydrogen. The latter method is based on chemical absorbing of hydrogen and involves complex metal hydrides and metal hydrides. Till now, complex metal hydrides (LiBH₄, NaAlH₄, LiNH₂) suffer from insufficient ability of absorbing and desorbing hydrogen under mild conditions. Metal hydrides have been extensively studied in the last three decades, particularly hydrides based on magnesium.

Mg seems to be perspective onboard hydrogen storage material for vehicular application due to its low weight, cost and high hydrogen content up to 7.6 wt. % corresponds to magnesium hydrid (MgH₂). However, pure magnesium suffers from very slow hydrogenation/dehydrogenation reaction. Moreover hydrogenation occurs at high temperature of order of 350 – 400 °C under a hydrogen pressure of more than 3 MPa [3] and for releasing hydrogen from MgH₂ temperature higher than 300 °C is necessary [4]. Many efforts have been made to improve the hydrogenation characteristics of magnesium, including alloying with appropriate...
elements (Ni, Al, Ti, Cu, La, Ce, Nd) [5-7], addition of transition metals oxides [8], mechanical alloying (MA) [9], preparing fine nanocrystalline or amorphous structure [10] and others.

There are several methods to synthesize Mg-based hydrides. Preparing hydrides by reaction of Mg-based alloy with gaseous hydrogen is the most mentioned method in literature [11,12]. However this method often requires elevated temperatures and high pressures of pure hydrogen. In addition the ball milling of Mg-based alloys is widely employed process to obtain better hydriding characteristics [13]. Therefore this method of preparing metal hydrides is technically and financially difficult.

In this work, a few investigated method of preparing metal hydrides - electrochemical hydriding - was tested. This method does not need any gaseous hydrogen and does not require high temperatures. The principle of electrochemical hydriding is electrolysis of a water solution, where the magnesium alloy serves as a cathode. So the atomic hydrogen directly enters the structure and could generate hydrides. Thus hydriding material can serve as a source of hydrogen [14,15].

2. EXPERIMENTAL

In this work, five binary and one ternary Mg-Ni-Mm-based alloys were investigated. The composition of alloys were as follows MgNi11, MgNi15, MgNi30, MgNi34, MgMm20 and MgNi24Mm5 (all concentrations are in wt. %). The Mm (mishmetal) contains 45 % Ce, 38 % La, 12 % Nd and 4 % Pr. The alloys were prepared by melting in a vacuum induction furnace under argon protective atmosphere. Cylindrical ingots of alloys of 100 mm in length and 20 mm in diameter were prepared by pouring the melt into a brass mould. The ingots were cut to thin samples of 0.5 mm in thickness. Surface of samples was treated by grinding on P180-P2500 abrasive papers before electrochemical hydriding tests. Pre-treated samples were immediately put in electrochemically hydriding cell.

Samples of alloys for electrochemical hydriding were connected to a DC source as a cathode. The platinum electrode was placed opposite to the hydriding side of sample and used as anode. Electrochemical hydriding was carried out in 6 mol/l KOH solution at 25 °C and 80 °C. The current density was maintained at 100 A/m². Hydriding time was 480 min.

Hydrogen concentration profile in hydrided alloys was determined by glow discharge spectrometer (GDS, Profiler 2). Due to the fact that hydriding was performed in a strongly alkaline bath, formation of magnesium hydroxide and/or complex hydroxide surface layers could be expected. In order to minimize the influence of such layers on results of hydrogen profile analysis, oxygen was also analyzed to determine the exact position of hydroxide/metal interface. The GDS analyzer was calibrated with respect to MgH₂. Sputtering rate was determined by measurement of surface profile after analysis.

Microstructure of samples was studied by the light microscope (Olympus PME-3) and the scanning electron microscope equipped by EDS analyzer (Hitachi S 450). Phase composition was determined by X-ray diffraction analyzer (XRD, X’Pert Pro).

3. RESULTS AND DISCUSSION

3.1 Structures of alloys

Fig. 1 illustrates the hypoeutectic structure of the as-cast alloys MgNi11 (Fig. 1a) and MgMm20 (Fig. 1b), eutectic structure of MgNi24Mm5 (Fig. 1c) and finally hypereutectic structure of MgNi34 (Fig 1d). Since the eutectic point of Mg-Ni alloys corresponds to the presence of 23.5 wt. % Ni, the structure of MgNi15 alloy is also hypoeutectic formed by primary denticles of Mg and fine Mg-Mg₂Ni eutectic. The structure of MgMm20 is formed by primary denticles of Mg and Mg-Mg₁₂Mm eutectic. In the case of ternary alloys Mg-Ni-Mm, these alloys contain three phases - Mg, Mg₂Ni and Mg₁₂Mm. As shown in Fig. 1d the structure of
hypereutectic MgNi34 is formed by Mg-Mg₃Ni eutectic and white shapes of Mg₃Ni. Very similar structure is obtained in the case of MgNi30 alloy.

Fig. 1. Microstructure of investigated alloys (light microscope) a) MgNi11, b) MgMm20, c) MgNi24Mm5, d) MgNi34

3.2 Hydrogen concentrations

Figure 2. Hydrogen concentration profile of MgMm20, MgNi11, MgNi30 and MgNi24Mm5 alloys after electrochemical hydriding (25 °C)

Hydrogen concentration profiles for MgMm20, MgNi11, MgNi24Mm5 and MgNi34 hydrided at 25 °C are presented in Fig. 2. These profile correspond to only hydrogen presents in metallic phase, it means there is zero concentration of oxygen.

The four alloys compared in Fig. 2 differ in amount of absorbed hydrogen. It can be seen that the binary MgMm20 alloy reached only about 0.2 wt. % of hydrogen on the surface and penetration depth of hydrogen is less than 10 μm. In the case of MgNi11 the value of hydrogen surface concentration is about 0.2 wt. % higher.
Therefore it can be assumed that Ni is more important element than Mm for electrochemical hydriding. The influence of Mm for hydriding becomes evident in the case of ternary alloy MgNi24Mm5. This alloy contains almost the same amount of magnesium as binary alloy MgNi30. In Fig. 2, one can see that the maximum hydrogen concentrations on the surface are almost identical for MgNi30 and MgNi24Mm5. The difference is in the shape of hydrogen curves. Whereas the hydrogen concentration in the depth of 10 μm corresponds to the same concentration as on the surface for MgNi24Mm5, in the case of MgNi30 this depth means fall-off in 0.2 % of hydrogen. Content of Mm probably positively influences the hydrogen diffusion inward the material. The positive role could also play almost pure eutectic structure of ternary alloy (see Fig. 1c).

In each hydrogen profile, we can determine two parameters, maximum surface concentration and penetration depth of hydrogen. For example for MgNi24Mm5, maximum surface concentration is 0.6 wt. % and penetration depth of hydrogen is 50 μm (see Fig. 2). These parameters are summarized for all hydrided alloys for two hydriding temperatures in Table 1.

### Table 1. Hydriding parameters of the alloys for two temperatures

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Hydriding temperature</th>
<th>H-surface conc. (wt. %)</th>
<th>H-penetration depth (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgMm20</td>
<td>25 °C</td>
<td>0.3</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>0.6</td>
<td>12</td>
</tr>
<tr>
<td>MgNi11</td>
<td>25 °C</td>
<td>0.3</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>0.4</td>
<td>40</td>
</tr>
<tr>
<td>MgNi15</td>
<td>25 °C</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>0.6</td>
<td>90</td>
</tr>
<tr>
<td>MgNi30</td>
<td>25 °C</td>
<td>0.6</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>1.0</td>
<td>120</td>
</tr>
<tr>
<td>MgNi34</td>
<td>25 °C</td>
<td>0.5</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>0.9</td>
<td>90</td>
</tr>
<tr>
<td>MgNi24Mm5</td>
<td>25 °C</td>
<td>0.6</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>0.8</td>
<td>90</td>
</tr>
</tbody>
</table>

The evident effect of temperature on the hydriding process can be seen in Table 1. As expected, the increasing of temperature accelerates hydriding rate. This is reflected by increasing the maximum hydrogen concentration and penetration depth for all of investigated alloys.

The best efficiency is observed for the binary MgNi30 alloy hydrided at 80 °C. The lowest hydrogen surface concentration for samples hydrided at 80 °C was measured for the binary MgNi11 alloy. The reason for this result may be in the low Ni-concentration, which causes a small volume fraction of eutectic. Although we supposed that higher content of Ni support the hydriding, the volume fraction of eutectic is more important parameter. From Table 1 it can be deduced that the higher volume fraction of eutectic is present at the structure of alloy, the better hydriding parameters are obtained. As was mentioned above the pure eutectic structure for Mg-Ni alloys corresponds to 23.5 wt. % of Ni. It means, that the structure of MgNi34 alloy contains less fraction of eutectic than MgNi30 alloy. Hence, the hydriding parameters are worse. We assume that neither primary Mg, nor grains of Mg2Ni play any significant role in electrochemical hydriding. This supposition confirms the XRD analysis after hydriding, which showed only presence of MgH2. No ternary or more complex hydrides, such as Mg2NiH4, Mg3MmNiH7 and other are found. This fact is probably caused by
faster formation kinetics of MgH$_2$ than in cases of other hydrides [16]. Nevertheless it should be noticed, that grow kinetics of MgH$_2$ support both Ni and Mm attendant in eutectic fraction.

4 CONCLUSIONS

In this work, various Mg-Ni-Mm alloys were electrochemically hydrided in an alkaline solution. The results of surface hydrogen concentration show that both Ni and Mm additions support hydriding. Elevated temperature also has positive effect of hydriding process. The penetration of hydrogen inward the structure of alloys poses diffusion controlled process. The key role of hydriding process plays the eutectic structure. The highest hydrogen concentration and maximum penetration depth was observed for the binary MgNi30 alloy, hydrided at 80 °C. Although the ternary MgNi24Mm5 alloy shows the pure eutectic structure, hydriding parameters are better in the case of binary MgNi30 alloy. In contrast to high-temperature and high-pressure hydriding processes, the only hydride formed during electrochemical hydriding was MgH$_2$.

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