EVALUATION OF HYDRIDING PARAMETERS IN MG–NI-BASED ALLOYS DOPED WITH TRANSITION METALS

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Abstract
There is a general hydrogen conception to overcome unstable production of electric energy from renewable resources, such as wind-power or solar-power plant. This conception consists in generation of hydrogen by using water electrolysis and its storing. However, there is a problem, how to store huge amount of hydrogen in a small volume. In this work, we performed water electrolysis to store nascent hydrogen in the form of magnesium alloys. Magnesium was alloyed by nickel, copper, zinc, cobalt and rare earths to improve kinetics of hydrogen absorption. Ingots of Mg-based alloys were prepared by vacuum induction melting. These were cut into thin coupons and electrochemically hydrided in KOH solution at 80 °C for 480 min. The structures and phase compositions of both as cast and hydried alloys were investigated by optical and scanning electron microscopy and by X-ray diffraction. Hydriding parameters for investigated alloys were measured by glow discharge spectrometer. The influence of doping transition metals on the ability of Mg-Ni-based alloys to absorb hydrogen was evaluated.

Keywords: Mg-based alloys, electrochemical hydriding, glow discharge spectrometry, mischmetal

1. INTRODUCTION
Hydrogen is considered to be a promising energy carrier especially for mobile applications. Simultaneously, hydrogen can serve as an agent for storage of the energy from renewable sources. It is the way how to overcome the production of hydrogen from fossil fuels which causes CO₂ release. However, the inaccessibility of safe, simple and cost-effective method of hydrogen storage limits the exploitation of hydrogen economy.

Storing hydrogen in the form of metallic hydrides seems to be promising due to the advantageous properties such as stability, safeness and easy handling. Magnesium-based hydrides have been taken great efforts in last two decades because magnesium is light, relatively inexpensive and capable to absorb up to 7.6 wt.% of hydrogen in the form of MgH₂. However, pure magnesium suffers from poor thermodynamics and slow kinetics of both hydrogenation and dehydrogenation. MgH₂ desorbs hydrogen very slowly if the temperature is below 573 K [1]. After the hydride layer is formed, MgH₂ prevents further diffusion of hydrogen into the material. Therefore the formation of MgH₂ is practically impossible in the bulk of pure magnesium [2]. Many efforts have been made to improve the hydrogenation characteristics of magnesium, including alloying with appropriate elements (Ni, Co, Al, Cu, La, Ce, Nd) [3-6], addition of transition metals oxides [7], mechanical alloying (MA) [8], preparing fine nanocrystalline or amorphous structure [9] and others.

Preparing hydrides by reaction of Mg-based alloy with gaseous hydrogen is the most common method [10]. 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 [11]. Therefore the synthesis of hydrides from metallic powder is expensive and dangerous.

In this work we present alternative method of synthesis of hydrides - electrochemical hydriding. 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. In this case the atomic hydrogen directly enters the structure and could generate hydrides. Our study focuses on electrochemical hydriding of various as-cast Mg-Ni-based alloys containing transition metals (Co, Cu and Zn) and rare earths (RE) that are known to positively affect hydrogen absorption. The structure and electrochemical hydriding efficiency of Mg-based alloys are characterized to identify the influence of alloying elements on the ability of Mg-based alloys to absorb hydrogen, when electrochemical hydriding is employed.

2. EXPERIMENT

In this work, three ternary Mg-Ni-M (M = transition metals Cu, Zn or Co) and one ternary Mg-25Ni-6Mm (Mm = mishmetal containing 45 % Ce, 38 % La, 12 % Nd and 4 % Pr) alloys (Table 1) were investigated. All concentrations in this paper are in units of wt.%. Table 1 shows that all investigated alloys contain approximately the same magnesium content. It means that ternary alloys were produced by nickel substitution with other element. 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 30 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 into electrochemically hydriding cell.

| Tab. 1 Chemical composition of hydrided magnesium alloys |
|-----------------|----------|----------|-------------|-------------|----------------|
| Alloy            | Ni (wt.%)| Zn (wt.%)| Cu (wt.%)  | Co (wt.%)   | Mm (wt.%)    |
| Mg-26Ni-6Zn      | 26.1     | 5.5      | -          | -           | -             |
| Mg-26Ni-6Cu      | 26.4     | -        | 6.0        | -           | -             |
| Mg-27Ni-5Co      | 27.3     | -        | -          | 4.9         | -             |
| Mg-25Ni-6Mm      | 25.1     | -        | -          | -           | 5.7           |

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 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 (GD 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.

Structure and phase composition of the as-cast and hydrided alloys were studied by the light microscope (Olympus PME-3), the scanning electron microscope (Tescan Vega 3) equipped by EDS analyzer (Oxford Instruments) and X-ray diffraction analyzer (XRD, X’Pert Pro).

3. RESULTS AND DISCUSSION

3.1 Structures of alloys

Light micrographs of investigated alloys are illustrated in Fig. 1. Every alloy exhibits hypereutectic composition and very similar structure, because Zn, Cu, Co and Mm are present particularly in eutectic mixture. It means that alloys are formed by light sharp-edged crystals which correspond to Mg₂Ni phase and by eutectic mixture with distinct composition. In the case of the Mg-26Ni-6Zn alloy (Fig. 1a) the eutectic is formed by α-Mg and Mg₂Ni phases (dark) where zinc is in the form of solid solution. The eutectic mixture...
(dark) of the Mg-26Ni-6Cu alloy (Fig. 1b) is composed by $\alpha$-Mg and Mg$_2$Ni phases too. EDS analysis indicated that copper is preferentially dissolved in the Mg$_2$Ni phase. Against copper, cobalt does not form solid solution. In the case of Mg-27Ni-5Co alloy, the eutectic is dominated by mixture of $\alpha$-Mg, Mg$_2$Ni and MgCo$_2$ phases (Fig. 1c). The eutectic in the microstructure of Mg-26Ni-6Mm alloy (Fig. 1d) is formed by $\alpha$-Mg, Mg$_2$Ni and Mg$_{12}$Mm phases.

![Fig. 1 Microstructures of investigated alloys (light microscope) a) Mg-26Ni-6Zn, b) Mg-26Ni-6Cu, c) Mg-27Ni-5Co, d) Mg-25Ni-6Mm](image)

It is observed that in all investigated binary and ternary alloys, there are relatively significant volume fractions of eutectic structures. These structures are very fine. It means there is a high area of phase boundaries which represent efficient paths for hydrogen diffusion in materials.

### 3.2 Hydrogen concentration

After GDS hydrogen analysis we obtain hydrogen profile for each alloy. In each profile, it can be determined the maximum hydrogen surface concentrations and the hydrogen penetration depths. From the profiles, it can be calculated the total mass of absorbed hydrogen, which is dependent on a course of hydrogen profile. Fig. 2 shows the measured hydrogen profiles of investigated alloys. Table 2 summarizes hydriding parameters obtained from these profiles including the maximum hydrogen concentrations present on the alloy surface, the hydrogen penetration depths and the total mass of hydrogen absorbed in the alloys during hydriding. Values of the last parameter in Table 2 are seemingly small, but it should be taken into account that hydrided volumes are very small.
The maximum values (the maximum hydrogen surface concentration and total mass of absorbed hydrogen) of the hydriding parameters are obtained for the Mg-27Ni-5Co alloy. The comparison with the Mg-25Ni-6Mm revealed that the maximum hydrogen surface concentration is more than twice higher. However the total mass of hydrogen absorbed in the Mg-25Ni-6Mm is almost the same as for the Mg-27Ni-5Co. This observation could be explained by the faster decreasing of H-concentration towards the alloy interior in the case of alloy with cobalt (Fig. 2), while the alloy with mischmetal behaves in different manner - the maximum surface hydrogen concentration (Cmax.) is the same in the depth of 20 µm and then starts gradually decrease. Both cobalt and mischmetal addition, into Mg-Ni-based alloy, support the hydrogen absorption, but in different way. Cobalt maximizes the maximum hydrogen concentration on the surface; therefore it probably supports hydrogen formation. The presence of mischmetal evidently decreases Cmax parameter. On the other hand, Mm probably support inward hydrogen diffusion, while does not participate in formation of hydrides (lower maximum surface concentration).

The data shown in Fig. 2 and the hydriding parameters in Table 2 indicate that Cu and Zn negatively influence the electrochemical hydriding performance. The Mg-26Ni-6Cu and Mg-26Ni-6Zn alloys have lower hydriding parameters than the others. For this reason, Zn and Cu addition are not suitable for supporting the electrochemical hydriding process.
3.3 Phase composition after hydriding
After electrochemical hydriding of investigated alloys the XRD analyses were carried out. The main hydriding product detected by XRD analyses, in all of investigated alloys, was MgH$_2$ binary hydride. It is surprising that no ternary or more complex hydrides, such as MmH$_3$, Mg$_2$MmNiH$_7$, Mg$_2$NiH$_4$ and other which are often detected after hydriding in gaseous hydrogen at high temperatures and pressures, were found. The one exception is Mg-27Ni-5Co alloy. We determined small amount of ternary Mg$_2$NiH$_4$ hydride by careful analysis of the pattern corresponding to the Mg-27Ni-5Co alloy. The presence of Mg$_2$NiH$_4$ is probably connected with the best hydriding efficiency in the case of Co-containing alloy, because hydrogen diffusion proceeds faster in this ternary hydride than in the binary MgH$_2$ phase. Therefore cobalt seems to be convenient doping element to enhance the electrochemical hydriding efficiency of Mg-Ni based alloys.

4. CONCLUSIONS
The results of this work show that the electrochemical hydriding of Mg-based alloys is a promising approach to simplify hydrogen storage. The electrochemical hydriding performance of as-cast Mg-based alloys strongly depends on the alloying elements when the structural compositions are very similar. In other words, the volume fraction of eutectic is almost the same in all of the investigated alloys. The alloying elements had the following effects on electrochemical hydriding:

1. Copper and zinc: Both elements influence the electrochemical hydriding performance negatively. The surface concentration of hydrogen and the total mass of absorbed hydrogen are lower than for the alloys with Co and Mm.
2. Mishmetal: The mixture of rare-earth metals has a positive effect on the electrochemical hydriding of Mg-Ni alloys in terms of maximizing the total mass of absorbed hydrogen. Mm probably supports inward hydrogen diffusion, but does not affect the formation of hydrides.
3. Cobalt: The alloy with Co addition (Mg-27Ni-5Co) achieved the best hydriding parameters. The maximum hydrogen concentration on the surface reached 1.5 wt.% of hydrogen. Cobalt probably changes the mechanism of hydriding, because, apart from MgH$_2$, XRD analyses revealed the presence of ternary Mg$_2$NiH$_4$ hydride.

Having identified the alloys with the most potential for electrochemical hydrogen storage, our next study will be devoted to designing cathodes for these alloys that are capable of storing high amounts of hydrogen and energy.

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