MAGNESIUM ALLOYS FOR HYDROGEN STORAGE

MAGNEZIJ ZA SKLADIŠČENJE VODIKA

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Several as-cast, binary Mg-Ni and ternary Mg-Ni-Mm (Mm = mischmetal) alloys were studied with respect to hydrogen storage. The alloys were hydrided using a new, electrochemical process to find the most promising alloy. The electrochemical hydriding process consisted of the electrolysis of a 6-M KOH solution in which the hydrided alloy was the cathode. The structures of both the as-cast and hydrided alloys were investigated by light microscopy, electron microscopy and x-ray diffraction. The hydrogen concentration was measured using glow-discharge spectrometry. It was observed that the structures of all the studied alloys contained a significant volume fraction of disperse eutectic mixtures that represented good paths for the inward hydrogen diffusion. The maximum hydrogen mass concentration of 1.6 % was thus achieved in the Mg-26Ni alloy with an almost purely eutectic structure. In the hypoeutectic and hypereutectic alloys the hydrogen concentrations were lower. The mechanism of the hydriding process is discussed in relation to the observed structural features of the alloys.

Keywords: hydrogen storage, magnesium, electrochemistry

Raziskano je bilo več litih binarnih Mg-Ni in ternarnih Mg-Ni-Mn (Mn = kovina) zlitin s stališča vezave vodika. Zlitine so bile hidrirane z novimi elektrokemijskimi procesi, da bi se našla najbolj primerna. Elektrokemijsko hidriranje se je izvršilo z elektrolizo v raztopini 6-M KOH s hidrirano zlitino kot katodo. Mikrostruktura je bila preiskana z optičnim in elektronskim mikroskopom in rentgensko difrakcijo. Koncentracija vodika je bila merjena s spektrometrijo tlivne razelektritve. Ugotovljeno je bilo, da vse raziskane zlitine vsebujejo pomemben volumenski delež dispergiranih evtektičnih zmesi, ki so imele dobro pot za difuzijo vodika navznoter. Največja masna koncentracija vodika 1,6 % je bila dosežena pri zlitini Mg-26Ni s skoraj čisto evtektično mikrostrukturo. V hipo- in hiperevtektičnih zlitinah je bila manjša koncentracija vodika. Mehanizem procesa hidriranja je obravnavan v odvisnosti od opaženih značilnosti mikrostruktur.

Ključne besede: skladiščenje vodika, magnezij, elektrokemija

1 INTRODUCTION

Magnesium alloys show a relatively high strength-to-weight ratio, making them of interest in many structural applications in automotive and aerospace industries. In addition, there are some potential non-structural applications of magnesium. Among them, hydrogen storage in magnesium alloys has been extensively studied.

Hydrogen is considered as one of the potential fuels for cars of the future. Great efforts have been exerted to find a simple, inexpensive and safe method for its storage. Today, three basic methods of hydrogen storage are considered[1]: 1. liquid hydrogen in heat-insulated tanks, 2. compressed hydrogen in pressure tanks, and 3. storage in the solid state, i.e., either adsorption in porous materials having a high specific surface or absorption in appropriate metals and alloys to form metallic hydrides. At present, the first method is commonly employed in the prototypes of "hydrogen cars". Hydrogen can be directly mixed with air and supplied to the engine, or it can be introduced into a fuel cell to produce electric power[1]. However, the main drawback of liquid-hydrogen storage is the high energy consumption associated with cooling to about –250 °C and liquefying. It was reported that this energy may represent up to 30 % of the total energy obtainable from the stored gas[1]. Moreover, another disadvantage is the continuous loss of hydrogen

through evaporation (about 1 % per day[1]). However, evaporation losses can be significantly reduced by storing liquid hydrogen in insulated pressure vessels (cryo-compressed hydrogen storage)[2]. The second approach does not need much energy but it achieves a relatively low gravimetric density of hydrogen – about 1 %[1]. In addition, there are safety risks arising from high pressure or liquid hydrogen storage.

For all these reasons, the storage of hydrogen in a solid phase has attracted a great deal of attention in the past three decades. In particular, systems based on magnesium hydrides have been extensively studied because magnesium is a light and relatively inexpensive metal and because MgH_2 achieves an excellent hydrogen gravimetric density of 7.6 %. During absorption, a magnesium alloy reacts with the gaseous hydrogen to form hydrides that are stable at room temperature. At elevated temperatures, the hydride is decomposed to evolve gaseous hydrogen, which can then be introduced either directly into a combustion engine or into a fuel cell. Pure MgH_2, however, suffers from a high thermodynamic stability, resulting in slow kinetics of the hydrogenation/dehydrogenation. Therefore, various attempts have been made to reduce its thermodynamic stability, mainly including alloying with transition or rare-earth metals (Ni, Fe, Nd, Ce)[3]. Although a lot of effort has been exerted in past years to develop inexpensive

hydrogen-storage materials based on magnesium, there is no commercially applied system at present.

There are several methods to synthesize Mg-based hydrides, but their common feature is that they involve the reaction of a metallic phase and gaseous hydrogen, usually at elevated temperatures and high pressures. Intensive milling of metallic powders in a hydrogen atmosphere has become a widely employed process[4]. However, from the technological and energy-consumption points of view, the synthesis of hydrides from metallic powder and hydrogen is inefficient, expensive and dangerous. For these reasons, it cannot compete with other hydrogen storage methods and fossil fuels.

In our work we present a new process of hydride production – electrochemical hydriding. Electrochemical hydriding overcomes the major drawbacks of traditional synthesis (summarized above), since it does not need gaseous hydrogen, high pressures and temperatures. Instead, hydrogen evolves from the water, which is a very cheap and easily available compound. In addition, this process occurs at mild temperatures. Atomic hydrogen, produced by the electrolysis of a water solution, directly enters a cathode made of an appropriate alloy, which can then serve as a source of hydrogen.

2 EXPERIMENT

In our work, several Mg-Ni-Mm (Mm=mischmetal containing 45 % Ce, 38 % La, 12 % Nd and 4 % Pr), see **Table 1**, were hydrided by an electrochemical process (hereafter, all concentrations are in mass fraction, $w/\%$). Mg-Ni alloys have been studied as prospective hydrogen-storage materials, because nickel is known to significantly support hydrogen absorption and desorption. Other alloys also contain mischmetal, i.e., an alloy containing rare-earth metals, which is also assumed to support hydriding behavior. The alloys were prepared by melting of pure metals in an induction furnace under argon. The ingots of 200 mm in length and 20 mm in diameter were gravity cast into a metal mould. Afterwards, the ingots were cut into 0.5-mm-thick coupons for electrochemical hydriding. Prior to the hydriding the surface of the coupons was mechanically polished.

Table 1: Chemical compositions (in $w/\%$) of hydrided magnesium alloys (Mm-mischmetal)
Tabela 1: Kemična sestava hidriranih zlitin magnezija (Mm – kovina) v masnih deležih, $w/\%$

alloy	element ($w/\%$)		alloy	element ($w/\%$)	
	Ni	Mm		Ni	Mm
Mg	–	–	Mg-35Ni	34.8	–
Mg-11Ni	10.9	–	Mg-10Ni-5Mm	10.3	5.4
Mg-26Ni	26.4	–	Mg-24Ni-5Mm	24.0	5.5

Electrochemical hydriding was performed in a 6-mol/l KOH solution at 80 °C and 100 A/m² current density. The hydriding time was 8 h. The alloys were immersed in the electrolyte, connected to a DC source

and polarized as the cathode, while a graphite rod of 10 mm in diameter and 100 mm in length was used as the anode. The current density was adjusted to prevent the excessive evolution of gaseous hydrogen.

The structure and phase composition of the as-cast and hydrided alloys were observed by using light (LM) and scanning electron microscopy (SEM, Tescan Vega 3), energy-dispersion spectrometry (EDS, Oxford Instruments Inca 350) and x-ray diffraction (XRD, X Pert Pro). To measure the concentrations of hydrogen, glow-discharge spectrometry (GDS, Profiler 2) was employed. The GDS analyzer was calibrated with respect to MgH₂.

3 RESULTS AND DISCUSSION

3.1 Structures

Light micrographs of the investigated alloys are illustrated in **Figure 1**. The Mg-11Ni alloy (**Figure 1a**) has a hypoeutectic composition and its microstructure is thus dominated by the α-Mg dendrites (light) and the α-Mg+Mg₂Ni eutectic (dark). The Mg-26Ni alloy (**Figure 1b**) approaches the eutectic point in the Mg-Ni phase diagram[5]; therefore, its structure is dominated by an α-Mg+Mg₂Ni eutectic mixture. In contrast, the structure of the hypereutectic Mg-35Ni alloy (**Figure 1c**) contains the α-Mg+Mg₂Ni eutectic mixture (dark) and also the primary Mg₂Ni phase (light). The MgNi10Mm5 alloy (**Figure 1d**) consists of the primary α-Mg dendrites (light) and a ternary α-Mg+Mg₂Ni+ Mg₁₂Mm eutectic mixture. The Mg₁₂Mm phase means a solid solution of
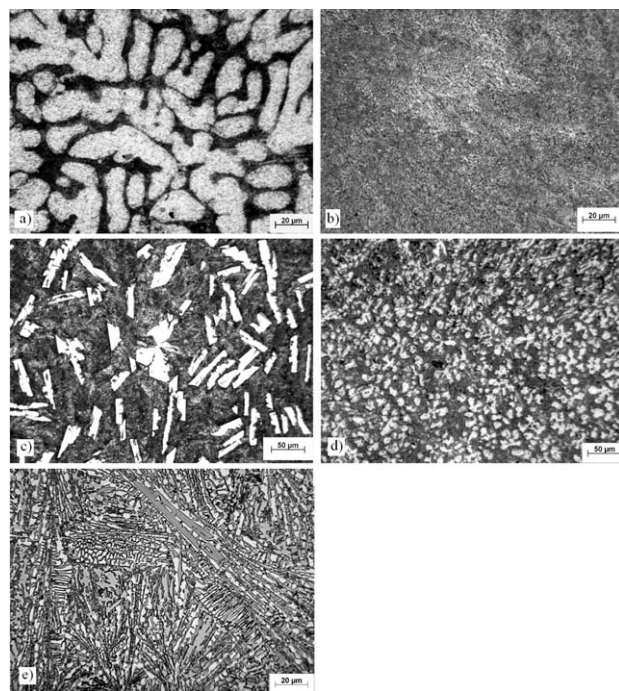

Figure 1: Microstructures of the investigated alloys: a) Mg-11Ni, b) Mg-26Ni, c) Mg-35Ni, d) Mg-10Ni-5Mm, e) Mg-24Ni-5Mm (LM)
Slika 1: Mikrostruktura raziskanih zlitin: a) Mg-11Ni, b) Mg-26Ni, c) Mg-35Ni, d) Mg-10Ni-5Mm, e) Mg-24Ni-5Mm (LM)

isostructural $Mg_{12}La$ and $Mg_{12}Ce$ (space group Immm) phases. The Mg-24Ni-5Mm alloy (**Figure 1e**) is dominated by the α-Mg+ Mg_2Ni+ $Mg_{12}Mm$ eutectic mixture. It is observed that in all the investigated binary and ternary alloys, there are relatively significant volume fractions of eutectic structures. These structures are very fine, despite the relatively slow cooling during gravity casting. Therefore, there is a high area of phase boundaries that represent efficient paths for hydrogen diffusion in materials.

3.2 Hydrogen concentrations

Hydrogen concentrations measured after 8-hour hydriding of the alloys are shown in **Figure 2**. It can be seen that the pure Mg cannot be hydrided by the electrochemical method, because the H concentration is below
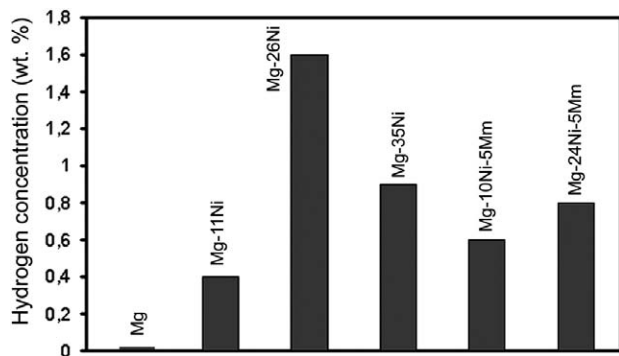

Figure 2: Hydrogen concentrations in the hydrided alloys (GDS)
Slika 2: Koncentracija vodika v hidriranih zlitinah (GDS)
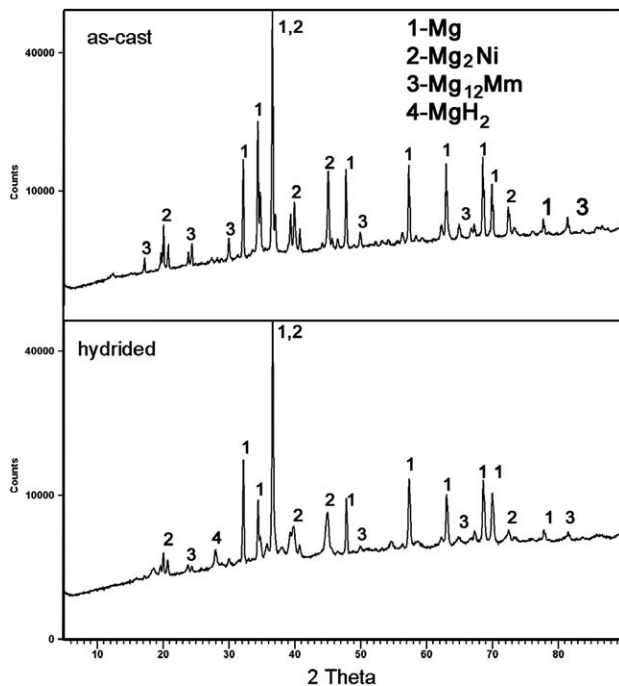

Figure 3: XRD patterns of the as-cast and hydrided Mg-24Ni-5Mm alloy
Slika 3: XRD-spekter lite in hidrirane zlitine Mg-24Ni-5Mm

the GDS detection limit. The best hydriding efficiency is observed for the binary Mg-26Ni alloy, which achieved a hydrogen mass concentration of 1.6 %. This concentration approaches those in common hydrides based on transition metals prepared by the pressure and high-temperature synthesis from elements (usually less than 2 %).

To reveal the electrochemical hydriding mechanism, an XRD pattern of the alloys was measured both before and after hydriding. The results are similar for all the alloys and are thus illustrated only for the Mg-24Ni-5Mm alloy in **Figure 3**. One can see that the XRD pattern of the as-cast alloy contains peaks of Mg, Mg_2Ni and $Mg_{12}Mm$ phases, which is in accordance with the structure in **Figure 1e**. In contrast, the hydrided alloy contains a new peak, which can be assigned to the MgH_2 phase. Other hydrides like, for example, Mg_2NiH_4, MmH_3, Mg_2MmNiH_7, often observed in Mg-Ni-Mm alloys hydrided in gaseous hydrogen[6,7], are not found after electrochemical hydriding, suggesting that all the hydrogen is chemically bonded only with magnesium. The reason is probably that the electrochemical hydriding temperature was not sufficient for the formation of complex or Mm-based hydrides.

A three-step mechanism of electrochemical hydriding of the Mg-Ni-Mm alloys can be suggested on the basis of the presented chemical and structural investigations:

First step: Electrochemical reaction on the cathode surface produces atomic hydrogen:

$$H_2O + e^- \rightarrow H + OH^- \qquad (1)$$

Second step: Atomic hydrogen enters the cathode. When it penetrates into the Mg phase, a layer of MgH_2 forms rapidly, due to the negligible solid solubility of the hydrogen in the magnesium. Such a layer would prevent hydrogen from further diffusion into the cathode material. For this reason the hydrogen concentration in the pure magnesium is negligible (**Figure 2**). In the binary and ternary alloys it is likely that hydrogen diffuses along boundaries between the Mg, Mg_2Ni and $Mg_{12}Mm$ phases and also inside the Mg_2Ni phase, where it forms an interstitial solid solution:

$$Mg_2Ni + X\,H \rightarrow Mg_2NiH_X \qquad (2)$$

The X value depends on the hydrogen content and it generally ranges between 0 and 0.3. Both Mg_2Ni and Mg_2NiH_X have a hexagonal crystal lattice (space group $P6_222$). For this reason, these phases are not distinguishable in the XRD patterns in **Figure 3**.

Third step: Atomic hydrogen diffusing inside the alloy reacts with the surrounding Mg phase to form MgH_2:

$$Mg + 2\,H \rightarrow MgH_2 \qquad (3)$$

With this mechanism the hydrogen is able to penetrate deeply into the material, which is necessary to achieve high hydrogen concentrations. The mechanism suggested explains why the highest hydrogen concentration is observed in the eutectic Mg-26Ni alloy (**Figure 2**).

This alloy contains a very fine eutectic mixture (**Figure 1b**) with a high volume fraction of phase boundaries, which represent good paths for hydrogen diffusion. The hypo- and hypereutectic Mg-Ni alloys contain primary crystals that slow down the inward penetration of the hydrogen. By comparing the eutectic Mg-26Ni and Mg-24Ni-5Mm alloys, one can see that the former achieved a higher H-concentration (**Figure 2**). One explanation may be in the more disperse eutectic structure of the binary alloy compared to the ternary one (**Figures 1b and 1e**).

4 CONCLUSIONS

The presented work demonstrates a new method of hydrogen storage in a solid phase – electrochemical hydriding. Using this method the electric current is directly transformed to metallic hydrides, like with electric batteries. In contrast to batteries, direct electro-chemical hydriding of the alloys with appropriate compositions may produce materials having a much higher density of stored energy. Such materials can serve as portable hydrogen sources, for example, for fuel cells in hydrogen-fuelled cars. Our work implies that appropriate alloys having fine eutectic structures can achieve H-concentrations approaching those in commercial hydrides. As a result they are promising materials for hydrogen storage.

Acknowledgements

5 REFERENCES

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