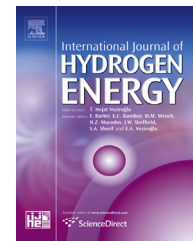Available online at www.sciencedirect.com

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Catalytic effect of Mg$_2$Ni and Mg$_{12}$RE on MgH$_2$ formation and decomposition

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ABSTRACT

In this study, several binary and ternary as-cast Mg—Ni-RE alloys were subjected to an electrochemical hydriding process to determine the catalytic effect of intermetallic phases on MgH$_2$ formation and decomposition. The alloys were electrochemically hydrided in a 6 mol/l KOH solution at 80 °C. To assess the catalytic effect of the Mg$_2$Ni and Mg$_{12}$RE phases on electrochemical hydriding performance, an optical emission spectrometer with glow discharge was employed. The temperature of dehydriding was observed by the temperature-programmed desorption technique. It was found that the only hydride formed after the electrochemical hydriding of all investigated alloys was MgH$_2$. Both the Mg$_2$Ni and Mg$_{12}$RE phases support hydrogen absorption but in different manners. The Mg$_2$Ni phase maximizes the hydrogen concentration beneath the surface of the binary alloys. In contrast, the Mg$_{12}$RE phase decreases the maximum hydrogen surface concentration but supports inward hydrogen diffusion. The influence of the Mg$_{12}$RE phase on hydrogen diffusion is most likely responsible for the reduction of the MgH$_2$ decomposition temperature by more than 190 K compared to commercial MgH$_2$.

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Introduction

Since LaNi$_5$-and FeTi-based hydrides were discovered and started to be used at the commercial level [1], the storage of hydrogen in metal hydrides has attracted considerable attention. Hydrides are stable and safe compounds that release hydrogen when heated to sufficient temperatures. In particular, hydrides based on magnesium, which can absorb approximately five times more hydrogen (in the form of MgH$_2$) than LaNi$_5$ [2], are prospective ideal storage materials. In addition, magnesium is a very light construction material and is relatively inexpensive compared to other hydride-formers (Ti, Zr, V). However, a well-known drawback of MgH$_2$ is its high thermodynamic stability, which is associated with slow hydriding/dehydriding kinetics and a high hydrogen release temperature above 300 °C. Therefore, various efforts have been made to destabilize the MgH$_2$ phase. It has been known for a long time that some Mg-RE-based (RE = rare earths-La, Ce, Nd, Pr) intermetallic compounds show better hydriding/dehydriding properties than pure magnesium [3]. The intermetallic compound Mg$_{17}$La$_2$ can absorb approximately the same amount of hydrogen as magnesium but at 150 °C [4]. However, the dehydriding temperature is similar to

magnesium hydride [5]. The addition of RE to Mg–Ni-based alloys could enhance hydriding properties [6]. Relatively few Mg–Ni-RE alloys have been studied, and the majority of them were prepared by ball milling [6–8] or rapid solidification [9–11]. Good results have been obtained predominantly by hydriding under a gas hydrogen atmosphere, where the formation of binary (MgH_2, REH_3), ternary (Mg_2NiH_4) and more complex hydrides have been observed [6,12]. It has been suggested that the formation of MgH_2 occurs prior to other hydrides [13], but the mechanism of the catalytic effect of Ni- and RE-based intermetallics on MgH_2 formation is unknown.

In the case of electrochemical hydriding, the temperature of a solution is limited to complete the full hydrogenation. Because electrochemical hydriding take place in a strong alkaline solution, the situation is complicated by a layer of formed Mg $(OH)_2$ that inhibits inward hydrogen diffusion into the material.

In this study, several as-cast Mg–Ni–RE-based alloys were prepared and subjected to electrochemical hydriding. The target of this study was to evaluate the catalytic effect of intermetallic phases on MgH_2 formation and decomposition.

Experiment

In our work, three binary Mg–Ni and five ternary Mg–Ni–RE alloys (RE = mixture of rare earth metals containing 45 wt.% Ce, 38 wt.% La, 12 wt.% Nd and 4 wt.% Pr) were hydrided by an electrochemical process. The compositions of the hydrided alloys are listed in Table 1 and all concentrations are in units of at.%. Ingots of alloys were prepared by the vacuum induction melting of pure Mg (99.9 wt.% purity), Ni (99.9 wt.% purity) and RE (99.0 wt.% purity) under a protective argon atmosphere. Cylindrical ingots 150 mm in length and 30 mm in diameter were gravity-cast into a brass mold. Subsequently, the ingots were cut into thin samples of 2 mm in thickness. Prior to hydriding, the surface of the alloys was treated by grinding on P180–P2500 abrasive papers. Pretreated samples were immediately put into an electrochemical hydriding cell.

Electrochemical hydriding was conducted in a 6 mol/l KOH solution at 80 °C for 480 min using a galvanostatic method with a current density of 100 A/m². The alloys were connected to a DC source and polarized as the cathode. A platinum electrode was placed opposite the hydriding side of the sample and used as the anode.

To determine the influence of Ni and RE addition on the hydriding process, a glow discharge spectrometer (Horiba Jobin-Yvon, GD Profiler 2 (GDS)) was employed. Depth-dependent hydrogen profiles were determined as the results. Due to the fact that hydriding was performed in a strongly alkaline solution, the formation of magnesium hydroxide and/or complex hydroxide surface layers could be expected. To minimize the influence of such layers on the results of hydrogen profile analysis, oxygen was also analyzed to determine the exact position of the hydroxide/metal interface (see Fig. 1). The evaluation of hydriding parameters such as the total mass of absorbed hydrogen and the maximum of hydrogen surface concentration is illustrated in Fig. 1. The GDS analyzer was calibrated with respect to commercial MgH_2. The sputtering rate was determined by the measurement of the surface profile after analysis. For the calculation of the total mass of absorbed hydrogen in sputtered volume, a numerical integration and the density of appropriate alloy were used.

The hydrogen evolution process of the hydrided samples was determined via a temperature-programmed desorption technique (TPD, MICROMETRICS AutoChem II 2920). In addition, we investigated the behavior of pure MgH_2 powder (20 μm, 98%, HiChem) under the same conditions. Each sample was pretreated in Ar gas at 273 K before hydrogen desorption. The desorption analysis was conducted in a reactor by heating under programmed temperature control from the ambient temperature to 673 K at a rate of 4 K min⁻¹ using argon (50 ml min⁻¹). The gas stream leaving the reactor was passed through a water-vapor trap at 210 K, and the evolution of the hydrogen was detected using a thermal conductivity detector.

The structures of as-cast alloys as well as the surfaces of hydrided alloys were investigated by optical (OM) and scanning electron microscopy (SEM, Tescan Vega 3) and energy dispersion spectrometry (EDS, Oxford Instruments Inca 350). The phase compositions both before and after hydriding were determined by X-ray diffraction (XRD, X Pert Pro, Co Kα radiation).

Results and discussion

Structures of alloys

Micrographs of the investigated alloys obtained by OM are presented in Fig. 2. The phase compositions of the alloys as determined by XRD were assigned to the components of structures by EDS. The structures of the binary Mg–Ni alloys (Fig. 2a–c) correspond to the structures of a typical eutectic system. The MgNi6 alloy is hypoeutectic (Fig. 2a) and consists of α-Mg dendrites (light) and α-Mg + Mg_2Ni eutectic (dark). Because the eutectic point of the Mg–Ni alloys corresponds to 13 at.% Ni [10], the binary MgNi14 and MgNi18 alloys are hypereutectic. However, the structures of these two hypereutectic alloys (Fig. 2b, c) are very different. While the structure of the MgNi14 alloy (Fig. 2b) is dominated by a very fine α-Mg + Mg_2Ni eutectic mixture and by very small white grains of

Table 1 – Chemical compositions of the studied Mg–Ni–RE alloys.						
Alloy	Element (at.%)					
	Ni	Ce	La	Nd	Pr	ΣRE
MgNi6	6.4	–	–	–	–	–
MgNi14	13.6	–	–	–	–	–
MgNi18	17.7	–	–	–	–	–
MgNi5RE1	5.1	0.6	0.5	0.2	0.1	1.4
MgNi13RE1	12.8	0.5	0.4	0.1	0.1	1.2
MgNi13RE2	13.4	0.9	0.8	0.2	0.1	2.0
MgNi13RE3	13.3	1.2	1.0	0.3	0.2	2.7
MgNi17RE1	16.8	0.5	0.4	0.1	0.1	1.2