Hydriding properties of a Mg-Al-Ni-Nd hydrogen storage alloy

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ABSTRACT:
This work presents the development of a Mg-Al-Ni-Nd alloy for hydrogen storage. The hydrogen storage properties of the alloy were analyzed using pressure-composition isotherms and hydrogen desorption kinetic curves at different temperatures. The characterization of the microstructures, before and after hydrogenation, were performed using X ray diffraction (XRD), scanning electron microscopy and energy dispersive spectrometer (SEM-EDS). Hydrogenation caused significant changes in the alloy microstructure. Two pressure plateaus were observed. The maximum hydrogen absorption/desorption capacity measured was 4 wt.% at 573 K. At this temperature the pressure plateaus were 0.3 and 0.4 MPa, respectively.

KEYWORDS: Magnesium alloy, hydrogen storage, metal hydrides, hydriding/dehydriding kinetics.

1. Introduction

Magnesium, as magnesium hydride (MgH₂), has the greatest theoretical hydrogen storage capacity among all the metals, 7.6 % in weight basis [1, 2]. However, magnesium has some shortcomings for practical use as a hydrogen storage medium, such as: slow hydrogen absorption/desorption kinetics, poor ability to dissociate the hydrogen molecules on its surface and strong bonds between hydrogen and magnesium atoms [3]. In order to overcome such problems, magnesium is usually alloyed with transition and rare earth elements [4, 5]. Mg-Nd and Mg-Pd-Nd alloys were studied by Yamada et al. [6]. The hydriding/dehydriding kinetics of these alloys were enhanced with Nd addition. The second one, produced by melt-spinning and annealed at 553 K showed better desorption kinetics than the binary Mg-Ni alloy, releasing approximately 80 % of the stored hydrogen in 17 minutes at 523 K. X ray diffractograms of a hydrided Mg-Ni-Nd alloy showed the formation of MgH₂, Mg₂NiH₄ and Nd₂H₅ hydrides [8]. The pressure-composition isotherms of the Mg-Ni-Nd alloy exhibited two plateaus. The plateau at the lower pressure was related to the MgH₂ formation and the plateau at the higher pressure was related to the Mg₂NiH₄ formation [8].

The present paper describes the behavior of a Mg-Al-Ni-Nd alloy upon hydrogenation. Aluminum alloying was chosen because this metal destabilize the magnesium hydride and reduces the desorption temperature [9].

2. Experimental methods

The Mg₈₂Al₈Ni₅Nd₅ (atomic %) alloy was produced by induction melting of commercial pure ingots (99.9 %) of magnesium, aluminum, nickel and neodymium. The melting process was performed under argon atmosphere, using quartz crucibles. In order to protect the quartz from magnesium chemical attack, the crucibles were internally coated with graphite. The samples were produced from the as-cast alloy.

The structural characterization of the samples, before and after hydrogenation, was performed by X ray diffraction, using CuKα radiation. The microstructure was analyzed by SEM-EDS (Jeol JSM-6460 LV). The hydrogen properties of the alloy were measured using a home-made Sievert’s type equipment. The activation of the samples was performed at 673 K under 7 MPa of hydrogen pressure. The
hydriding/dehydriding kinetics and the pressure-composition isotherms of the samples were measured in the temperature range between 573 and 673 K.

3. Results and discussion

The X ray diffractograms of the samples in the as-cast, hydried and dehydrided states are shown in Figure 1.

Figure 1. X ray diffractograms of the Mg-Al-Ni-Nd alloy: a) as-cast b) hydried and c) dehydried.
Five crystalline phases were identified in the as-cast state: Mg, Mg_{12}Nd, AlNiNd, AlNi_{3} and Nd, as shown in Figure 1(a). The Mg_{2}Ni phase was not observed. The absence of Mg_{2}Ni also occurred in the Mg-Ni-Nd alloy studied by Yin et al. [7]. The aluminum addition leads to AlNiNd and AlNi_{3} formation.

The hydrogenation process caused important microstructural changes. New crystalline phases were identified: MgH_{2}, Nd_{2}H_{5}, Mg_{2}NiH_{4} and Al_{3}Ni_{2}, additionally some unreacted Mg and MgO were also observed, as it is shown in Figure 1(b). The dehydrogenation didn’t completely restore the phases present in the as-cast state and some hydrides still remained. The crystalline phases observed after dehydrogenation were Mg, Mg_{2}Ni, Nd_{2}H_{5}, Al_{3}Ni_{2}, MgO and, in a minor proportion, MgH_{2}, Figure 1(c).

Figure 2 presents the microstructure of the as-cast sample. In order to analyze qualitatively the chemical composition of the compounds, EDS mappings were performed.

The EDS elemental mappings of magnesium, aluminum, nickel and neodymium are shown in Figure 3. This unveiled that the dendritic grains are composed mostly by magnesium; the interdendritic network is composed mainly by magnesium and neodymium and the needle-like structures are composed by aluminum, nickel and neodymium.
Further topological analysis showed that the needle-like structures had, in fact, a blade-like morphology. EDS analysis showed that the white small spots observed in Figure 2 were neodymium particles.

The microstructure of the alloy partially hydrogenated is showed in Figure 4. The interdendritic network is not homogenous any more. It resembles a eutectoid feature, and the dendritic grains show dark and light gray regions.

![Figure 4. SEM image of Mg-Al-Ni-Nd alloy after partial hydrogenation.](image)

Analyzing the results obtained by XRD and the microstructures observed by SEM and EDS, before and after hydrogenation, changes in the microstructure were evidenced. The as-cast Mg$_{12}$Nd interdendritic network was decomposed into two new phases, MgH$_2$ and Nd$_2$H$_5$ hydrides, upon hydrogenation. The decomposition occurred via the following disproportionation reaction [7, 8]:

$$\text{Mg}_{12}\text{Nd} \rightarrow \text{Nd}_2\text{H}_5 + \text{MgH}_2$$  \hspace{1cm} (1)

The morphology of these new phases is similar to a eutectoid microstructure, as is observed in Figure 4. In this case, the transformation of one solid phase into two new solid phases was induced by hydrogenation and not by temperature or pressure changes, as is the case in the eutectoid reaction.

The other phase present in the as-cast sample is AlNiNd, initially forming smooth blades, Figure 5(a). This phase after hydrogenation becomes irregular, fractured and also presented a morphology that resembles that of a eutectoid microstructure, as can be seen in Figure 5(b). Upon hydriding the following reaction takes place in the blades:

$$\text{AlNiNd} \rightarrow \text{Al}_3\text{Ni}_2 + \text{Nd}_2\text{H}_5$$  \hspace{1cm} (2)

![Figure 5. SEM image detailed of AlNiNd phase a) before b) after hydrogenation.](image)
The dendritic grains, mainly composed of magnesium, Figures 2 and 3, were partially hydrogenated. The reversible reaction occurred by formation of magnesium hydride, is as showed in Equation 3:

\[
\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2 \quad (3)
\]

The different grades of gray were noticeable on the dendritic grains, resulted from partial hydrogenation. The dark gray areas, in the grains periphery, had more hydrogen than the light gray areas, in the grain center, showing that hydrogen diffusion was faster in the interdendritic network.

Among the hydrogen properties, hydrogen desorption rate is noteworthy. In average, 97 % of the stored hydrogen was released during the first 5 minutes at 673 K. At the same temperature and using desorption kinetics equations proposed by Douglas [10], the hydrogen desorption curve fits very well with a phase-boundary controlled process, as is observed in Figure 6.

![Figure 6. Control mechanisms of hydrogen desorption kinetics from Mg-Al-Ni-Nd alloy at 673 K.](image)

The desorption pressure-composition isotherms obtained in the temperature range between 673 and 573 K are showed in Figure 7.

![Figure 7. Pressure-composition isotherms of the Mg-Al-Ni-Nd alloy.](image)
The desorption pressure-composition isotherms of this alloy exhibit two-plateaus, more clearly visible at 623 K. Probably the first plateau is associated to MgH₂ decomposition, Equation 3, and the second one is associated to Mg₂NiH₄ decomposition, Equation 4 \[8\].

\[
\text{Mg}_2\text{NiH}_4 + 2\text{H}_2 \xrightarrow{\text{U}} \text{Mg}_2\text{NiH}_4 \tag{4}
\]

The enthalpy and entropy changes associated to the MgH₂ hydride, obtained by the use of van't Hoff diagrams, \( \Delta H^\circ = -72.4 \text{ kJ/mol H}_2 \) and \( \Delta S^\circ = -138.4 \text{ J/mol H}_2\text{K} \), are in reasonable agreement with those reported in the literature, \( \Delta H^\circ = -74.8 \text{ kJ/mol H}_2 \) and \( \Delta S^\circ = -135 \text{ J/mol H}_2\text{K} \) \[6, 8, 11\].

The hydrogen desorption capacity measured was close to 4 wt.% at 573 K and the pressure plateaus were 0.3 and 0.4 MPa, respectively.

In the hydrogen absorption/desorption cycle, shown in Figure 8, a very small hysteresis was observed in the pressure plateau related to MgH₂ formation. The hysteresis gap was more noticeable in the pressure plateau related to Mg₂NiH₄ hydride formation.

![Figure 8. Absorption and desorption pressure-composition isotherms for the Mg-Al-Ni-Nd alloy at 623 K.](image)

As mentioned before, a drawback of magnesium as a hydrogen storage medium is the slow hydrogen desorption rate. However, the Mg-Al-Ni-Nd alloy presented a reasonably fast hydrogen desorption rate; approximately 97 % of the hydrogen stored was released in the first 5 minutes at 673 K, as shown in Figure 6. A detailed analysis of the relation among the microstructures, phase structures, before and after hydrogenation, and hydrogen storage properties of the Mg-Al-Ni-Nd alloy shows that hydrogen desorption kinetics is influenced by the catalytic effect of the Nd addition, as was evidenced in previous studies \[6, 7, 12\]. Upon hydrogenation, NdH₃ is formed. After dehydriding the trihydride decomposes to the very stable Nd₂H₅ hydride \[7\]. This reversible reaction, shown in Equation 5, has catalytic effect on the hydrogen desorption rate of the nearby Mg and Mg₂Ni phases.

\[
2\text{Nd}_2\text{H}_5 + \text{H}_2 \xrightarrow{\text{U}} 4\text{NdH}_3 \tag{5}
\]

The NdH₃ hydride phase is not perceptible in the X ray diffractograms, possibly due to crystalline structural similarity between Nd₂H₅ and NdH₃ and to the fact that the NdH₃ phase may be quickly decomposed to the lower hydride Nd₂H₅ when the sample is removed from the reactor for XRD analysis \[6\].

To evidence the existence of NdH₃ phase in the Mg-Al-Ni-Nd alloy after hydrogenation, further studies will be performed with Differential Scanning Calorimetry (DSC).

The hydrogen desorption rate is also improved because hydrogen diffusion is faster in the interdendritic network than in the magnesium grains. The interface between the AlNiNd blades and the dendritic matrix also generate a preferential pathway for hydrogen diffusion. In Figure 9, cracks are observed along the blades close to the surface. The boundary between the blades and the matrix didn’t withstand the stress resulting from the volumetric changes associated with the phase changes in the hydrogenation/dehydrogenation process.
Studies associated with Mg-Al-Ni-Nd quaternary alloy are not reported in the literature. The difference between these alloy and the Mg-Ni-Nd ternary alloys reported by others [7, 8] is that the addition of aluminum to the chemical composition results in the formation of AlNiNd phase in blade form, which generates pathways that enhance the hydrogen diffusion into and from the interior of the magnesium alloy matrix.

![SEM image close to surface of a Mg-Al-Ni-Nd alloy after hydrogenation. The AlNiNd phase is detailed associated to cracks.](image)

4. Conclusions

The Mg-Al-Ni-Nd quaternary alloy studied in this work, which has not been previously reported, has fast hydrogen desorption rate. The kinetics is controlled by phase boundary mechanism. The Nd$_2$H$_5$ hydride, formed mainly by disproportionation reactions, has a catalytic effect on the hydriding/dehydriding kinetics and assists the formation and decomposition of magnesium hydride. Although the hydrogenation of Nd$_2$H$_5$ produces NdH$_3$, this hydride was not identified by XRD, probably due to its rapid decomposition to Nd$_2$H$_5$.

The hysteresis in absorption/desorption cycle is very small in the first plateau, favoring the reaction reversibility of magnesium hydride.

Additional studies will be addressed towards the understanding of the effects of alloying elements on the destabilization of magnesium hydride, in order to develop alloys with smaller hydrogen desorption temperatures at atmospheric pressure.

5. Acknowledgements

The authors sincerely acknowledge the financial support provided by RENAULT (Contracts COPPETEC no. PEMM 029 and 803), CNPq (Grant nos. 309174/2003 and 141597/03-8) and FAPERJ (Grant no. E-26/152.396/2002).
6. References


