Hydrogen desorption process in Mg_2Ni hydrides

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One of the most interesting intermetallic compounds investigated for energy storage purposes has been the Mg_2Ni alloy which was prepared by mechanical alloying. Hence it was used here for hydriding-dehydriding implied mechanisms studies. Hydrogenation of milling prepared Mg_2Ni alloy samples under a 1 MPa H_2 flux at 473K for 5 min allowed the formation of two Mg_2Ni-hydrides which were identified by the empirical formulae Mg_2NiH_4 and $Mg_2NiH_{0.3}$ [1]. Dehydriding behavior along the temperature range from 298 to 623K was recorded by Thermo Gravimetric Analysis (TGA). TGA spectrum exhibited two weight decrease peaks. The maximum hydrogen amount desorbed was 3.95 ± 0.01 wt%. Isotherms between 470 and 600K, every 30K, were obtained by using the same technique, showing a discontinuity which might be associated with a dehydriding process taking place in two steps. Approximately 40-50% of the total H_2 content seems to be desorbed in the first faster step. The present results might confirm that the two hydrides formed present a differentiated desorption outline.

Keywords: Mg_2Ni alloy; hydriding/dehydriding; hydrogen storage material; dehydriding rates; intermetallic hydrides.

El Mg_2Ni es uno de los compuestos intermetálicos que han despertado mayor interés para el almacenamiento de energía por medio de ciclos de adsorción-desorción de hidrógeno. En el presente trabajo, la aleación Mg_2Ni se obtuvo por molienda mediante el aleado mecánico y la hidrogenación se llevó al cabo de acuerdo a lo reportado [1]. Mediante la hidrogenación, bajo un flujo de H_2 a 1 MPa y 473K durante 5 min., se obtuvieron dos hidruros: Mg_2NiH_4 y $Mg_2NiH_{0.3}$ en la proporción 77.9/14.9% el otro 7.2% lo constituía Ni sin reaccionar. Por medio del análisis termogravimétrico (ATG), se determinó la rapidez de la desorción del hidrógeno con el aumento de la temperatura de 293 a 623K. El espectro de ATG mostró dos máximos. Los resultados muestran una capacidad máxima de hidrogenación de 3.95 ± 0.01% en peso. También por medio de la técnica ATG se obtuvieron isotermas entre 470 y 600K. Las curvas correspondientes presentaron una discontinuidad, lo cual se asoció con dos etapas de deshidrogenación. Se observó que en la primera etapa, la más rápida, el hidrógeno se desorbío aproximadamente entre 40-50%. Los resultados parecen indicar que los dos hidruros formados presentan su propio esquema de desorción.

Descriptores: Aleación Mg_2Ni; hidrogenación/deshidrogenación; hidrógeno almacenado; tasa de deshidrogenación; hidruros intermetálicos.

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1. Introduction

The liquid or gas compressed hydrogen [2], as a nonpolluting substitutive source of energy, has been used in course for several decades as a storage system. On the other hand, because of their greater safety and relatively low price, metal hydrides are being developed as an alternative method to the traditional compressed hydrogen storage systems [2]. These advanced methods require the use of large hydrogen diffusivity and storage capacity metals. In addition, hydriding must be reversible at high reaction rates [3-5]. Thus, a detailed knowledge of the microscopic picture of hydrogen motion in these materials is important.

While hydrogen storage capacity of pure metals is relatively reduced, much progress has been achieved in understanding hydrogen diffusion mechanisms in these systems [2-3]. In contrast, in intermetallic compounds, those mechanisms become more complex. In this kind of compound, hydrogen may occupy sites inside or outside the unit cell [6-8]. Yet several alloys exhibit interesting properties, such as a high capacity to adsorb large quantities of hydrogen. However, hydriding reactions, in most of them, are not reversible, in which case the problem is to establish a recycling procedure [9,11].

Some reports show the Mg_2Ni compound to be quite an attractive prospect for investigating the stability and reversibility of intermetallic hydrides. Conventionally prepared polycrystalline Mg_2Ni absorbs hydrogen only after activation by a series of heating-cooling cycles, at temperatures between 523 and 623K, and high hydrogen pressures, *i.e.* from 1.5 to 5.0 MPa [12]. As stated by other recent investigations, a mechanical alloying preparation of Mg_2Ni enhances its hydrogen absorption capacity up to 2.5-3.5wt% in mild conditions [13]. Moreover, Martinez [1] observed the formation of two hydrides; whose empirical formulae are Mg_2NiH_4 and $Mg_2NiH_{0.3}$, coexisting with no reacted Ni in the ratio 77.9wt% Mg_2NiH_4, 14.9wt% $Mg_2NiH_{0.3}$ and 7.2 wt% Ni. Accordingly, Thermogravimetric Analysis Technique (TGA) was used here to define dehydriding conditions of Mg_2Ni-hydrides. Isotherms performed in the 470-600K temperature range made it possible to assume dehydriding rate constants.

2. Experimental

Stoichiometric quantities of elemental Mg (nominally 99.9% purity, particle size < 500) and Ni (99.9%, <100) were subjected to mechanical alloying to obtain the alloy whose empirical formula was Mg_2Ni. Powder mixtures were milled

in tool steel vials under argon atmosphere, in a high-energy SPEX vibratory mill, model 8000-D. Products of the milling were stored in argon filled glass vials.

Stoichiometric ratio and particle size of alloy samples were determined by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectrometry (EDS) and Transmission Microscopy (TEM). The Rietveld method was used in the same way to estimate quantitatively the formation of hydrides and their percentage. Nanocrystalline Mg_2NiH_4 and $Mg_2NiH_{0.3}$ were confirmed to be present in the ratio 77.9/14.9; the remaining 7.2% (Wt) was unreacted Ni. In order to detect any change occurring during the treatment of samples, the procedure indicated elsewhere [1] was followed. Prior to hydrogenation, samples were outgassed for at least 30 min at an achievable vacuum pressure of 10 kPa. The hydriding process was carried out in a 50 mL stainless steel PAAR micro-reactor, model 4592, by exposing the powder samples to gaseous H_2 (99.99% nominal purity) at 473K under an H_2 pressure of 1.0 MPa for 5 min.

In order to determine dehydriding conditions, Thermo Gravimetric Analysis (TGA) spectra were recorded throughout the temperature range from 293 to 623K at 10 K/min. Furthermore, dehydriding isotherms, recorded between 470 and 600K in 30K steps, made it possible to infer hydrogen desorption kinetics.

Prior to record isotherms of the alloy hydride samples, a sample weight, optimal for the TGA technique, was established (see Table I). Afterwards, a sample weight of 12 mg. was maintained the same throughout the experimentation. Subsequently, samples of Mg_2Ni-hydrides were heated in the TGA equipment. Graphs of weight decrease as a function of time, at constant temperature, were obtained.

3. Results and discussion

Two hydrides, Mg_2NiH_4 and $Mg_2NiH_{0.3}$, were found to be formed by the hydrogenation of the milling prepared alloy Mg_2Ni. Stability of both intermetallic hydride compounds was confirmed by repeated Thermo Gravimetric Analysis (TGA) measurements to one and the same sample. Thermographs of the sample, fresh prepared and 30 days later, were identical. Hence it was concluded that, at room temperature no release of H_2 occurs, nor does the presence of oxygen alter hydrogen content in the alloy.

On the other hand, reproducible chromatography spectra, recorded by coupling the micro-reactor to the Gaschromatographer, demonstrated that weight decrease during TGA experiments was exclusively due to desorbed H_2.

Hydrogen total content in Mg_2Ni-hydrides was determined to be ≈ 3.953wt% (more than 2000 mol H_2/Mol Mg_2Ni), since in all experiments the heating of 12 mg hydrogenated alloy samples produced a total weight diminution of 0.476 mg. Continuation of heating, beyond that point, produced a light increase in weight, attributed to the adsorption of carrier gas, N_2, by the sample.

TABLE I. Total weight decrease by H_2 desorption as weight of Mg_2Ni-hydride samples varied from 10 to 20 mg.

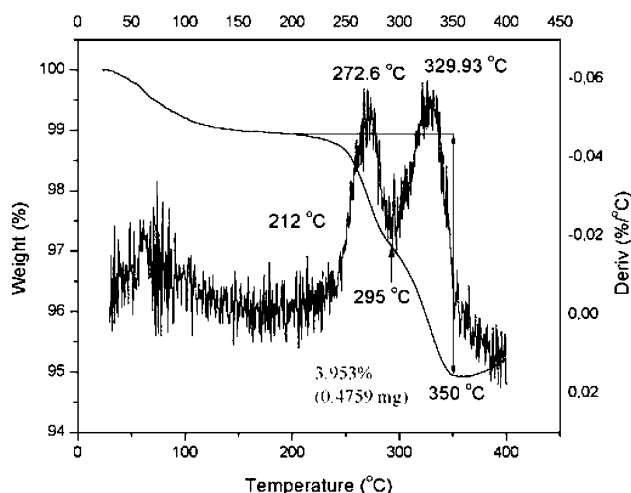| Weight of Mg_2Ni hydrides (mg)	Hydrogen desorbed (wt%)	Hydrogen desorbed (mg)
10	3.754	0.378
12	3.953	0.476
15	3.947	0.592
20	3.814	0.765
Average	3.867 ± 0.01	

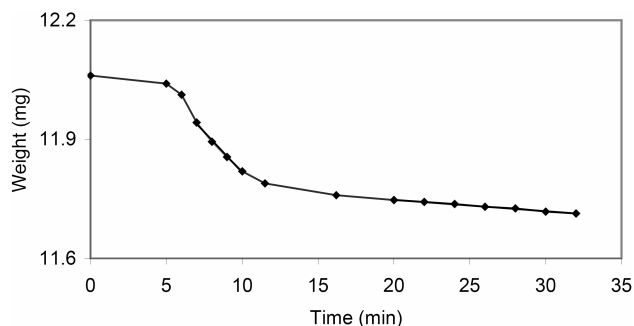FIGURE 1. Thermogravimetric analysis spectrum of Mg_2Ni-hydrides.

FIGURE 2. Representative isotherm of H_2 desorption at temperatures between 530 and 565K. Mg_2Ni-hydride weight is plotted as a function of time. Temperature was kept constant for 40 min.

Repeated Thermo Gravimetric Analysis experiments resulted in the thermograph of Fig. 1. As it can be observed on the graph, above and beyond a first weight decrease at low temperature, which is due to adsorbed humidity during sample handling, two maxima are to be noted. The first one, at 545.6K, begins at 515K and ends at 568K. At this point, the second one starts, whose peak is at 602.93K, ending at 623K. The presence of two maxima on the spectrum seems to match up with two hydrogen desorption processes. This result would be in agreement with the detection of two magnesium-nickel hydrides.
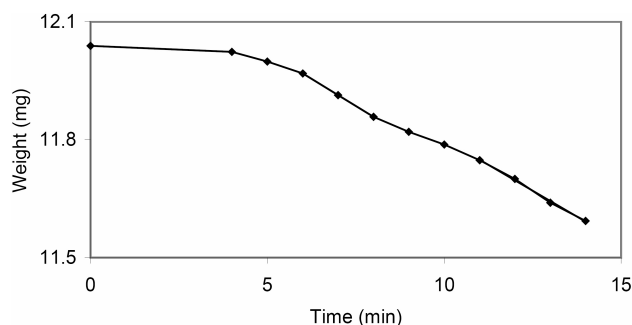
FIGURE 3. Weight decrease of Mg$_2$Ni hydrides as a function of time. Temperature was maintained at 593K for a 40 min period time.

In addition, isotherms in the range of 470 to 600K in steps of 30K were recorded. Temperature was maintained constant for 40 min lapses. At temperatures falling into the first part of the thermograph of Fig. 1, *i.e.* from 470 to 510K, isotherms showed, at the most, a very slight weight decrease, which augmented as temperature was higher. This result may be associated to the stability of Mg$_2$Ni-hydrides, showing that efficient reversible adsorption-desorption cycles on Mg$_2$Ni alloy would require excessive long heating periods time at those relatively low temperatures.

Figure 2 shows an isotherm curve which typified the H$_2$ desorption behavior in the range of 530 to 565 K. Desorption seems to proceed in two steps; the one at the beginning, occurs at a rate of $\approx$0.04 mg/min. Although at this rate the total liberation of hydrogen would be completed in 20 min, at approximately 12 min a discontinuity appears. At this

point, more or less 0.18 mg of H$_2$ seems to have been desorbed, that is to say $\approx$40% of the total H$_2$. This percentage roughly equals the area of the first desorption peak observed at 545.6K in Fig. 1. The remaining $\approx$60% would be desorbed during the second step which seems to be much slower; hence depletion of H$_2$ would take several hours.

Figure 3 shows the isotherm at 593K. Temperature was maintained constant for a 40 min period time. In spite of this, on the curve it may be appreciated that after 15 min heating 0.48 mg of weight has vanished, which corresponds to 3.95wt%, the maximum H$_2$ amount absorbed by the alloy samples in the present experimentation. All the same, two parallel slopes are observable on the curve, probably indicating, as in the preceding case, two desorption processes associated with the decomposition of two Mg$_2$Ni- hydrides.

4. Conclusions

As compared to the polycrystalline alloy, prepared by mechanical alloying Mg$_2$Ni prove to absorb relatively high amounts of H$_2$, *i.e.* 3.95% which represents more than 2 thousand Mol H$_2$ per 1 Mol Mg$_2$Ni. The hydriding proved to be a reversible process which was achievable commencing around 500K.

Hydriding of nanocrystalline Mg$_2$Ni prepared by mechanical alloying produced two hydride structures, namely Mg$_2$NiH$_4$ and Mg$_2$NiH$_{0.3}$. Accordingly, two dehydriding steps were observed at temperatures ranging from 533 to 593K.

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