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Hydrogen absorption and desorption in nanocrystalline $LaMg_2Ni$

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Abstract

Hydrogen absorption and desorption properties in $LaMg_2Ni$ compound are presented. Nanostructured phases have been obtained by means of ball milling in order to study the influence of the microstructure on the absorption/desorption properties. The structural and hydriding properties were examined by X-ray diffraction, thermal analysis, hydrogen pressure–composition and thermal desorption measurements. Ball milling of as-cast compound gives a significant refinement of the microstructure. Hydrogenation at 443 K leads to the formation of $LaMg_2NiH_7$, but at higher temperatures (523 K) LaH_2 is produced. Two hours of ball milling promote the formation of LaH_2 under hydrogenation at 443 K. Thermal desorption up to 983 K of hydrogenated samples leads again to parent $LaMg_2Ni$ phase.

Keywords: Nanostructured materials; Hydrogen absorbing materials; Mechanical alloying

1. Introduction

Hydrogen energy systems have been proposed as means to reduce greenhouse gas and other harmful emission from stationary and mobile sources [1]. The goals are to pack hydrogen as close as possible, i.e. to reach the highest volumetric density by using as little additional material as possible, and reach the reversibility of uptake and release of hydrogen by the system. The most common storage systems are high pressure gas, with possible problems about safety, and liquid hydrogen, which needs very large amount of energy for liquefaction. It is well known that absorption of hydrogen on interstitial sites in a host metal or alloy can store more hydrogen in a safe and efficient way with respect to liquid or high pressure gas phase [2].

In particular, Mg-based alloys have been intensively studied as promising candidates for hydrogen storage due to their high theoretical storage capacity (7.6 wt.%), light weight and low cost [3]. Mg_2Ni is a well known intermetallic compound for hydrogen storage, however high operating temperatures and slow kinetics prevent practical applications. So, in order to move towards more convenient operative conditions, ternary intermetallic compounds may be considered. In order to obtain useful microstructures for improving the kinetics of hydrogen absorption/desorption a mechanical grinding of as-cast alloy has been suggested: ball milling gives rise to the creation of fresh surfaces and cracks, which are highly effective for the kinetic improvement in initial hydriding properties. Furthermore, ball milling produces nanocrystalline materials which may increase hydrogen solubility and hydrogen diffusion rate at the grain boundaries [4].

The aim of this work is the study of the absorption–desorption of hydrogen in $LaMg_2Ni$ intermetallic compound [5]. The addition of the Lanthanum to Mg_2Ni is due to the well known absorption properties of this element and, in particular, of the La–Ni alloys (i.e. $LaNi_5$) [6]. The role of alloy microstructure on absorption–desorption properties, i.e. hydrogenation kinetics, will be outlined.

2. Experimental

$LaMg_2Ni$ coarse crystals have been obtained by slowly cooling the liquid alloy (closed in a BN crucible to reduce magnesium evaporation) in an induction furnace. Nanostructured powders have been obtained by mechanical grinding of the as-cast alloy for different time using a Spex-Mill mod 8000. The methodology employed to quantify the dynamics of the mechanical treatment has been fully described in previous works [7–10] and will not be discussed here in detail. The milling runs were carried out at 875 rpm (impact frequency $29\,s^{-1}$) by employing a special hardened steel vial and only one hardened steel milling ball at work—mass of 7.74 g and 9.5 mm in diameter. Powder batches of 8 g were employed. The resulting ball impact energy was about 0.07 J per hit due to a ball impact velocity of 4.3 m/s.

The structure was analysed by X-ray powder diffraction (XRPD), performed using Cu Kα on a Philips PW3020; Rietveld refinement was used to analyse diffraction pattern by means of MAUD software [11]. Absorption–desorption

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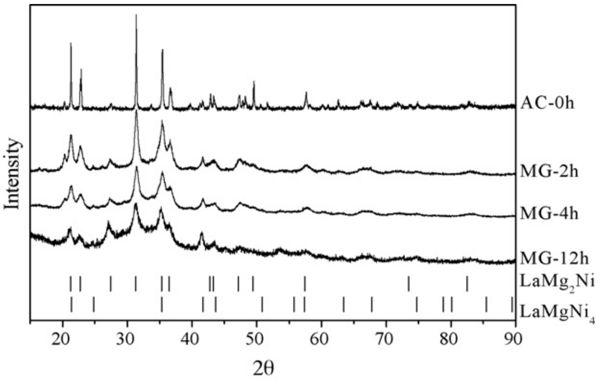

Fig. 1. XRPD patterns of $LaMg_2Ni$ after different milling times. AC: as-cast; MG: mechanical ground.

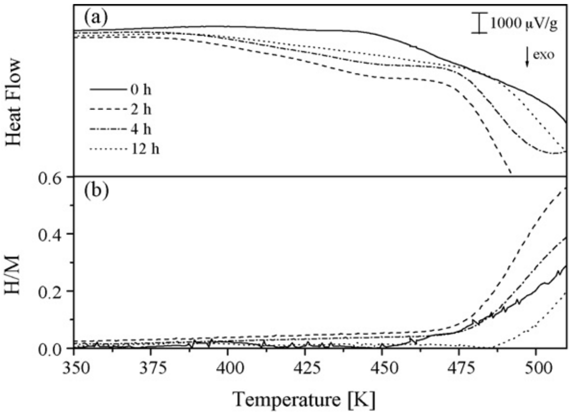

Fig. 2. DSC signal (a) and H/M values (b) for hydrogen absorption in as-cast and milled $LaMg_2Ni$ as a function of temperature. The initial hydrogen pressure was 1.45×10^4 Pa. The heating rate was 2 K/min.

experiments were performed in a quartz vacuum line ($P < 1.01 \times 10^5$ Pa). In order to follow the heat involved in absorption–desorption processes, the reaction was carried out in a Setaram C80 DSC. The system was calibrated for volume, so that the amount of hydrogen in the sample can be calculated from standard *P–V–T* relationship. Desorption process was also obtained with a Perkin-Elmer DSC7 equipped with a TPD, constituted by a hydrogen analyser of the exhausted gas which allows to determine the amount of hydrogen desorbed.

3. Results and discussion

The as-cast sample was basically composed of $LaMg_2Ni$ compound, with additional contributions from impurities of $LaMgNi_4$ phase, as evidenced in the XRPD pattern shown in Fig. 1. A strain content of 1×10^{-5} and an average size of 90 nm was obtained for the $LaMg_2Ni$ coherent scattering domains. The as-cast alloy was milled for different times (2, 4 and 12 h) and the results of the XRPD analysis are shown in Fig. 1.

Rietveld analysis of XRPD patterns leads to the microstructural results resumed in Table 1. The extent of the coherent domain scattering appears progressively reduced as a function of milling time, reaching a final value of 12 nm after 12 h. On the other hand, the corresponding strain content increases significantly, reaching a final value of 7×10^{-3} after 12 h. So, it is clear that mechanical grinding acts as a suitable system to strongly refine the microstructure of the $LaMg_2Ni$ intermetallic compound.

In order to identify the temperature range for $LaMg_2Ni$ hydride formation, as-cast and milled samples have been heated at 2 K/min in the DSC under an initial hydrogen pressure of 1.45×10^4 Pa. The results are reported in Fig. 2, where a clear correspondence between exothermic DSC signals and hydrogen absorption can be evidenced. For the as-cast sample, the hydrogen absorption starts at about 450 K and it becomes more pronounced at about 500 K. On the other hand, for the samples milled for 2 and 4 h, the first absorption phenomena appear at about 390 K. The DSC signal reaches a sort of plateau between 450 and 475 K and, at higher temperatures, further absorption phenomena appear. The amount of hydrogen absorbed by the compound shows that samples milled for 2 and 4 h reach higher hydrogen-to-metal (H/M) values with respect to the as-cast sample, but the sample milled for 12 h displays a decrease of absorption kinetics. The XRPD analysis (not shown here) has evidenced the formation of $LaMg_2NiH_7$ after hydrogen absorption in as-cast sample in the temperature range from 450 to 500 K. On the contrary, after absorption of hydrogen at 525 K, the formation of LaH_2 has been observed.

In order to understand the role of the microstructure on the hydrogen absorption kinetics, experiments have been carried out in isothermal conditions at 443 K on powders ground for different milling times. The calorimetric signals and the corresponding amount of absorbed hydrogen are shown in Fig. 3 as a function of time. It is worth noting that the results reported in Fig. 3 are related to the first cycle of absorption, when the sample is in contact to an initial hydrogen pressure of 8.68×10^3 Pa. The first cycle of hydrogen absorption in as-cast samples is completed after about 3000 s; 2 h of ball milling increase significantly the absorption kinetics so that a value of H/M equal to 0.27 is easily reached after about 1000 s. Such an increase of hydrogen absorption properties after mechanical grinding is related to the significant refinement of the microstructure, as evidenced in Fig. 1. The increased fraction of grain boundaries promotes

Table 1
Phase analysis and coherent domains scattering (CDS) and strain content in the phase $LaMg_2Ni$ after different milling times

Milling times [h]	$LaMg_2Ni$			$LaMgNi_4$ [%]	La_2MgNi_2 [%]	La_2O_3 [%]
	%	CDS [nm]	Strain [10^{-5}]			
0	86	90	1	10	4	–
2	89	17	400	4	7	–
4	91	13	700	7	–	2
12	84	12	700	8	–	8

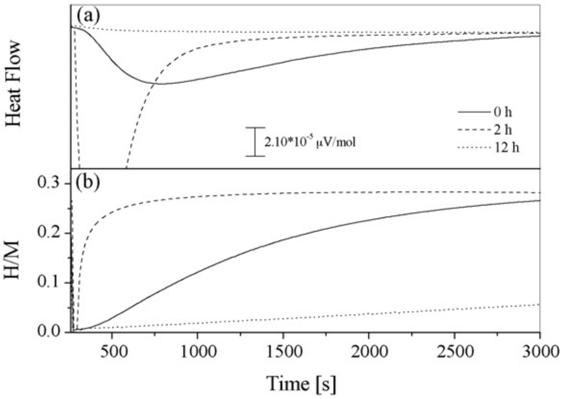

Fig. 3. DSC signal (a) and H/M values (b) obtained at 443 K as a function of time for $LaMg_2Ni$ under different ball milling conditions. The initial hydrogen pressure was 8.68×10^3 Pa.

hydrogen absorption in the alloy and may acts as nucleation sites for hydride phases formation [3]. On the contrary, 12 h of ball milling reduce the hydrogen absorption kinetics. This effect is likely due to surface contaminations, which promote the formation of oxide layers at the surface as evidenced by XRPD analysis (Table 1). In fact, it is known that MgO and La_2O_3 surface layers slow down hydrogen absorption in Mg–La–Ni alloys [12].

The equilibrium values of H/M and the phase analysis of XRPD patterns after complete hydrogen absorption at 443 K are resumed in Table 2. The results show that only for the as-cast alloy the formation of single $LaMg_2NiH_7$ hydride phase was observed, giving a value of H/M = 5.6, which is lower than that reported for the same compound after hydrogenation in different conditions [5]. The grinding of the as-cast alloy promotes the formation of LaH_2 phase during hydrogenation at 443 K but significantly reduces the maximum hydrogen uptake (H/M = 1.8 for 2 h milled powder). This result suggests an activation of the compound due to ball milling, which promotes the formation of LaH_2 at lower temperatures with respect to as-cast sample, in agreement with DSC data shown in Fig. 2. After hydrogenation at 443 K of the powder milled for 12 h, a significant amount of $LaMg_2NiH_7$ phase is obtained and the quantity of LaH_2 is lower than that observed for 2 h milled powder (Table 2). This result confirms some oxide contamination for high milling times, as evidenced from XRPD analysis (Table 1) and hydrogen absorption experiments (Fig. 2). The surface activation due to ball milling, gives easily to La-oxide formation, even during hydrogenation experiments. In fact an increased fraction of La_2O_3 is observed after hydrogenation, together with Ni-rich $LaMgNi_4$ compound (Table 2).

Table 2
Phase analysis and H/M values of $LaMg_2Ni$ ball milled for different times after isothermal hydrogenation at 443 K

Milling times [h]	Phase [%]				H/M
	LaH_2	$LaMg_2NiH_7$	$LaMgNi_4$	La_2O_3	
0	–	100	–	–	5.6
2	51	17	15	17	1.8
12	27	45	13	15	3.1

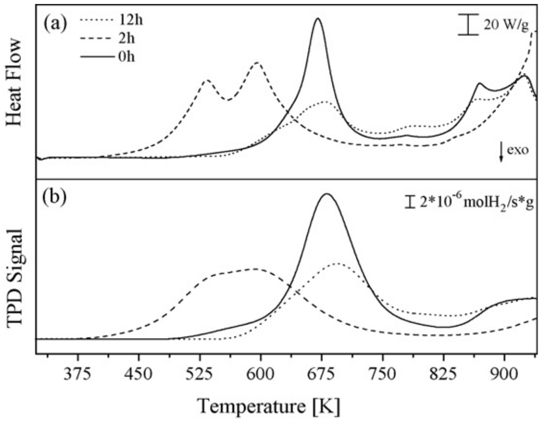

Fig. 4. DSC (a) and TPD (b) signal as a function of temperature for as-cast and milled $LaMg_2Ni$ samples after hydrogenation at 443 K. The heating rate was 20 K/min.

Coupled DSC–TPD desorption experiments have been carried out heating at 20 K/min as-cast and milled samples hydrogenated at 443 K, and the results are shown in Fig. 4. A clear correspondence between the DSC and the TPD signals is observed. The endothermic DSC signals appear very intense even because the hydrogen desorption in the calorimetric cell containing the sample modifies significantly the thermal conductance of the flowing gas, so that the heat of desorption cannot be measured accurately [13]. The as-cast hydrogenated sample shows a main signal, with a maximum at about 675 K, followed by a second event at higher temperature. The sample milled for 2 h shows a much faster desorption kinetics as evidenced by a desorption signal beginning at about 400 K, which appears composed by two reactions from the DSC signal. The desorption of hydrogen from the sample milled for 12 h is very similar to that of the as-cast sample. After annealing up to selected temperatures in DSC, a XRPD analysis has been carried out. The main desorption reaction of all samples leads to the formation of LaH_2 phase, leaving some Mg_2Ni. When the samples are heated up to 983 K, the formation of parent $LaMg_2Ni$ is observed, because of the decomposition of LaH_2 and successive reaction with Mg_2Ni.

4. Conclusions

Nanostructured $LaMg_2Ni$ have been obtained by ball milling an as-cast alloy. The coherent scattering domain appears progressively reduced as a function of milling time, reaching a final value of 12 nm after 12 h. Hydrogenation of as-cast alloy at 443 K leads to the formation of $LaMg_2NiH_7$, but treatments at higher temperatures (523 K) lead to the formation of LaH_2. Two hours of ball milling increase significantly the absorption kinetics with respect to as-cast sample, but higher milling times appear to slow down hydrogen absorption. Ball milled powders hydrogenated at 443 K form LaH_2, because of an activation of the compound during ball milling. Thermal desorption up to 983 K of hydrogenated alloys leads again to parent $LaMg_2Ni$ phase.

Acknowledgements

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