Journal of Alloys and Compounds 580 (2013) S159–S162

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Study on La–Mg based ternary system for hydrogen storage

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ARTICLE INFO

Article history:
Available online 26 February 2013

Keywords:
Ternary alloys
Rare earth
Metal hydride
Hydrogen storage

ABSTRACT

An explorative study on the hydriding/dehydriding characteristics of the $La_2(Mg,Pd)_{17}$ ternary alloy, with different Pd content, is presented. All the samples were prepared by induction melting of the selected elements, characterized with scanning electron microscopy and X-ray powder diffraction, to detect present phases, and subsequently milled with a high-energy shaker apparatus. The hydrogen reaction kinetics and thermodynamics properties have been investigated by means of a volumetric Sievert's apparatus. The measured H_2 gravimetric capacity of the alloy varied with the Pd content, being the highest for the sample without Pd (>4.5 wt%). A possible correlation between the constituent phases individuated with microanalysis and the variation in the hydrogenation behaviour is proposed.

1. Introduction

Different metallic ternary systems containing magnesium and a rare earth metal have been examined in recent years, with respect to phase analyses, structural chemistry and other peculiar properties [1 and references therein]. In the outlook of a broad investigation of light alloys for solid state hydrogen storage, their hydrogenation behaviour turns out to be a feature worth of notice [2–5].

Among these, some compounds with a high Mg content reveal interesting hydrogenation properties, due to recognized Mg characteristics, as low weight and H_2 affinity. On the other hand, rare earths have been reported to have good influence on hydrogen absorption/desorption (a/d) of metals, including magnesium [6].

Among Mg–La compounds, La_2Mg_{17} was initially alleged to have capacity similar to pure Mg, being able to exchange hydrogen at lower temperature [7], but subsequent studies [8 and references therein] proved it otherwise and underlined that this alloy disproportionates during hydriding and then behaves according to the reactions:

$$La_2Mg_{17} + 20H_2 \rightarrow 2LaH_3 + 17MgH_2 \tag{1}$$

$$2LaH_3 + 17MgH_2 \leftrightarrow 2LaH_x + (20 - x)H_2 + Mg \tag{2}$$

The step in (1) was also studied and confirmed by means of in situ X-ray diffraction, where the large difference in enthalpy between the original compounds and the products is proposed as the motivation for this reaction [9]. The second step (2) is the reason why the reaction temperature is close to that of magnesium. Improved performances of La_2Mg_{17} with the addition of Ni have been proved by mechanically alloying the base material with other compounds such as $LaNi_5$ [10] or introducing it in a metallurgical preparation [11].

In order to investigate the influence of another transition metal as Pd on La_2Mg_{17} hydrogen a/d properties, a study in the Mg-rich corner of the La–Pd–Mg system has been undertaken. Pd is known from the literature to have a beneficial effect on the kinetics of hydrogen reaction with Mg based materials (see, e.g. [12,13]).

2. Experimental

The alloys have been prepared from >99.9% pure elements (La and Pd were supplied by Newmet Koch, Waltham Abbey, England, and Mg by MaTecK, Jülich, Germany), weighting the exact amount in an analytical balance in such a way to obtain the nominal compositions reported in Table 1; the alloys lay on the $La_2(Mg_{1-x}Pd_x)_{17}$ compositional line.

The samples, each one with a total weight of about 3 g, were prepared by induction melting, with the stoichiometric amounts of the constituent metals held in small arc-sealed tantalum crucibles. The sealing, made under argon flow, was needed to avoid evaporation of Mg during melting, which was repeated three times in order to ensure homogeneity.

The as-cast samples were analyzed with a scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDXS) and X-ray diffraction (XRD). These techniques were applied to investigate the microstructure and uniformity of the alloy, in addition to the morphology and crystal structure of the phases. The SEM apparatus used was an EVO 40 Carl Zeiss, equipped with a Pentafet Link EDXS microanalysis system. Smooth alloys surfaces suitable for the microscopic examinations were obtained by means of SiC papers and diamond pastes with particle size decreasing from 6 to 1 µm. The diffraction patterns were measured with a Philips X'Pert MPD, using Cu Kα radiation (wavelength $\lambda = 1.5406$ Å) with Bragg–Brentano geometry.

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http://dx.doi.org/10.1016/j.jallcom.2013.02.079

Table 1
List of the prepared samples, their atomic and morphologic composition, and milling time.

Sample	Nominal composition	Phases	Milling time (h)
1	$La_{10.5}Mg_{89.5}$	La_2Mg_{17} $LaMg_3$	12
2	$La_{10.5}Pd_4Mg_{85.5}$	$La_2(Pd,Mg)_{17}$ $LaMg_3$ $La_{12.7}Pd_{12.1}Mg_{75.2}$	15
3	$La_{10}Pd_{16}Mg_{74}$	$La_2(Pd,Mg)_{17}$ $La_{17.5}Pd_{7.5}Mg_{75.0}$ $La_{6.4}Pd_{20.2}Mg_{73.4}$	24

The samples were milled in a Spex SamplePrep 8000M high-energy shaker mill, with a ball-to-powder ratio of 10:1, using a hardened steel vial and stainless steel spheres. Different milling times, listed in Table 1, were used to ensure a significant powdering of the as-cast samples.

The powders were subsequently tested in a volumetric Sievert's apparatus by AMC, Pittsburgh. All powders were handled in an MBraun Labstar glove box with Ar atmosphere.

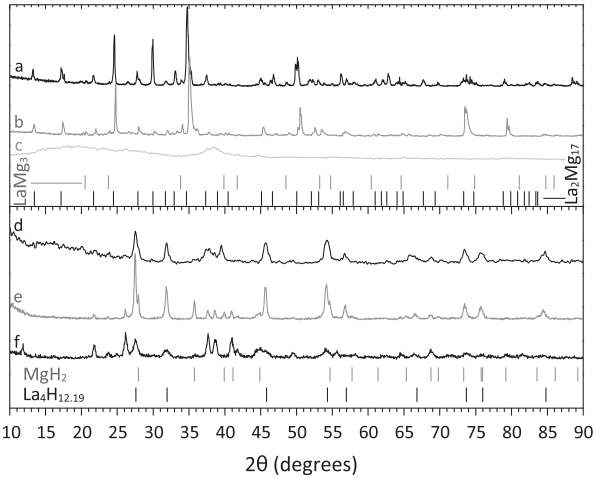

Fig. 2. XRD patterns of samples 1 (a), 2 (b) and 3 (c) after milling and of samples 1 (d), 2 (e) and 3 (f) after subsequent hydrogenation.

3. Results and discussion

Some useful information can be retrieved from the micrographs shown in Fig. 1, which were taken on the alloys before milling. The morphological information is complemented by quantitative microanalysis. Sample 1 is shown in Fig. 1a, where the most abundant grey phase is La_2Mg_{17} (measured composition: $La_{11.0}Mg_{89.0}$) and the clearer phase is $LaMg_3$ (measured composition: $La_{22.6}Mg_{77.4}$). In Fig. 1b, sample 2, it is possible to distinguish three different phases: the main grey one is the substitutional solid solution $La_2(Mg,Pd)_{17}$ (measured composition: $La_{11.0}Pd_{3.2}Mg_{85.8}$), the small white dendritic crystals are constituted by $LaMg_3$ (measured composition: $La_{24.1}Mg_{75.9}$) as in the previous sample, and the light grey phase at the grain boundaries is a ternary phase with measured composition $La_{12.7}Pd_{12.1}Mg_{75.2}$. Finally, sample 3 is shown in Fig. 1c, with a majority of the grey phase corresponding to $La_2(Mg,Pd)_{17}$ (measured composition: $La_{10.7}Pd_{16.3}Mg_{73.0}$), and two secondary phases with compositions about $La_{17.5}Pd_{7.5}Mg_{75.0}$ (light grey) and $La_{6.4}Pd_{20.2}Mg_{73.4}$ (dark). The crystal structures of the new ternary phases found in these samples are under investigation together with the constitutional properties of the Mg-rich region of the La–Pd–Mg system.

In the XRD patterns of Fig. 2a and b, recorded on the milled powders before hydrogenation, the only identifiable phases are La_2Mg_{17} and $LaMg_3$, and the presence of Pd in the crystal lattice is only resulting in a small shift of the La_2Mg_{17} peaks. Comparing pattern 'a' (sample 1) with 'b' (sample 2), it is possible to distinguish the mentioned small shift to the right of La_2Mg_{17} peaks due to the presence of Pd in the lattice. Pattern 'c' (sample 3) does not present sharp peaks owing to a reduced grain size as a consequence of the more prolonged milling required by the higher hardness of the sample.

Considering the XRD patterns of hydrogenated specimens, it is interesting to see how the hydrogenation reaction leads to the formation of the hydride following the path (1) proposed in [9]. In fact pattern 'd' of sample 1, pattern 'e' of sample 2 and pattern 'f' of sample 3 (all after hydrogenation) display peaks of MgH_2 and LaH_3, and some residuals of the starting $La_2(Mg,Pd)_{17}$.

Sample 3 reaches a maximum quantity of stored H_2 of 1.2 wt% in a time range that approaches one hour. In Fig. 3a it is possible to notice how absorption rate and final quantity at 310 °C and 2 MPa of H_2 are improved after the first cycles. Desorptions at 20 kPa and 310 °C shown in Fig. 3b do not present appreciable changes with cycling and evidence that after more than three hours the undesorbed quantity is fluctuating around 0.2 wt%.

Moving towards a lower amount of Pd there is some improvement: for sample 2 the amount of hydrogen stored during the cycles of Fig. 3c is close to 2.5 wt% and there is also a similar kinetics (about 20 min to reach 90% of the maximum capacity). This sample exhibits an increase in the storage capacity with cycling, while the desorption reaction, at the same temperature and low pressure, can be completed in about one hour and half (Fig. 3d).

Finally, the a/d cycles for sample 1, where slightly lower temperature settings (270 °C and 290 °C) were used, are depicted in Fig. 3e and f. The maximum total amount of hydrogen is almost

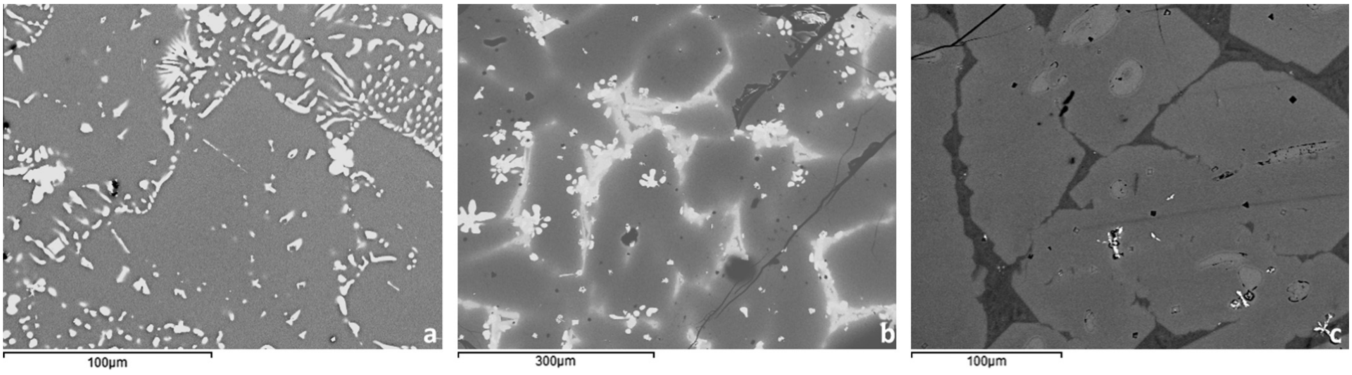

Fig. 1. SEM images (BSE mode) of the microstructure of samples 1 (a), 2 (b) and 3 (c).