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# Metallography and hydrogenation behaviour of the alloy Mg-72 mass%–Ni-20 mass%–La-8 mass%

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## Abstract

Alloy having the composition of Mg-72 mass%–Ni-20 mass%–La-8 mass% prepared by vacuum-induction melting was studied by means of optical microscopy, scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction analysis. Metallographic investigations evidence that the alloy has a fine and uniform grain structure which corresponds to the structure of a ternary eutectic alloy. The surface of a metallographic cross section of the alloy was subjected to hydrogenation in various conditions and studied by means of the mentioned methods. It is shown that during the initial stage of hydrogenation the phase $La_2Mg_{17}$ is decomposed at first. Then the phase $LaH_3$ is formed, while the formation of the $MgH_2$ phase proceeds at a slowest rate. This hydrogenation behaviour is explained by taking into account the microstructure peculiarities of the alloy.

*Keywords:* Hydrogen absorbing materials; Metal hydrides; Magnesium alloys; Metallography

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## 1. Introduction

Magnesium-based reversible hydrides are promising materials for solid state hydrogen storage [1]. However, the up-to-date hydride-forming materials have a number of shortcomings and do not meet all requirements for reversible hydrogen storage [2]. They need a temperature of about 300 °C to provide the required hydrogen output and have a poor kinetics of the hydrogenation/dehydrogenation (H/D) processes. Magnesium-based alloys, such as Mg–Ni–Mm(La), are prospective materials to improve these disadvantages. These alloys, due to their highly dispersed structure and the synergetic influence of nickel and rare-earth metals, may offer besides the high hydrogen sorption capacity (more than 5 mass%), a high hydrogenation/dehydrogenation rate and the possibility to decrease the hydrogenation temperature (down to 200 °C). This would allow to avoid the sintering of alloy beds. The Mg-based alloys have been prepared by different methods such as melt-spinning [3], hydriding combustion synthesis [4], mechanical and vacuum induction alloying [5] to ensure nanocrystalline structure and fast kinetics of H/D processes [3]. In particular, La–Ni–Mg composites prepared by hydriding combustion synthesis showed attractive H/D characteristics [4] which were attributed to their multiphase structure and to the catalytic influence of $LaNi_5$ and $LaH_{3-x}$ on the hydrogen exchange rate. For the Mg–La–Ni alloys obtained by conventional methods an activation procedure is usually required. Thus, Tarasov et al. demonstrated [5] that a Mg-72 mass%–Ni-20 mass%–Mm(La) alloy, which was prepared by induction melting, reversibly absorbed up to 5.5 mass% of hydrogen, and the system MgMmNi–$H_2$ demonstrated a much faster H/D kinetics when compared to the non-modified Mg–$H_2$ system. It was also reported that binary alloys $Mg_2Ni$ and $La_2Mg_{17}$ needed several activation cycles to reach the maximum hydrogen storage capacities: 3.55 mass% for $Mg_2Ni$ and 5.44 mass% for $La_2Mg_{17}$ [6]. Hence, the activation of an as-cast Mg–La–Ni alloy needs to be studied in detail with respect to the

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microstructure, the phase composition of the resulting material and its performance characteristics in the H/D processes.

In the present work, we report the hydrogenation behaviour of the alloy Mg-72 mass%–Ni-20 mass%–La-8 mass% during the activation stage studied by means of metallographic investigation of the surface of a section of a compact piece of the alloy, as well as on the same surface of this alloy subjected to hydrogenation in various conditions. The surface microstructure and phase composition of both the initial and the hydrogenated alloy were examined using optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction analyses. This approach provides complementary information to the studies of the hydrogenation of the powdered samples.

## 2. Experimental

An alloy having composition of Mg-72 mass%–La-8 mass%–Ni-20 mass% (later referred to as Mg–La–Ni) was prepared by induction melting in vacuum as described in detail by Tarasov et al. [5]. The purity of magnesium, nickel and lanthanum used were of 99.95, 99.99 and 99.79%, respectively.

Metallographic sections were made on a side of the compact pieces of every studied alloy. The sections were prepared by grinding and polishing. The final polishing procedure was carried out with a diamond suspension of 1 μm particle size. Some of the prepared specimens were examined by means of optical microscopy on an Aristomet Olympus microscope. Before the examination the specimens were etched using acetic glycol at room temperature for 4 s.

Non-etched specimens were employed for further hydrogenation investigations. Hydrogen absorption was performed in a high-pressure chamber at controlled temperatures and pressures. Stepwise series of hydrogenation charging experiments were carried out for two specimens of the alloy. The specimen A was placed in the chamber at 280 °C and 3 MPa of hydrogen and the specimen B at 350 °C and 2 MPa of hydrogen. Before the first hydrogenation step the specimens were activated in vacuum. After every step of hydrogenation the specimens were removed from the chamber and examined by means of scanning electron microscopy and X-ray diffraction (XRD) analysis. XRD analysis was carried out on a STOE $\theta$–$\theta$ diffractometer, Cu K$\alpha$ radiation, at 40 kV, 30 mA. The diffraction angle range was $2\theta = 18$–$70°$, step: 0.03°, integration time: 5 s/step. The intensities of the peaks in a XRD pattern were normalized using the most intense – Mg (1 0 1) – line of this pattern. XRD pattern were evaluated using the PDF-2 ICDD database: Mg—card 65-3365, space group $P6_3/mmc$ (No. 194); $Mg_2Ni$—card 75-1249, space group $P6_222$ (No. 180); $La_2Mg_{17}$—card 17-399, space group $P6_3/mmc$; $MgH_2$—card 89-7887, space group $P4_2/mnm$ (No. 136); $LaH_3$—card 65-3741, space group $Fm\bar{3}m$ (No. 225); $Mg_2NiH_4$—card 37-1159, space group $Fm\bar{3}m$. SEM studies and energy dispersive X-ray spectroscopy analysis of the specimens were performed on CamScan MV2300 and Jeol JSM-5310LV scanning electron microscopes equipped with energy dispersive X-ray spectrometers INCA Energy (Oxford Instruments) and EDS Noran, respectively. Data of the line-scan EDX chemical analyses of the specimens were normalized by the mean values for each spectrum. It should be noted that all experimental results obtained in the present paper are related to samples covered by oxygen. The surface of a specimen before hydrogenation is always covered by a thin oxide layer. Furthermore, because of the stepwise hydrogenation, after every stage of the process, the specimens were removed from the reaction vessel into the atmosphere, implying that the surface of the hydrogenated specimen gets partly oxidized as well. This oxidation significantly decreases the hydrogenation rates of the specimens.

## 3. Results and discussion

The optical microscopy and SEM (BSE mode) images of a metallographic section of the as-cast alloy, shown on Fig. 1, evidence the fine grain and uniform structure of the alloy. The SEM pattern is uniform down to the scale of about 1 μm. As the analyzed volume of the electron microprobe is comparable to that size, the EDX spot elemental analysis will not provide reliable results. The EDX analysis performed from an area 300 μm × 300 μm gives the following elemental composition: Mg 71.8 ± 0.5 wt%, Ni 20.1 ± 0.4 wt%, La 8.1 ± 0.3 wt%, that agrees well with the bulk composition of the alloy. XRD pattern of the alloy (Fig. 2a) contains diffraction peaks associated with three phases: Mg, $Mg_2Ni$ and $La_2Mg_{17}$. Minor additions of non-identified phases are also present. Thus, the data of XRD and SEM analyses show that the alloy has a ternary eutectic

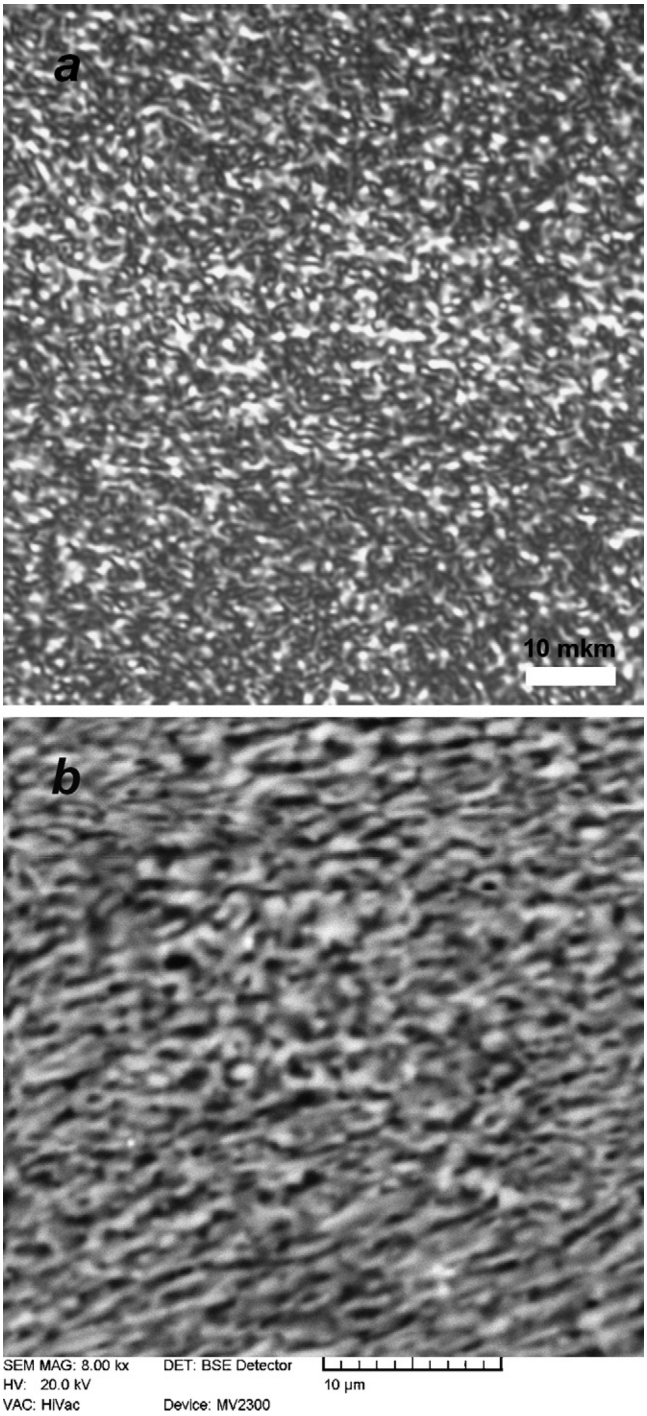

Fig. 1. Optical microscopy (a) and scanning electron microscopy (BSE mode, b) images of a metallographic section of the alloy Mg–La–Ni.

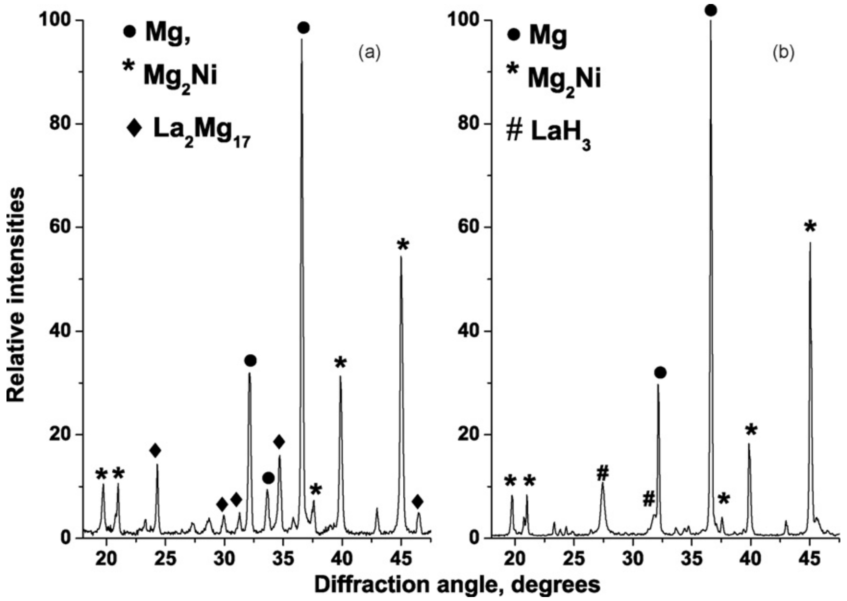

Fig. 2. XRD data for the as-prepared (a) and hydrogenated (b) specimens of the alloy (see text). Cu Kα radiation.

structure $Mg+Mg_2Ni+La_2Mg_{17}$. This fact is in good agreement with the earlier work by Tarasov et al. [5], where it was shown that a diffractogram from the powdered sample of the alloy Mg-72 mass%–Ni-20 mass%–Ln-8 mass% is consistent with the presence of the following three phases: Mg, $Mg_2Ni$, and $Ln_2Mg_{17}$ (Ln = La, Mm).

The surface of the as-prepared metallographic section of the alloy has a typical metallic appearance and a light-grey colour. After hydrogenation during 1 h at 623 K and 3 MPa of $H_2$ the surface gets a yellowish-bronze tint. SEM data measured from the surfaces of both the as-prepared metallographic section of the alloy and the hydrogenated one does not show noticeable changes in the microstructure of the alloy during the initial hydrogenation stage. This was confirmed by the microprobe chemical line-scan analysis of elemental distribution along a certain selected line on the surface of the alloy (Fig. 3). The X-ray diffraction pattern collected from the surface of the hydrogenated specimen shows that the peaks corresponding to $La_2Mg_{17}$ intermetallic have vanished and the peaks associated with lanthanum hydride appear (see Fig. 2b). The other diffraction peaks corresponding to Mg and $Mg_2Ni$ do not show visible changes. Also, the peaks related to the phases $MgH_2$ and $Mg_2NiH_4$ are not observed. This indicates that the hydrogenation of the Mg–La–Ni alloy starts from the decomposition of $La_2Mg_{17}$. As indicated by EDX line-scan analysis (Fig. 3), the distribution of La in the material is uniform as compared to Ni. Since the relative amount of the $La_2Mg_{17}$ phase in the alloy is rather small, this means that the crystallites of the phase $La_2Mg_{17}$ have sizes small enough to ease the decomposition of $La_2Mg_{17}$ species in the course of hydrogenation. Such a uniform distribution of $La_2Mg_{17}$ and, consequently, $LaH_3$ in the H absorbing material may contribute to the explanation of the catalytic role of La in the hydrogenation process observed in [4].

Darriet et al. studied in detail the hydrogen interaction with the $La_2Mg_{17}$ phase [7]. However, the overall equation of the

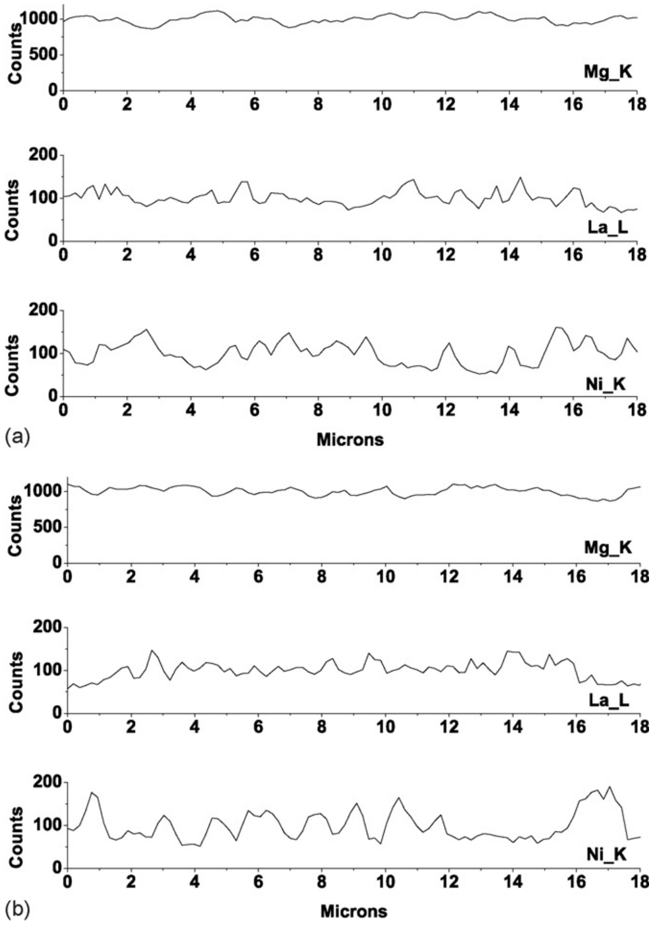

Fig. 3. EDX line-scan data for the as-prepared (a) and hydrogenated (b) specimens of the alloy (see text).

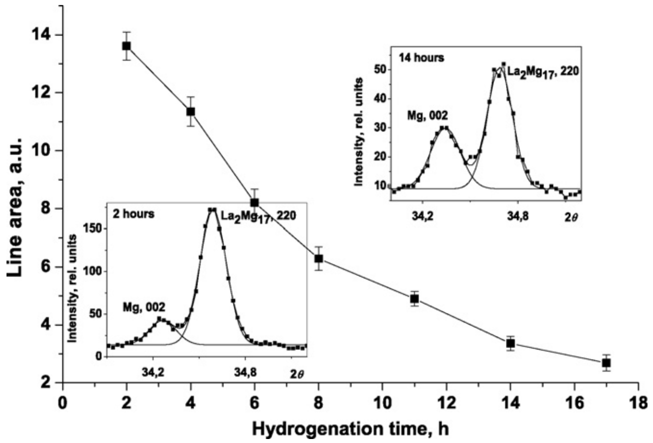

Fig. 4. Hydrogenation time dependence of the relative integral intensity of the 220 XRD peak of the $La_2Mg_{17}$ phase component of the alloy, specimen A.

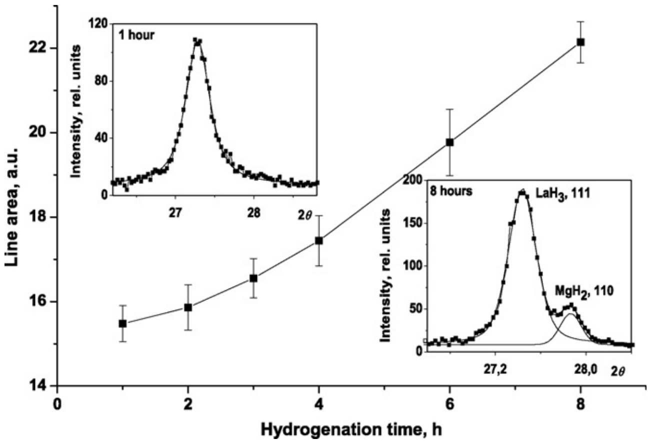

Fig. 6. Hydrogenation time dependence of the relative integral intensity of the 111 XRD peak of the $LaH_3$ phase component of the alloy, specimen B.

hydrogenation reported in [7]:

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

does not reveal the sequence of the formation of the hydride phases during the disproportionation of $La_2Mg_{17}$. The stepwise series of H absorption experiments performed in present study for the specimens A and B of the alloy allow revealing further details of this process.

During hydrogenation of the alloy the hydrogen diffusion through the grain and interphase boundaries well exceeds its diffusion into the grains. The hydrogenation conditions for the specimens were selected to ensure that the hydrogen uptake proceeds deep enough in the surface layer of the specimen, but without breaking it, in order to make possible both XRD and SEM studies. An essential decrease of the content of $La_2Mg_{17}$ in the sample was observed at the hydrogenation temperature of 280 °C (specimen A, Fig. 4). The decomposition of the $La_2Mg_{17}$ leads to the formation of $LaH_3$, manifested by the appearance and growth with time of the strongest peak for $LaH_{3-x}$ (1 1 1) in the XRD pattern (Fig. 5). The reaction rate seems to be quite slow, with changes in the amount of $La_2Mg_{17}$ observed even after 14 h of interaction (see Fig. 5). At higher hydrogenation temperature, 350 °C (specimen B), the decomposition of $La_2Mg_{17}$ proceeds much faster and is completed in 1 h within the first hydrogenation step. However, the formation of the phase $LaH_3$ lasts much longer. Growth of its amount is observed during all the hydrogenation time of the specimen B, 8 h (Fig. 6). Assuming that the phase conversion and transport processes in the alloy during hydrogenation have temperature dependence of Arrhenius type, these data evidence differences between the fast decomposition rate of $La_2Mg_{17}$ and the rather slow process of nucleation and growth of the $LaH_{3-x}$ binary hydride.

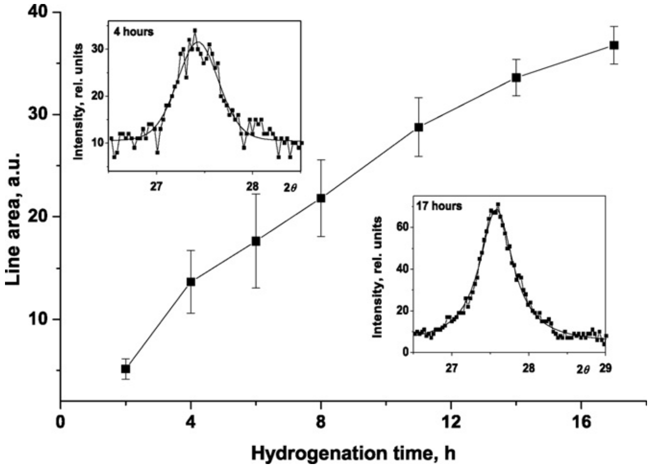

Fig. 5. Hydrogenation time dependence of the relative integral intensity of the 111 XRD peak of the $LaH_3$ phase component of the alloy, specimen A.

Fig. 6 shows that no XRD-detectable amount of $MgH_2$ was formed during the hydrogenation period of up to 6 h. This is because hydrogen mobility in Mg-based alloys is limited by the rate of its diffusion [8] and is very slow in the bulk samples used for the measurements at the indicated temperatures.

It is noteworthy that the data obtained in the present work evidence in general the same hydrogenation behaviour of the alloy as was reported for the powdered alloy Mg-72 mass%–Ni-20 mass%–Mm(La) by Tarasov et al. [5]. In Ref. [5] it has been shown that the activation of the alloy leads to the formation of three hydride phases: $Mm(La)H_3$, $MgH_2$ and $Mg_2NiH_4$, while $Mm(La)_2Mg_{17}$ is subjected to decomposition to form the magnesium hydride and the mischmetal hydride or lanthanum hydride.

## 4. Conclusions

Metallographic investigations performed in the present work showed that the alloy Mg-72 mass%–Ni-20 mass%–La-8 mass% has a fine grain and uniform structure of a ternary eutectic alloy. This structure has peculiar hydrogenation properties. During the activation stage of the hydrogenation process, the decomposition of the $La_2Mg_{17}$ was found to occur first and faster than the formation of $LaH_3$. A slowest rate was observed for the reaction $Mg \rightarrow MgH_2$.

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