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Formation of nanostructured LaMg₂Ni by rapid quenching and intensive milling and its hydrogen reactivity

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ABSTRACT

The formation of the nanostructured orthorhombic LaMg₂Ni phase using the melt-spinning and the intensive ball milling routes has been studied for the $La_{25}Mg_{50}Ni_{25}$ and $La_{20}Mg_{50}Ni_{30}$ compositions. By controlled heat treatment of glassy melt-spun ribbons the formation of the LaMg₂Ni phase proceeds at $T_A \ge 220 \circ C$ (T_A = annealing temperature) for La₂₅Mg₅₀Ni₂₅ via the initial formation of LaMg₃, but occurs for La₂₀Mg₅₀Ni₃₀ already at $T_A \ge 200 \,^{\circ}$ C in a single reaction. Crystallite sizes of LaMg₂Ni of \approx 30 nm were achieved. The formation enthalpies of LaMg₂Ni were estimated to $\Delta H = -320.8$ kJ/mol for La₂₅Mg₅₀Ni₂₅ and $\Delta H = -230.0$ kJ/mol for La₂₀Mg₅₀Ni₃₀. Intensive ball milling of inductively molten master alloys using a planetary RETSCH mill for 30 h resulted in a crystallite size reduction, e.g. up to 15 nm for LaMg₂Ni. The formation of the complex hydride LaMg₂NiH₇ was studied for both alloy compositions by annealing rapidly guenched and crystallised as well as intensively ball milled powder under hydrogen. However, the most effective method for achieving the complex hydride as single phase was found to be intensive ball milling in a planetary RETSCH mill under a 0.5 MPa hydrogen atmosphere. The hydride formation reaction was completed within 3 h for La₂₀Mg₅₀Ni₃₀ and within 7.5 h for La₂₅Mg₅₀Ni₂₅. The hydrogen desorption from intensively milled LaMg₂NiH₇ powder proceeds in two steps. At first, the LaMg₂NiH₇ decomposes into LaH₂₋₃ and Mg₂NiH_{0.2-0.3} at $T_A > 450 \,^{\circ}\text{C}$ with a decomposition enthalpy of $\Delta H \approx 48 \,\text{kJ/mol}$ and the recombination of LaMg₂Ni starts at $T_A > 540 \,^{\circ}$ C. Above 625 $\,^{\circ}$ C the LaMg₂Ni decomposes by the sublimation of Mg.

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1. Introduction

The search for new hydrogen storage materials, which reversibly form hydride compounds at low temperatures via gas phase reaction or electrochemical charging-discharging, is one of the key research areas today. In the last years mainly metallic alloys based on the hexagonal Mg₂Ni-compound (RG: P6₂22 [1]) have been investigated. It forms the complex hydride (Mg₂NiH₄ [2]), which corresponds to a theoretical hydrogen content of 3.6 wt.% or a theoretical discharge capacity for MH electrodes of 1000 mAh/g. However, these theoretical values are by far not reached under real conditions. Microstructural refinement by ball milling or rapid quenching leading to grain sizes of Mg₂Ni, at the nanoscale or to amorphization [3,4,5], has been found to be beneficial for the hydrogen sorption characteristics. Moreover, additional alloying elements, i.e. transition metals like Ti [6] or Zr [7] and also rare earth elements like Y, Ce, La, Nd [8] improve the reversible hydrogenation process. For example, fundamental studies on Mg-Ni-Y alloys [9,10,11,12] revealed that in particular samples with

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nanostructured-amorphous structure exhibit good hydrogenation properties, e.g. 1.3 wt.% absorbed hydrogen and maximum discharge capacities much higher than 200 mAh/g, which is reported for additive-free nanocrystalline Mg₂Ni-containing alloys.

However, more recent studies focus on La-Mg-Ni phases as promising hydrogen storage compounds, though the phase reactions and the phase diagram of this ternary system are so far only partially known [13,14]. Of particular interest is the orthorhombic LaMg₂Ni phase of type MgAl₂Cu (RG Cmcm) [15], which was only recently structurally characterised in detail by Renaudin et al. [16]. From all La-Mg-Ni alloys investigated so far the LaMg₂Ni phase shows the highest hydrogen absorption capacity. The inductively molten alloy absorbs at pressures < 8 bar and temperatures < 200 °C up to 2.8 wt.% hydrogen [16], which is not only higher than the practical values reported for Mg₂Ni, but also by far higher than the values for conventional low temperature hydrogen storage media, e.g. LaH₃ (2.13 wt.%), LaNi₅-H_x (1.5 wt.%), TiV₂-H_x (1.7 wt.%). The hydrogen absorption corresponds with the formation of the monoclinic LaMg₂NiH₇ of space group P2₁/c, which represents only a small lattice distortion of ca. 0.3° of the original orthorhombic cell [16,17]. In the hydride two hydrogen bonding states exist: (i) [NiH₄]^{4–} complexes (similar as in the complex transition metal hydride Mg₂NiH₄) and (ii) interstitial hydrogen in La₂Mg₂ tetra-

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hedral sites. This is a new hydride type with mixed ionic-covalent character, which represents an interesting new target for hydrogen storage studies.

Moreover, it is known for several years that La–Mg–Ni is a glassforming system in the concentration ranges of 10–40 at.% Ni and 5–30 at.% La with maximum glass-forming ability for La₂₀Mg₅₀Ni₃₀ [18,19]. Therefore, rapid quenching or ball milling may be also in this case suitable processing routes for amorphization and formation of nanostructured LaMg₂Ni, which may exhibit enhanced hydrogen sorption reactivity. But until now, the crystallisation behaviour of La–Mg–Ni glasses has only been scarcely investigated.

First studies regarding nanostructuring of LaMg₂Ni and its hydrogenation behaviour have been conducted by Di Chio et al. [20,21,22]. They found that intensive milling of inductively molten stoichiometric pre-alloys with LaMg₂Ni main phase and minor phases leads to strong grain refinement. Spex milling can enhance the subsequent hydrogen absorption, but significantly reduces the fraction of LaMgNiH₇ due to preferential formation of impurity phases. Spex milling under hydrogen was found to lead always to LaH₂ and an amorphous phase. Amorphous ribbons were obtained by rapid quenching, which crystallise under formation of various phases – among them nanocrystalline LaMg₂Ni. However, limited microstructural effects on the hydrogen absorption were detected.

In the present paper we report on our first studies on the $Mg_{50}Ni_{25}La_{25}$ and $Mg_{50}Ni_{30}La_{20}$ alloys, which aim at preparing the nanostructured LaMg₂Ni phase by following the rapid quenching plus annealing route and the intensive milling route with a planetary ball mill, respectively. Hydrogenation experiments were conducted to obtain the LaMg₂NiH₇ phase and the subsequent desorption behaviour was observed. We demonstrate that the formation of these phases of interest depends very sensitively on the alloy composition and processing conditions. Single phase LaMg₂Ni was obtained in a one-step crystallisation of rapidly quenched glassy La₂₀Mg₅₀Ni₃₀ resulting in a mean grain size of 27 nm and also by intensive milling of La₂₅Mg₅₀Ni₂₅ leading to a mean grain size of 15 nm. Complete formation of LaMg₂NiH₇ was achieved by reactive milling of both alloys under hydrogen.

2. Experimental details

Master alloys with the nominal composition $La_{25}Mg_{50}Ni_{25}$ and $La_{20}Mg_{50}Ni_{30}$ were prepared by induction melting of the pure elements Ni and La and subsequent cold crucible casting of the re-molten binary alloys under addition of Mg. This way losses of Mg due to evaporation could be minimized. Ribbons with a width of about 4 mm and a thickness of 0.03 mm were prepared by single-roller melt-spinning (BUEHLER melt spinner) under highly purified argon atmosphere. The chemical compositions of the master alloys and of the melt-spun ribbons were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The methodical deviation in the composition is about 0.5 wt.%. The IRIS Advantage High resolution device (Thermo Electron GmbH) was used.

DSC measurements were carried out using a NETZSCH and a Perkin Elmer DSC7 device under Ar atmosphere at a heating rate of 10 K/min.

The microstructure of the as-quenched samples was studied using transmission and high resolution electron microscopy (HRTEM, Tecnai F30). EDX studies were used to obtain the elemental composition of the investigated sample region.

The thermal behaviour was observed by using an in situ high temperature X-ray attachment XRK900 (PAAR) and an X'Celerator semiconductor detector. The accuracy of the temperature was controlled by the calibration with various substances up to 900 °C. The temperature stability was found to be ± 1.5 K. The temperature treatment was carried out with a heating rate of 10 K/min up to 100 °C followed by steps of 10 K to the next temperature with the same heating rate. The X-ray diffraction measurements, using Cu-K_{α} radiation, were started after a holding time of 2 min at the chosen temperature in the 2Θ region 20–100° and in a time window of only about 12 min. Before heating, the ribbon samples were reduced to small pieces by using a mortar. The crystallisation behaviour of the melt-spun samples was investigated using 0.05 MPa helium atmosphere and the gas-solid reaction with hydrogen was observed under 0.5 MPa hydrogen atmosphere at elevated temperatures. After the heat treatment XRD patterns were recorded for the determination of the lattice constants by using a X'Pert MPD system with a PW3040 diffractometer and Co-K $_{\alpha}$ radiation. For data analysis the PANalytical X'Pert HighScore Plus software package 2.2 was used. The grain sizes were estimated from the XRD profile using the Pseudo Voigt function by means of a LaB₆ standard.

The algorithm of this analysis is given by the PAN alytical X'Pert HighScore plus software package 2.2 with

$$D_i = \left(\frac{\pi}{180}\right) \frac{\lambda}{\sqrt{W_i - W_{\rm std}}} \tag{1}$$

and ε_i

$$\varepsilon_i = \frac{\sqrt{(U_i - U_{\text{std}}) - (W_i - W_{\text{std}})}}{1/100(180/\pi)4\sqrt{2\ln 2}}$$
(2)

The peak broadening FWHM (full width at half maximum) is defined as H_k with

$$H_k = \sqrt{U \tan^2 \Theta + V \tan \Theta + W} \tag{3}$$

U, V and W are parameters, which are refined stepwise.

 U_i contains the information about the strain broadening and the W_i parameter contains a possible grain size broadening [23].

Formation enthalpies and transformation enthalpies of the Mg-hydrides were determined using the thermal desorption method coupled with a mass spectrometer (Leybold) at heating rates of 5, 10 and 20 K/min. Heating rates of 5, 10, 20, 30, 40, 60 and 100 K/min were used for the Kissinger analysis [24]. The pre-activation of the ribbon surface was performed in 0.1 M HF solution for 30 s to eliminate passive films.

High-energy ball milling was carried out for achieving a fine grained alloy microstructures. A RETSCH PM4000 planetary ball mill and stainless steel vials were used. The crushed master alloy powders were milled under Ar atmosphere up to 30 h with 200 rpm using a ball to powder ratio of 10:1. High-energy ball milling under hydrogen atmosphere was performed using similar milling parameters for achieving the complex hydride. A hydrogen pressure of 0.5 MPa was used. After 30, 60, 90, 120, 180, 300 and 450 min milling time the process was interrupted and a small amount of the sample powder was taken for XRD measurements to follow the phase reactions.

3. Results and discussion

3.1. Nanostructured LaMg₂Ni by rapid quenching and annealing

The XRD patterns of the master alloys reveal only the equilibrium phase LaMg₂Ni for the stoichiometric composition La₂₅Mg₅₀Ni₂₅ (Fig. 1a) and a phase mixture of LaMg₂Ni, LaMg₃ and La₂Mg₁₇ for the Ni-rich alloy La₂₀Mg₅₀Ni₃₀ (Fig. 1b). Small fractions of La₂O₃ were also detected in some cases. The average lattice constants and the unit cell volume of the LaMg₂Ni phase were determined for samples of both alloy compositions (Table 1). These estimated values are in a good agreement to the reported lattice constants of Di Chio et al. [22]. However, the results differ from the single crystal values, which were determined by Renaudin et al. [16] and which are also given in Table 1. A deviation of the La diditional consumption of La by the formation of La₂O₃. Thus, a range of homogeneity of LaMg₂Ni is assumed. The mean crystallite



Fig. 1. XRD patterns of the master alloys $La_{25}Mg_{50}Ni_{25}$ (a) and $La_{20}Mg_{50}Ni_{30}$ (b) obtained by inductive melting and subsequent cold crucible casting.

Table 1

Lattice constants of the LaMg₂Ni phase determined from inductively molten master alloys and from rapidly quenched ribbons annealed at 200 °C for La₂₀Mg₅₀Ni₃₀ and 220 °C for La₂₅Mg₅₀Ni₂₅, respectively.

	Phases	Lattice constants of LaMg ₂ Ni (Å)			Unit cell volume, V (Å ³)
		а	b	С	
LaMg ₂ Ni ICSD [11]	LaMg ₂ Ni single crystal	4.227	10.303	8.380	364.96
La ₂₅ Mg ₅₀ Ni ₂₅ master alloy	LaMg ₂ Ni minor phases La ₂ O ₃	4.222 ± 0.002	10.275 ± 0.002	8.346 ± 0.003	362.15 ± 0.3
La ₂₀ Mg ₅₀ Ni ₃₀ master alloy	LaMg ₂ Ni minor phases La Mg ₃ La ₂ Mg ₁₇	4.220 ± 0.002	10.278 ± 0.002	8.353 ± 0.003	362.30 ± 0.3
La ₂₅ Mg ₅₀ Ni ₂₅ in situ HTXRD 250 °C, 0.05 MPa He	LaMg2Ni minor phases La Mg3 (La,Mg)Ni2	4.207 ± 0.001	10.275 ± 0.001	8.357 ± 0.001	361.2 ± 0.2
La ₂₀ Mg ₅₀ Ni ₃₀ in situ HTXRD 200 °C 0.05 MPa He	LaMg_2Ni Minor phases La Mg_3 (La,Mg)Ni_2	4.162 ± 0.001	10.267 ± 0.001	8.347 ± 0.001	356.7 ± 0.2

size *D* and lattice strain ε were estimated to about $D = (90 \pm 20)$ nm and $\varepsilon = (0.02 \pm 0.01)\%$.

After rapid quenching of the two master alloys the XRD patterns of the ribbon samples (Fig. 2) show diffuse maxima only without differences between the two alloys. Amorphous/nanocrystalline microstructures were obtained as can be seen exemplarily in a HRTEM image of a LaMg₂Ni ribbon sample (Fig. 3) and the corresponding electron diffraction pattern (inset Fig. 3). The nanocrystals of 2–7 nm size are embedded in the amorphous matrix. The chemical analysis of the melt-spun ribbons proved correspondence with the nominal compositions within the error limits of the method.

DSC measurements of the rapidly quenched ribbons (Fig. 4) exhibit an endothermic glass transition T_g and an undercooled liquid regime followed by two exothermic crystallisation peaks for La₂₅Mg₅₀Ni₂₅ at T_{x1} = 206.6 °C and T_{x2} = 227.3 °C and only one for La₂₀Mg₅₀Ni₃₀ at T_x = 215.3 °C. The temperature span (ΔT_x) between $T_{g(onset)}$ and $T_{x1(onset)}$ reaches for La₂₅Mg₅₀Ni₂₅ from 35 K for 3 K/min (see Fig. 4) to 42 K for 40 K/min. The temperature span (ΔT_x) for La₂₀Mg₅₀Ni₃₀ reaches from 43 K for 3 K/min (see Fig. 4) to 56 K for 40 K/min, which is in a good agreement to the values. which were found by Inoue et al. [18] for this composition. Furthermore, in situ high temperature XRD measurements under 0.05 MPa helium atmosphere were performed up to 360 °C to observe the phase evolution of the melt-spun ribbons. Sequences of XRD patterns recorded at elevated temperatures are shown in Fig. 5 for La₂₅Mg₅₀Ni₂₅ and in Fig. 6 for La₂₀Mg₅₀Ni₃₀. The crystallisation of La25Mg50Ni25 starts above 200°C. At first, the LaMg3 phase is formed. The crystallisation of the LaMg₂Ni phase sets in only at $T_A > 220 \,^{\circ}$ C. Above 240 $^{\circ}$ C the LaMg₃ phase decomposes and at $T_{\rm A}$ = 260 °C the LaMg₂Ni is found nearly as single phase. In contrast, the annealing of the glassy La₂₀Mg₅₀Ni₃₀ alloy leads directly to the formation of LaMg₂Ni as single phase at $T_A > 200 \circ C$. Above 260 $\circ C$



Fig. 2. XRD patterns of rapidly quenched La–Mg–Ni alloys of different master alloy compositions.



Fig. 3. HRTEM image of a rapidly quenched La₂₅Mg₅₀Ni₂₅ sample showing an amorphous matrix with embedded nanocrystals of 2–7 nm; inset: electron diffraction pattern of the selected area.

additional La-oxides were detected as impurities in both cases. The LaMgNi₄ phase, which was described by Di Chio et al. [22] as a minor phase occurring during the annealing of stoichiometric melt-spun ribbons was not found. The lattice constants of the crystallised LaMg₂Ni phase were estimated after an isothermal heat treatment at $T_A = 250$ °C for La₂₅Mg₅₀Ni₂₅ and at $T_A = 200$ °C for La₂₀Mg₅₀Ni₃₀ (Table 1). The obtained values differ from the lattice constants deter-



Fig. 4. DSC curves of rapidly quenched $Mg_{50}Ni_{25}La_{25}$ and $Mg_{50}Ni_{30}La_{20}$ alloys recorded at 3 K/min.



Fig. 5. Sequence of *in situ* high temperature XRD patterns of $La_{25}Mg_{50}Ni_{25}$ meltspun ribbons recorded during heating under 0.05 MPa helium; at first the $LaMg_3$ phase is formed at $T_A > 200$ °C and the $LaMg_2Ni$ phase crystallises at $T_A > 220$ °C; the LaMg₃ phase decomposes again above 230 °C; (X) LaMg₃, (\blacksquare) LaMg₂Ni.

mined for the phase in the master alloys. Also differences between these parameters obtained from the two annealed samples have to be noticed. Especially, the unit cell volume of the annealed ribbon samples is much lower than that of the single crystal and that of the LaMg₂Ni phase in the master alloys. It is assumed that a remaining amorphous fraction exists in the ribbon samples after annealing, which is enriched in La. Therefore, a range of homogeneity of the LaMg₂Ni phase is concluded.

The formation enthalpies ΔH of the LaMg₂Ni and LaMg₃ phases were determined using the Kissinger method, which analyses the heating rate dependence of the crystallisation temperatures $T_{x(onset)}$ in the DSC experiment [24]. In Fig. 7 the Kissinger plot obtained from different heating rate experiments is shown. The ΔH of the direct LaMg₂Ni phase formation from the Ni-rich composition La₂₀Mg₅₀Ni₃₀ (\Box) with ΔH = -232 kJ/mol has a much lower value than that of the LaMg₂Ni formation from the La₂₅Mg₅₀Ni₂₅ alloy (\blacksquare) with ΔH = -320 kJ/mol, which is preceded by the primary crystallisation of LaMg₃ (\blacktriangle). The formation enthalpy of LaMg₃ was also determined to be ΔH = -269 kJ/mol.



Fig. 6. Sequence of *in situ* high temperature XRD patterns of $La_{20}Mg_{50}Ni_{30}$ meltspun ribbons recorded during heating under 0.05 MPa helium; the $LaMg_2Ni$ phase is formed at $T_A > 200 \,^{\circ}C$ as single phase. At $T_A > 250 \,^{\circ}C$ a small amount of La_2O_3 is additionally detected; (\bigcirc) La_2O_3 , (\blacksquare) $LaMg_2Ni$.



Fig. 7. Kissinger plot for the determination of the formation enthalpies of the LaMg₂Ni (\Box, \blacksquare) and LaMg₃ (\blacktriangle) phases for the different starting compositions La₂₅Mg₅₀Ni₂₅ (filled symbol) and La₂₀Mg₅₀Ni₃₀ (unfilled symbol) from DSC data.

3.2. Nanostructured LaMg₂NiH₇ by annealing of rapidly quenched samples under hydrogen

In order to study the hydrogen reactivity of rapidly quenched and subsequently annealed alloy samples comprising the nanostructured orthorhombic LaMg₂Ni main phase in detail, gas phase reactions under *in situ* XRD observation were conducted.

The phase reactions of the melt-spun La25Mg50Ni25 and La₂₀Mg₅₀Ni₃₀ samples were investigated first with helium and then with hydrogen in a one-step procedure in an in situ high temperature XRD (HTXRD) equipment to avoid an additional contamination with oxygen. The temperature and time management of the crystallisation under helium and the subsequent reaction under hydrogen was defined considering process conditions already reported [16] and own results as described above. For La₂₅Mg₅₀Ni₂₅ the isothermal crystallisation to LaMg₂Ni was performed at 250 °C under helium to skip the formation of the LaMg₃ phase. After 3 h heat treatment at 250 °C the crystallite size was $D \approx 30$ nm and the lattice strain (\approx 0.020% as estimated from XRD data. The sample was cooled down to room temperature and reheated to 190 °C. The hydrogen was filled in the chamber up to 0.5 MPa and the isothermal measurement started after a further heating to 210 °C. A higher temperature was not reasonable due to the favoured formation of LaH₂₋₃ and a lower temperature would cause a very slow phase reaction to LaMg₂NiH₇. For La₂₀Mg₅₀Ni₃₀ the heating conditions were changed according to the crystallisation behaviour that we observed (see above). An isothermal crystallisation was performed at 200 °C for 7 h under helium. The crystallite size of LaMg₂Ni was $D \approx 27$ nm and the lattice strain was ($\approx 0.025\%$. This was followed by an isothermal heat treatment at 180 °C under 0.5 MPa hydrogen. Fig. 8 shows the XRD patterns of a melt-spun La₂₀Mg₅₀Ni₃₀ sample (a), which was crystallised under helium to LaMg₂Ni single phase (b) and of the hydrogenated samples for both starting compositions (c and d). The gaseous phase reaction was interrupted after 37 h for La25Mg50Ni25 and after 18 h for La20Mg50Ni30 due to the increasing fraction of LaH₂₋₃. A small remaining amorphous fraction is assumed to be present in the crystallised melt-spun ribbon samples, which favourably reacts with the introduced hydrogen to LaH₂₋₃. In contrast, the reaction of the LaMg₂Ni phase to LaMg₂NiH₇ proceeds very slowly under the chosen conditions. Therefore, from the XRD pattern of the Ni-rich composition (Fig. 8c) a Mg₂NiLaH₇ concentration of only about 25 wt.% was estimated. In the case of Mg₅₀Ni₂₅La₂₅ only about 10 wt.% was observed (Fig. 8d).

The formation of the LaMg₂NiH₇ hydride is obviously strongly dependent on the initial hydrogen pressure. That can be concluded

Table 2

Lattice constants of LaMg₂NiH₇ prepared by intensive ball milling under hydrogen and ball milling under argon and subsequently annealing under hydrogen, respectively, in comparison to the values from the literature.

Treatment origin	Phases	Lattice constants of LaMg ₂ NiH ₇ (Å)				Unit cell volume, $V(Å^3)$
		a	b	с	eta°	
Renaudin et al. [16]	LaMg ₂ NiH ₇ neutron diffraction	13.9789 (7)	4.7026 (2)	16.0251 (8)	125.24	860.39 (8)
La ₂₅ Mg ₅₀ Ni ₂₅ milling master alloy 30 h + <i>in situ</i> HTXRD 0.5 MPa H ₂	≈67 wt.% LaMg₂NiH7 ≈24 wt.% LaH2 ≈9 wt.% LaMg₂Ni	13.969 ± 0.004	4.719 ± 0.001	16.075 ± 0.003	124.89	869.25
La ₂₅ Mg ₅₀ Ni ₂₅ milling of the master alloy for 7.5 h, 0.5 MPa H ₂	LaMg ₂ NiH ₇ single phase	13.956 ± 0.002	4.716 ± 0.002	16.061 ± 0.002	124.86	867.38
La ₂₀ Mg ₅₀ Ni ₃₀ milling of the master alloy for 3 h, 0.5 MPa H ₂	LaMg ₂ NiH ₇ single phase	13.959 ± 0.002	4.715 ± 0.002	16.061 ± 0.002	124.83	866.93

when comparing the results obtained here under 0.5 MPa hydrogen with the results of Di Chio et al. [22] for the hydride formation under 3 MPa hydrogen.

3.3. Nanostructured LaMg₂Ni and LaMg₂NiH₇ by intensive ball milling

The master alloys were intensively ball milled aiming at achieving fine grained powders with enhanced hydrogen reactivity of the LaMg₂Ni phase. Fig. 9 shows the XRD patterns of the crushed La25 Mg50 Ni25 starting alloy (a) in comparison to the powder milled for 30 h (b) with a strong peak broadening. The mean crystallite size D and the lattice strain ε of the LaMg₂Ni phase in dependence on the milling time is presented in the inset of the Fig. 9. First, the crystallite size decreases drastically from about (90 ± 20) nm to (25 ± 13) nm within the first 5 h and decreases further to about (15 ± 1) nm after 30 h. At the same time the lattice strain ε increases from about $\varepsilon = (0.02 \pm 0.01)\%$ to $\varepsilon = (0.32 \pm 0.04)\%$. After 30 h of intensive milling a small amount of La2O3 and La4Ni3O10 was detected. The powder milled for 30 h was used as starting material to form the complex LaMg₂NiH₇ phase. This was firstly conducted by means of the in situ high temperature XRD (HTXRD) device under 0.5 MPa hydrogen. The heat treatment was performed at $T_A = 180 \circ C$ for 34 h. The first reaction could be observed already after 3.5 h. In Fig. 9c the XRD pattern taken after the isothermal heat treatment of pre-milled La₂₅Mg₅₀Ni₂₅ powder under hydrogen is shown. After



Fig. 8. Formation of LaMg₂NiH₇ from the rapidly quenched state analysed by using *in situ* HTXRD: (a) typical melt-spun alloy, (b) after annealing of La₂₀Mg₅₀Ni₃₀ ribbons at $T_A = 200^{\circ}$ C under helium (for La₂₅Mg₅₀Ni₂₅ at $T_A = 250^{\circ}$ C); (c) La₂₀Mg₅₀Ni₃₀ sample after additional annealing under 0.5 MPa hydrogen at $T_A = 180^{\circ}$ C for 18 h; (d) La₂₅Mg₅₀Ni₂₅ sample after additional annealing under 0.5 MPa hydrogen at $T_A = 180^{\circ}$ C for 37 h.

34 h we detected \approx 67 wt.% LaMg₂NiH₇, \approx 24 wt.% LaH₂ and \approx 9 wt.% residual LaMg₂Ni. La-oxides were not formed. This deviates from results of Di Chio et al. [20], who obtained 45 wt.% LaMg₂NiH₇, 27 wt.% LaH₂, 13 wt.% LaMgNi₄ and 15 wt.% La₂O₃ after milling in a SPEX mill for 12 h and subsequent hydrogenation under \approx 9 MPa hydrogen pressure. The differences are related to the various sample histories and the different hydrogen pressures. The lattice constants of the achieved hydride were determined by using the XRD method (Table 2). The estimated values deviate from those, which were reported by Renaudin et al. [16]. A high degree of lattice imperfections induced by the milling process of the master alloy is assumed, which leads to a higher unit cell volume. For the Ni-rich La₂₀Mg₅₀Ni₃₀ alloy a quite similar behaviour can be predicted.

Another way to form the LaMg₂NiH₇ phase was the direct intensive ball milling of the coarse grained master alloy under a 0.5 MPa hydrogen atmosphere. Fig. 10 shows the XRD patterns of the La₂₅Mg₅₀Ni₂₅ master alloy in the induction molten and crushed and sieved state and after milling times of 90, 120 and 450 min under hydrogen. The master alloy shows only the LaMg₂Ni single phase. The first reflections of the evolving LaMg₂NiH₇ phase were observed after 90 min. The XRD pattern shows a small amount of the remaining LaMg₂Ni phase and some additional peaks belonging to an unknown phase. After a further milling up to 120 min the fractions of the LaMg₂Ni phase and the unknown phase decrease and the quantity of LaMg₂NiH₇ increases. After 450 min the phase reac-



Fig. 9. Formation of $LaMg_2NiH_7$ by intensive ball milling of a master alloy under helium atmosphere and subsequent annealing under 0.5 MPa hydrogen using the *in situ* HTXRD: (a) XRD pattern of the starting alloy $La_{25}Mg_{50}Ni_{25}$, (b) XRD pattern after 30 h intensive ball milling; (c) XRD pattern after an *in situ* isothermal high temperature treatment at 180 °C for 32 h: (**■**) $LaMg_2Ni$, (**○**) LaH_{2-3} , (**●**) $LaMg_2NiH_7$; the crystallite sizes *D* and lattice strains ε in dependence on milling time are shown in the inset.



Fig. 10. XRD patterns after intensive ball milling of $La_{25}Mg_{50}Ni_{25}$ under 0.5 MPa hydrogen: after 90 min the first peaks of the Mg_2NiLaH_7 phase (x) were detected plus unknown additional phases; after 450 min (=7.5 h) the $LaMg_2NiH_7$ is detected as single phase; $\blacksquare = LaMg_2Ni$, o = unknown phases, x = $LaMg_2NiH_7$.

tion to the hydride was complete. Only the LaMg₂NiH₇ was detected in the XRD pattern. The same milling procedure was also performed for the La₂₀Mg₅₀Ni₃₀ starting alloy. In Fig. 11 the XRD patterns after milling for 30, 60 and 180 min are shown together with that of the induction molten, crushed and sieved starting alloy. The first phase reaction can be seen already after 30 min milling time. The formation of the LaMg₂NiH₇ phase was completed already after 180 min. i.e. much earlier than for the La₂₅Mg₅₀Ni₂₅ alloy. That indicates a strong dependence of the hydride forming reaction on the starting composition. The lattice constants of these prepared hydrides were determined from the XRD pattern taken after the milling process. In comparison to the values which were determined by Renaudin et al. [16] we found some deviations and a higher unit cell volume in both cases due to the high lattice defect concentration induced by the milling preparation (Table 2). The estimated lattice constants of the hydride formed from the La₂₀Mg₅₀Ni₃₀ alloy are similar to those of the hydride formed from the La25Mg50Ni25 starting



Fig. 11. XRD patterns after intensive ball milling of $La_{30}Mg_{50}Ni_{20}$ under 0.5 MPa hydrogen: the master alloy shows the $LaMg_2Ni$ peaks only; after 30 min the first peaks of the $LaMg_2NiH_7$ phase were detected; the other peaks belong to the remaining $LaMg_2Ni$ phase; after 180 min (=3 h) the $LaMg_2NiH_7$ is detected as single phase; $\blacksquare = LaMg_2Ni$, $\Delta = La_2Mg_{17}$, $v = LaMg_3$, $x = LaMg_2NiH_7$.



Fig. 12. Thermal desorption analysis: phase reaction of $LaMg_2NiH_7$ (obtained by milling under hydrogen) in dependence on the temperature. The endothermal peaks represent the concentration of the effusing hydrogen; the dots represent the temperatures, at which the XRD patterns (Fig. 13) were taken: (a) 360 °C, (b) 450 °C, (c) 540 °C, (d) 625 °C, (e) 700 °C, (f) 750 °C.

alloy. The hydrogen concentrations of the LaMg₂NiH₇ samples were estimated to be $[H] \approx (3.0 \pm 0.5)$ wt.% in both cases. The calculated hydrogen concentration in LaMg₂NiH₇ is 2.8 wt.%. It is assumed that the additionally measured hydrogen fraction is adsorbed at grain boundaries.

3.4. Desorption behaviour of the Mg_2NiLaH_7 using the thermal desorption analysis

The desorption behaviour of the LaMg₂NiH₇ powders obtained by milling under hydrogen was studied using thermal desorption analysis (TDA). The already reported results of Di Chio et al. [21] were taken into account. Fig. 12 shows the desorption curve for the La₂₅Mg₅₀Ni₂₅ sample, which was intensively ball milled under hydrogen until complete LaMg₂NiH₇ formation, recorded at a heating rate of 20 K/min. Several endothermic peaks indicate the successive effusion of hydrogen and consequently, the gradual decomposition of the hydride into other phases. XRD patterns were taken after heating to different temperatures to follow the phase reactions. The symbols at selected temperatures in the TDA curve mark the pre-heating conditions after which corresponding XRD patterns were taken (Fig. 13). In general, the transformation reaction of LaMg₂NiH₇ is characterised by two steps: (i) the decomposition of LaMg₂NiH₇ into LaH₂ and Mg₂NiH_{0.2-0.3} and (ii) the desorption of hydrogen from these hydrides. In both cases a large amount of hydrogen effuses from the sample. After 360 °C a part of the adsorbed hydrogen is already removed. However, the LaMg₂NiH₇ phase remains unchanged (see Fig. 13a). Also its lattice constants did not change. This reaction was observed for different heating rates and seems to be systematically. We assume that the removed hydrogen was additionally adsorbed on special lattice planes of the hydride. Such behaviour was already reported by Li et al. [25] for surfaces energies of different lattice planes in Fe-Ni alloys. A further hydrogen desorption can be observed between 360 and 450 °C. However, the XRD measurement shows the LaMg₂NiH₇ phase only indicating that the hydrogen removes in the same manner as before (Fig. 13b). Above 450 °C the LaMg₂NiH₇ phase decomposes into LaH₂₋₃ and Mg₂NiH_{0.3} (see Fig. 13c). The maximum hydrogen desorption occurs at 528 °C. The lattice constants of the observed phases were estimated from the XRD pattern, which was taken after cooling from 540 °C to room temperature and provide a = 5.650 Å for the LaH₂₋₃ phase and a = 5.230 Å and c = 13.32 Å



Fig. 13. XRD patterns taken after successive thermal desorption (see Fig. 12); (a) and (b): the LaMg₂NiH₇ (o) is unchanged after 360 °C and a further hydrogen release at 450 °C; (c) at 540 °C: decomposition of the hydride into LaH₂₋₃ (v) and Mg₂NiH_{02-0.3} (x); (d) at 625 °C: the recombination of LaMg₂Ni (**■**) has already started; (\triangle) Mg₂Ni, (**●**) La(OH₃, (**□**) LaNi₃; (e) at 700 °C: decomposition of the LaMg₂Ni by sublimation of Mg: La₂Ni₂Mg (**★**) additional.

for the detected Mg₂NiH_{0.3} phase. This is in a good agreement with the reported values by Darriet et al. [2]. The next phase reaction starts at 620 °C. XRD patterns were recorded after 625 and 700 °C (Fig. 13d and e). Several processes are overlapped in this temperature range: at first, further hydrogen desorption from $Mg_2NiH_{0.3}$ to Mg_2Ni and the decomposition of the residual LaH_{2-3} were observed. Additionally, the recombination of La and Mg₂Ni into the starting LaMg₂Ni alloy occurred. A small amount of La₂MgNi₂ is also observed, its formation can be caused by the evaporation of Mg. A small amount of La-oxides and hydroxides were also detected. An amorphous phase appearing during the desorption process as described by Di Chio et al. [21] could not be observed. At 750 °C (see also Fig. 12(f)) the LaMg₂Ni phase is decomposed completely. Only LaNi, La₂Ni₃ and a small amount of La₂Mg₁₇ were found and Mg evaporates strongly. The reaction was interrupted at this temperature to avoid a further contamination of the desorption cell. The complete phase reaction sequence can be described as following:

$$\begin{split} \text{LaMg}_2\text{NiH}_7 &\stackrel{>450^{\circ}\text{C}}{\longrightarrow} \text{LaH}_{2-3} + \text{Mg}_2\text{NiH}_{0,2-0,3} + 2.3 - 2.4\text{H}_2 \uparrow \\ &\stackrel{\geq 620^{\circ}\text{C}}{\longrightarrow} \text{Mg}_2\text{Ni} + \text{La} + 1.2 - 1.6\text{H}_2 \uparrow \stackrel{\geq 700^{\circ}\text{C}}{\longrightarrow} \text{LaMg}_2\text{Ni} \\ &\rightarrow \text{La}_2\text{MgNi}_2 + \text{Mg} \uparrow \stackrel{\geq 750^{\circ}\text{C}}{\longrightarrow} \text{LaNi} + \text{La}_2\text{Ni}_3 + \text{La}_2\text{Mg}_{17} + \text{Mg} \uparrow \end{split}$$

From the hydrogen desorption peaks the transformation enthalpies could be calculated using the Kissinger method (Fig. 14). The first value of $\Delta H \approx 11$ kJ/mol is related to desorption peak I in Fig. 12 and represents the hydrogen desorption from special lattice planes in LaMg₂NiH₇. The second value of $\Delta H \approx 48$ kJ/mol represents the desorption enthalpy of two overlapping reactions, i.e. desorption peaks Ia and II. That means the further hydrogen desorption from special lattice planes of LaMg₂NiH₇ without changing lattice constants of the hydride (Ia) and the decomposition of the hydride into LaH₂₋₃ + Mg₂NiH_{0.2-0.3} (II). It can be presented only as an average value. The reaction above 625 °C is not only related with hydrogen desorption, but also with Mg evaporation. For that reason, the decomposition enthalpy cannot be estimated.



Fig. 14. Desorption enthalpies of LaMg₂NiH₇, estimated from the TDA using the Kissinger analysis for different heating rates and the first and second peak in Fig. 12; the first hydrogen effusion peak provides a desorption enthalpy of about 11 kJ/mol in every case; the decomposition enthalpy of LaMg₂NiH₇ into LaH₂ and Mg₂NiH_{0.2-0.3} provides an average value of ΔH = 48 kJ/mol.

The achieved results are strongly dependent on the sample history and the methodical conditions.

4. Summary

The La₂₅Mg₅₀Ni₂₅ and La₂₀Mg₅₀Ni₃₀ alloys have been subjected to studies regarding phase formation by induction melting, rapid quenching plus annealing and intensive milling as well as regarding the hydrogenation and desorption behaviour of structurally refined states.

By induction melting of the stoichiometric alloy composition a single phase state of $LaMg_2Ni$ was obtained, whereas the Ni-rich alloy comprised additional minor phases. Rapid quenching led for both alloys to amorphous phases with a few embedded nanocrystals. Upon heat treatment $La_{25}Mg_{50}Ni_{25}$ crystallised in two steps, i.e. firstly to $LaMg_3$ at 220 °C then to $LaMg_2Ni$ with mean grain size of 30 nm at 260 °C. For $La_{20}Mg_{50}Ni_{30}$ the single phase $LaMg_2Ni$ with mean grain size of 27 nm was obtained in one crystallisation step at 200 °C. The enthalpy of crystallisation and the lattice constants of the $LaMg_2Ni$ phase have been determined. Intensive milling of the pre-alloys in a planetary ball mill led to strong grain size reduction down to 15 nm combined with strong lattice strain increase up to 0.32%.

The formation of the complex $LaMg_2NiH_7$ phase was studied using several methods:

- (a) from the glassy melt-spun state using the *in situ* HTXRD device in a one-step procedure: first, crystallisation of the LaMg₂Ni phase under helium at 250 °C or 200 °C, respectively and subsequent hydrogenation under 0.5 MPa hydrogen at 190 °C or 180 °C, respectively. The LaMg₂NiH₇ phase is formed from the La₂₀Mg₅₀Ni₃₀ alloy at 180 °C after 18 h with about 10 wt.% and from the La₂₅Mg₅₀Ni₂₅ alloy at 190 °C only after 36 h with a very small amount. The differences between the crystallisation temperature of the LaMg₂Ni phase from the two alloys are related to the varying reaction mechanisms: while for La₂₀Mg₅₀Ni₃₀ the LaMg₂Ni phase forms directly from the glassy state in the case of La₂₅Mg₅₀Ni₂₅ the formation proceeds via intermediate LaMg₃ formation.
- (b) via intensive ball milling of the master alloys in a planetary RETSCH mill for 30 h under argon to obtain a nanocrystalline microstructure with crystallite sizes of $D \approx 15 \pm 1$ nm and subsequent heat treatment in the *in situ* HTXRD device under 0.5 MPa

hydrogen at $T_A = 180$ °C for 34 h. Then we detected ≈ 67 wt.% LaMg₂NiH₇, ≈ 24 wt.% LaH₂ and ≈ 9 wt.% residual LaMg₂Ni. Laoxides were not formed. This deviates from results of Di Chio et al. [20], who obtained 45 wt.% LaMg₂NiH₇, 27 wt.% LaH₂, 13 wt.% LaMgNi₄ and 15 wt.% La₂O₃ after milling in a SPEX mill for 12 h and subsequent hydrogenation under ≈ 9 MPa hydrogen pressure.

(c) via intensive ball milling of the master alloys in a planetary RETSCH mill directly under 0.5 MPa hydrogen. Only in that case the LaMg₂NiH₇ phase was formed as single phase. Differences in the reaction time were observed and are caused by the different chemical compositions of the starting alloys. The formation of the complex hydride is already complete after 3 h for La₂₀Mg₅₀Ni₃₀ and after 7.5 h for La₂Mg₅₀Ni₂₅. The unit cell volume of the obtained LaMg₂NiH₇ is similar in both cases, but larger as the reported values from the literature due to a high degree of lattice imperfections generated by the milling process. In contrast, Spex milling under hydrogen [21] was found to lead always to LaH₂ and an amorphous phase.

The desorption behaviour of these prepared $LaMg_2NiH_7$ phases was studied by TDA.

The thermal reaction of LaMg₂NiH₇ is characterised by two steps: the decomposition of LaMg₂NiH₇ into LaH₂ and Mg₂NiH_{0.2-0.3} above 450 °C and the hydrogen desorption from these formed hydrides above 540 °C. The recombination of LaMg₂Ni is observed already at 625 °C, but the Mg sublimates during this process and the LaMg₂Ni phase is decomposed at 750 °C completely. The influence of an alloying constituent substitution on the formation and the thermal stability of LaMg₂Ni and its hydride, and on the desorption properties is a subject of ongoing studies.

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