Figure

Fig. 1

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Fig. 5

Fig. 6a

Fig. 6b

Fig. 7a

Fig. 7b

Fig. 7c

Hydrogen induced amorphization of LaMgNi₄ phase in metal hydride alloys

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Abstract

Hydrogen induced amorphization (HIA) of the LaMgNi₄ phase at 30°C was found in three LaMgNi₄/LaNi₅ two-phase metal hydride (MH)-forming alloys. The amorphization happened at the first dehydrogenation cycle from a fully hydrided alloy, and the process is reversible after annealing at 250°C for 1 h. The hydrogen storage capacity of the LaMgNi₄ phase in an amorphous state is higher than in its crystalline form. A scanning electron microscope study did not observe any significant changes in the shape of grains as a consequence of HIA and re-crystallization. A transmission electron microscope study confirmed the amorphous structure of the LaMgNi₄ phase after HIA. These findings suggest a new way to improve the performance of MH alloys when used in electrochemical applications.

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1. Introduction

Newly developed metal hydride (MH) alloys, both AB_2 - and A_2B_7 -based superlattice alloys, used as negative electrode active materials for nickel/metal hydride (Ni/MH) batteries and can be considered as phase-change materials. The conventional chalcogenide-based phase change materials has been pursued by Energy Conversion Devices Inc. for more than fifty years because of the wide range of applications in the consumer market, including rewriteable optical disks (with focused laser beams) and non-volatile memory (with electrical current pulses). The microstructure of this group of materials can be altered between polycrystalline and amorphous by applying a pulse of energy. A reversible hydrogenation process can be considered as a source of pulsed energy and may be applicable for phase change media. In the past hydrogen-induced-amorphization (HIA) has been extensively studied, especially for AB_2 C15-Laves phase alloys [1] with atomic radii ratio $R_A/R_B > 1.37$ [2]. Previous study results indicate that typical HIA and recrystallization temperatures are around 300°C and 400°C, respectively [2, 3], and both processes occur at relatively high hydrogen pressures rather than at high hydrogen concentrations [4]. Li et al [5] reported HIA in both A_2B_7 and A_5B_{19} phases for the multiphase $La_{0.8}Mg_{0.2}Ni_{3.5}$ MH alloy; the origin of HIA was attributed to the significant lattice distortion during hydrogenation, rather than to thermal activation. In our current study, the HIA phenomenon was found for the $LaMgNi_4$ phase materials to occur at a particularly low temperature (30°C), which supports the Li et al. argument about the non-thermal origin of HIA.

Mg-containing rare earth-based superlattice MH alloys have attracted much attention recently as replacements for conventional AB_5 alloys with higher storage capacity, lower self-discharge, and extended cycle stability [6–9]. These superlattice multi-component alloys consist of alternating structural AB_5 and A_2B_4 slabs stacked along the c -direction. Denys, Yartys, and Webb reported the hydrogen can be stored in both the AB_5 slab ($AB_5H_{5.2}$) and A_2B_4 slab ($LaMgNi_4H_{7.9}$) [10]. Same report also pointed out a spatial framework is formed by connected the NiH_4 tetrahedral and MgH_6 octahedral by sharing H-vertices [10]. Among other phases such as AB_2 , AB_3 , A_2B_7 , A_5B_{19} , AB_4 , and AB_5 , $AA'B_4$ phase is also found when a single rare earth (RE) element was used instead of a misch-metal in the A-site [11, 12]. The structure, electrochemical properties, and chemical modifications of the RE-MgNi₄ MH alloys, such as YMgNi₄ [13–16], LaMgNi₄ [17–22], CeMgNi₄ [18, 23], PrMgNi₄ [18, 24], NdMgNi₄ [17, 18, 25], GdMgNi₄ [15, 19], and SmMgNi₄ [26, 27], have been studied, and some of these alloys have shown reasonable cycle stability, while others went through HIA when hydrided at a relatively higher temperature. When approximated for pseudo AB_2 stoichiometry, the LaMgNi₄ has a R_A/R_B of 1.39 using the 12-coordinate metallic radii, which is slightly higher than the threshold for HIA (1.37) [2]; HIA for LaMgNi₄ has been reported only when hydrided at 5 MPa H_2 and 100°C [19]. The ball-milled amorphous LaMgNi₄ phase showed a stable 400 mAh g⁻¹ discharge capacity [28] and was considered accordingly as a candidate to replace the A_2B_7 MH alloy. In this paper, a study of a metastable LaMgNi₄ phase in a LaNi₅ matrix, its HIA, and recrystallization by annealing at 250°C will be presented.

2. Experimental setup

Ingots were prepared in a 2-kg capacity induction furnace from raw elemental materials (except for Mg, for which MgNi₂ was used to suppress the evaporation of Mg) in a helium atmosphere at 0.1 MPa. Extra 22% Mg was added to compensate for the loss of Mg in vapor form during melting. Annealing was performed in vacuum by a diffusion pump at 960°C for 5 h. A Philips *X'Pert Pro* x-ray diffractometer (XRD) using Cu-K_α as the radiation source and a 2θ scanning range between 10 and 80° was used to evaluate phases in a cast structure and a JEOL-*JSM6320F* scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) capability (Noran System 7) was used to study the phase distribution and composition. A primary electron beam at 20 kEV and 300 pA was used for EDA analysis. An FEI Titan 80-300 analytical transmission electron microscope was also used for structure and phase characterization. Pressure-concentration-temperature (PCT) characteristics for each sample were measured using a Suzuki-Shokan multi-channel PCT system. For the PCT analysis, each sample (of about 2 g) was first soaked in H₂ at 2.5 MPa and 300°C for 4 h and then cooled down to room temperature at 2.5 MPa H₂ pressure. H₂ pressure in the 66 cc reservoir was 4 MPa before opening the valve and stabilized to 2.4 MPa in 0.5 h. Sample was continuous pumped by a rotary pump for 1 h followed by a rest for 0.5 h.

3. Results and discussion

3.1 Finding HIA during gaseous phase cycling

Several (La, Mg)Ni_x MH alloys (E series) with $x = 3.1$ to 3.3 were prepared, and their target compositions are listed in Table 1. Thirty gaseous phase hydride/dehydride cycles in the PCT apparatus were performed to study the mechanical and chemical stability of these alloys. Results for a few alloys in this study are plotted in Fig. 1 and compared with an AB₅ sample of the composition of La_{10.5}Ce_{4.3}Pr_{0.5}Nd_{1.4}Ni_{60.0}Co_{12.7}Mn_{5.9}Al_{4.7}. The maximum storage capacity for alloy E14 is close to other similar MH alloys reported before [29–31]. Capacities of other E-alloys are smaller due to different composition design with Al-incorporation [32]. While the reversible hydrogen storage capacity of the AB₅ alloy was very stable, those from Mg-containing E-alloys experience capacity loss, which, as identified in our previous work, was due to contamination from pump oil during a 1 h pump process at room temperature [11]. The surface of the Mg-containing E-alloy is more reactive compared to that of the Mg-free AB₅ alloy.

XRD analysis is essential for the research of multi-phase MH alloys [33–35].

XRD patterns of the E-alloys before PCT cycling are shown in Fig. 2a–2d. While the annealed Al-free E14 alloy shows a typical multi-phase superlattice structure composed of AB₂, AB₃, A₂B₇, A₅B₁₉, and AB₅ phases (see the study of Alloy A in [11] for a detailed analysis), other Al-containing alloys (E26, E29, and E32) show two phase structures (LaNi₅ and LaMgNi₄) before the cycling. XRD patterns of the Al-containing E-alloys after 30 hydride-dehydride cycles are shown in Fig. 2e–2g and composed of only LaNi₅ phase. Four possible mechanisms were considered to explain the apparent

disappearance of LaMgNi₄ phase on X-ray scans: amorphization, **decomposition**, severe pulverization, and selective oxidation. **Decomposition was reported in some hydrides [36] but was ruled out due to lack of new phase in the XRD pattern.** In order to investigate this phenomenon, seven consecutive PCT measurements were performed at 30°C on a newly activated E26 alloy. Between each measurement, the desorption isotherm was stopped at 0.001 MPa and the test chamber was not directly opened to the mechanical pump to avoid the contamination from the pump oil. Between cycles 6 and 7, the alloy was annealed in vacuum (degassing) at 250°C for 1 h. The resulting PCT isotherms from cycles 1, 2, 6, and 7 are plotted in Fig. 3. As the figure shows, the PCT isotherms **basically** follow the same trend, with a small shift in the maximum capacity in cycle 7. **The initial decrease in the equilibrium pressure with the increase in the hydrogen content in the first absorption cycle (curve Cycle 1A in Fig. 3) is due to the fact that sample is not fully activated in the beginning of the PCT analysis and the system is not at equilibrium within our maximum waiting time per PCT step (2 h).** The amount of reversible hydrogen storage (from 2.4 MPa to 0.005 MPa during desorption) obtained from each cycle is plotted in Fig. 4. From this figure it is clear that the reversible hydrogen capacity initially increases, then stabilizes, and finally decreases to near the original value after annealing at 250°C. It appears that the disappearance of the LaMgNi₄ crystalline phase between the first and second cycle is caused by full-hydrogenation-dehydrogenation, with the phase reappearance after annealing at 250°C, which leads to a near full recovery of the capacity loss. The discovery of crystalline restoration eliminates the possibility of severe pulverization and selective oxidation of the LaMgNi₄ phase, and the HIA mechanism remains as the only plausible explanation.

In order to further studying the HIA phenomenon, XRD analysis was performed at four different stages of the PCT cycling experiment; the resulting XRD scans are shown in Fig. 5. The phase abundances in each stage are calculated from a **full-pattern analysis with the XRD data** (Table 2). From these results, it is clear that the cast alloy was composed of 91.4% LaNi_5 and 8.6% LaMgNi_4 before hydrogenation (Fig. 5a). In the first PCT cycle, with an equilibrium hydrogen pressure at 0.004 MPa, 75% of the LaMgNi_4 phase was hydrided (from α to β phase), while the LaNi_5 phase remained unhydrided (Fig. 5b). At the end of the absorption of Cycle 1 (2.4 MPa), both LaNi_5 and LaMgNi_4 phases are fully hydrided (Fig. 5c). After the first complete PCT cycle (0.001 MPa), the XRD pattern only shows peaks from the LaNi_5 phase (same as Fig. 2e). These results indicate that the HIA happened during the dehydrogenation and not during hydrogenation. This agrees with most of the earlier HIA work on the C15 AB_2 alloys: HIA happens after a full hydrogenation during a temperature ramp up and it occurs at a very high hydrogen concentration. The only major difference between our finding here and the previous reported HIA is that the temperature was significantly lower (at 30°C) when the HIA occurred. Our hypothesis explaining HIA in AB_2 alloys with larger R_A/R_B ratios is as follows: In the original AB_2 structure, electron transfer from atom A to atom B is occurring to compensate for the deviation from the ideal R_A/R_B ratio. During hydrogenation, atom A has a higher affinity for the electron donated by the absorbed ionized hydrogen and pushes the effective R_A/R_B ratio further away from the ideal ratio, increasing the instability of the Laves phase and reducing the stability of the Laves phase structure, especially at the point where maximum amount of hydrogen is absorbed.

However, the absorbed hydrogen at various interstitial sites increases the stability of the hydride crystal structure. During dehydrogenation, when hydrogen leaves the host alloy, the crystal structure of the hydrogen-hosting phase collapses under high stresses and an amorphous phase is formed instead.

The XRD pattern of the same alloy after a 1 h at 250°C degassing is shown in Fig. 5d. The full-pattern analysis yields a complete de-hydrated LaNi_5 phase (92.3 wt%) and an almost complete de-hydrated LaMgNi_4 (7.1 wt.%) phase and a very small amount of $\text{LaMgNi}_4\text{H}_{0.75}$ (0.5 wt.%). The LaMgNi_4 phase recrystallizes after the 250°C thermal treatment and thus proves the HIA in LaMgNi_4 is reversible. The crystallite size of the LaMgNi_4 phase decreases after the HIA-and-recrystallization process as seen from the increase in the peak width of the diffraction peak.

The hydrogenation behavior of a pure LaMgNi_4 alloy was studied before [19]. The $\text{LaMgNi}_4\text{H}_{3.8}$ was formed at room temperature but not reversible up to 300°C and no HIA was found. Since the dehydrogenation, which is critical to HIA, in the alloy never occurred and therefore no HIA was observed. In our case, apparently the hydrogen stored in the LaMgNi_4 phase can be released through the main LaNi_5 phase, which enables HIA process.

The amorphous LaMgNi_4 apparently has a higher hydrogen storage capacity (from Fig. 4) and lower reversibility (Fig. 3) in comparison with its crystalline counterpart. In the literature, there is no consensus on storage properties of the

amorphous form (by quenching, ball-milling, and annealing) versus its crystalline form of the same chemical composition, e.g., different results include lower capacity [2, 37–41], similar capacity [42], higher capacity [43], faster desorption rate [39, 43], and better high-rate dischargeability [37, 40]. It will be interesting to find that, although the impact of HIA to capacity is controversial, the improvement to the high-rate capability from HIA is universal. Therefore, our finding encourages the use of HIA to improve both the capacity and the rate capability of the MH alloys used as negative electrodes in Ni/MH batteries.

3.2 SEM observation

SEM micrographs in the backscattering electron image (BEI) mode of a sample after 6 PCT cycles (with vacuum degassing at 25°C between cycles) and a sample with additional annealing at 250°C in vacuum are shown in Fig. 6a and 6b, respectively. From both micrographs, it is evident that the main LaNi_5 phase, with the average composition of $\text{Mg}_{0.8}\text{La}_{16.5}\text{Ni}_{73.1}\text{Co}_{3.1}\text{Al}_{6.3}$, went through a severe pulverization after the cycling. The LaMgNi_4 phase, with a slightly darker contrast compared to the LaNi_5 phase, remained intact after 6 PCT cycles with no obvious changes in the shape and uniformity after re-crystallization of this phase. According to the EDS measurements, besides the main AB_5 phase and secondary LaMgNi_4 phase in both samples, there exists a third LaNi phase with an average composition of $\text{Mg}_{16.6}\text{La}_{40.4}\text{Ni}_{52.4}\text{Co}_{0.3}\text{Al}_{0.2}$ (and with the brightest BEI contrast). The volume fraction of the third phase is too small to be detected by XRD study and there is no change in this phase as observed after the re-crystallization.

3.3 TEM observation

A TEM sample was prepared by embedding the powder of E26 after 30 PCT cycles in epoxy; the powder (in curried epoxy) was mechanically thinned and then ion milled. With the help of EDS spectral measurements, a region with a composition close to LaMgNi_4 was identified (Fig. 7a). As seen in Fig. 7b, the electron diffraction pattern from the region (selected with 150 nm diameter aperture) shows a halo of continuous intensity without visible diffraction spots, indicating that the region is a metallic amorphous phase. To support the diffraction results, a high resolution TEM image from the same area was obtained (Fig. 7c); the image shows an orange-peel textured amorphous structures. This measurement demonstrate that after 30 PCT cycles the LaMgNi_4 phase was turned into amorphous structure.

4. Conclusions

Combining the XRD, SEM, and TEM studies, we conclude that the disappearance of the crystalline LaMgNi_4 peaks in the XRD pattern is due to a hydrogen-induced amorphization process. XRD analysis also shows that the amorphization happened at the first dehydrogenation when the fully hydrided crystalline $\text{LaMgNi}_4\text{H}_x$ phase turned into an amorphous LaMgNi_4 structure at room temperature. The process is reversible by a thermal annealing treatment at 250°C. The TEM study reveals that small crystal particles

remain in the area mainly occupied by the amorphous LaMgNi_4 phase and may act as nucleation centers upon recrystallization.

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Figure Captions

Fig. 1

Gaseous phase cycling experiment performed at 30°C for AB5 (a commercially available La-rich MH alloy) and a series of superlattice alloys.

Fig. 2

XRD patterns using Cu- K_{α} as the radiation source from E14 (a), E26 (b), E29 (c), and E32 (d) before gaseous phase cycling and E26 (e), E29 (f), and E32 (g) after 30 gaseous phase cycles. Vertical lines are used to indicate the position of the LaMgNi₄ phase, which is absent in samples after cycling.

Fig. 3

PCT isotherms of E26 alloy at cycle 1, 2, 6 and 7. Open and solid symbols indicate absorption and desorption curves, respectively.

Fig. 4

Plot of reversible hydrogen storage as a function of cycle number for alloy E26. It clearly shows the increase in the capacity due to the crystalline-to-amorphous transition of the LaMgNi₄ phase from the first to the second cycle and the decrease in the capacity after an amorphous-to-crystalline transition from annealing.

Fig. 5

XRD patterns from E26 alloy before PCT (a), equilibrium at 0.004 MPa H₂ (b), equilibrium at 2.4 MPa H₂ (c), and after annealing at 250°C in vacuum (d).

Fig. 6

SEM back-scattering electron images for E26 alloy after 6 PCT cycles without (a) and with annealing at 250°C in vacuum (b). The three vertical bright bands are artifacts from our equipment produced when micrographs were taken. Areas indicated by ①, ②, and ③ are LaNi, LaNi₅, and LaMgNi₄ phases, respectively. LaMgNi₄ phase (the brightest contrast) in (a) and (b) are in amorphous and poly-crystalline states, respectively.

Fig. 7

Large area TEM micrograph (a) for E26 alloy after 30 PCT cycles, 150 nm diameter aperture used to select area (b inset) and its associated electron diffraction pattern (b), and a high magnification TEM image from the same area for the diffraction pattern. The red spot in (a) indicates the position of the electron beam for EDS measurement.

Table 1 Design composition (in at%) of superlattice alloys used in this study.

	La	Zr	Mg	Ni	Co	Al	Fe	B/A ratio
E14	16.28	0.00	6.98	65.11	11.63	0.00	0.00	3.30
E26	17.07	0.00	7.32	68.29	2.44	4.88	0.00	3.10
E29	16.93	0.02	7.33	68.40	2.44	4.88	0.00	3.12
E32	16.81	0.02	7.28	67.90	2.43	4.83	0.73	3.15

Table 2 The phase abundances (in wt%) for alloy E26 at different stages of hydrogenation obtained from a full-pattern analysis with the XRD data. ND denotes non-detectable.

	LaNi ₅	LaNi ₅ H ₆	LaMgNi ₄	LaMgNi ₄ H _{0.75}	LaMgNi ₄ H _{3.7}	LaMgNi ₄ H _{4.85}
PDF number	00-55-0277	04-017-3206	04-016-5766	04-016-5767	04-016-5768	04-016-5769
Space group	P6/mmm (191)	P6/mmm (191)	F-43m (216)	F-43m (216)	Pmn21 (31)	F-43m (216)
Structure type	Hexagonal	Hexagonal	Cubic	Cubic	Orthorhombic	Cubic
Lattice constant	5.0167, 3.9783	5.28, 4.181	7.17027	7.27871	5.1257, 5.52436, 7.45487	7.6584
As-prepared E26	91.4	ND	8.6	ND	ND	ND
α -phase @ 0.004 MPa	83.2	8.3	ND	2.1	6.4	ND
β -phase @ 2.4 MPa	ND	83.7	ND	ND	ND	16.3
After 1 cycle PCT	100	ND	ND	ND	ND	ND
After 7 PCT cycles w 250°C degas	92.3	ND	7.1	0.5	ND	ND