Degradation Characters of La-Mg-Ni-Based Metal Hydride Alloys: Corrosion and Pulverization Behaviors

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Abstract

Degradation behaviors of three typical La-Mg-Ni alloys, La_2MgNi_9 , $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ and $\text{La}_4\text{MgNi}_{19}$, were studied. $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ with $(\text{La},\text{Mg})_2\text{Ni}_7$ as main phase presents better discharge capacity and cycling stability. The three alloys suffer severe pulverization and corrosion after electrochemical cycles, which are considered to be the significant factor attributing to the capacity deterioration. However, the overall corrosion extent of the three cycled alloys aggravates successively, which is inconsistent with the result that La_2MgNi_9 presented poor cycling stability and also the assumption that alloy with high Mg content is easy to be corroded. The intrinsic anti-corrosion and anti-pulverization characteristics of the three alloys are mainly focused in this work. Immersion corrosion experiments demonstrate that the Mg-rich phases are more easily to be corroded. The corrosion resistance of the three alloys presents an improved trend which is inversely proportional to abundance of the Mg-rich phases. However, the anti-pulverization abilities present an inverse trend, which is closely related to the mechanical property of various phase structures. LaNi_5 with the highest hardness is easy to crack, but the soft $(\text{La},\text{Mg})\text{Ni}_2$ is more resistant to crack formation and spreading. Thus, the weaker corrosion of La_2MgNi_9 after electrochemical cycling is attributed to the better intrinsic anti-pulverization capability though the anti-corrosion is poor. As $\text{La}_4\text{MgNi}_{19}$ possesses excellent corrosion resistance, enhancement of the anti-pulverization ability is urgent for improvement in the cycling stability.

Keywords La-Mg-Ni-based alloys · Degradation behaviors · Corrosion · Pulverization

1 Introduction

RE-Mg-Ni-based alloys have received substantial attentions over the past decades owing to their excellent electrochemical performances in the nickel/metal hydride (Ni/MH) battery [1–5]. To date A_2B_7 -type RE-Mg-Ni alloys have been applied successfully in the commercial Ni/MH batteries [3]. However, AB_2 and AB_3 -type RE-Mg-Ni alloys present poor cycling stability though the theoretical

discharge capacities are higher than A_2B_7 -type alloys [6–8]. In addition, A_5B_{19} -type alloys have been reported to possess good electrochemical performances, but the cycling stability still need further development to meet the practical requirements [9, 10].

Degradation of the discharge capacity is considered to be mainly attributed to pulverization and corrosion of the electrode alloys during the reversible electrochemical cyclings [11, 12]. Corrosion of the alloys leads to direct degradation of the discharge capability, and pulverization improves corrosion due to the fresh surface of the alloy particles continuously exposing to the electrolyte. As to the RE-Mg-Ni alloys, it is found that these alloys are easily to be corroded into $\text{RE}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ [13–15]. And these kinds of corrosion products are loose and passive which cannot protect the matrix from further corrosion [15, 16]. Severe pulverization of RE-Mg-Ni alloys during cycling had also been reported in numerous works [13–17]. Degradation process of La-Mg-Ni-Co alloys has been classified into three stages: the pulverization and Mg

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oxidation stage, the Mg and La oxidation stage and the oxidation and passivation stage [14]. Thus, further improvement in the anti-pulverization and anti-corrosion resistant of the RE–Mg–Ni-based alloys is considered to be significant for the cycling stability. In addition, degradation of the hydrogen storage alloys is also demonstrated to be affected by the structural distortion upon the hydrogenation cyclings. Our previous works demonstrated that La–Mg–Ni alloys suffered hydrogen-induced amorphization (HIA) which remarkably worsened both the gas–solid and electrochemical storage capability [18, 19].

There are several compounds including AB_2 -, AB_3 -, A_2B_7 - and A_5B_{19} -type phases existing in the RE–Mg–Ni system, which makes the phase constitution of these alloys more complex [4, 5]. It is well accepted that A_2B_7 -type structure has better cycling stability than other phases. Li et al. reported that AB_3 phase was easily corroded by KOH [20]. Liu et al. [21] prepared single phase La–Mg–Ni alloys by stepwise powder sintering method and found that La_3MgNi_{14} with A_2B_7 -type phase presented good cycling stability, which was closely related to the pulverization trend of the alloys. Though the overall degradation characters of the RE–Mg–Ni-based alloys have been investigated in quite a number of works, diversity of the degradation characteristics of various compounds in this system is still lacking. In particular, coexisting of pulverization, corrosion and the structural distortion during the charge/discharge cycles makes it difficult to illustrate the degradation mechanisms of the individual phase.

Accordingly, understanding the distinction of degradation behaviors of the individual phase is the precondition for improvement in the cycling stability of the RE–Mg–Ni-based alloys. In the present study, degradation mechanisms of three typical La–Mg–Ni alloys: La_2MgNi_9 , $La_{1.5}Mg_{0.5}Ni_7$ and La_4MgNi_{19} have been systematically investigated. Corrosion and pulverization behaviors of the alloys, especially the intrinsic characteristics of the AB_3 -, A_2B_7 - and A_5B_{19} -type La–Mg–Ni phases during absorption/desorption cycling were generated.

2 Experimental

The as-cast La_2MgNi_9 , $La_{1.5}Mg_{0.5}Ni_7$ and La_4MgNi_{19} alloys were prepared using induction levitation melting in an argon atmosphere. Excessive Mg was added since some Mg would evaporate in the melting process. The alloys were melted two times and metallographic observation in large areas (about 5 mm × 5 mm) showed a uniform character indicating the microstructural homogeneity of the ingots, as displayed in Fig. S1 in the supplementary information. Then the as-cast alloys were annealed at 1143,

1173 and 1193 K, respectively, for 6 h protected in argon atmosphere.

The compositions of the ingot were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) using a ThermoFisher iCAP-6300 system. Metallographic microstructure of the alloys was observed using a laser scanning confocal microscope (LSCM, Olympus-OLS4000) and a scanning electron microscope (SEM, FEI-Qanta 400). Chemical composition was studied by energy dispersive spectroscopy (EDS). A Bruker-D8 Advance X-ray diffractometer (XRD) was used to detect the crystal structure of the alloys. The microstructural and crystallographic information were also measured by a field-emission transmission electron microscope (TEM, JEOL-2100 and FEI-F20).

Particle size of the cycled alloys was tested under a laser particle size analyzer (Malvern-Mastersizer 3000). Oxygen content of the electrochemical cycled and immersed alloys was performed on a nitrogen/oxygen tester (NCS-ON3000). Before the oxygen test, the samples were immersed in deionized water for 24 h, then washed using pure alcohol twice to remove the residual KOH and dried in a vacuum drying oven. Vickers hardness of various phases was tested by a FUTURE-TECH FM-300 micro-hardness tester under 10 and 25 gf with a keeping time for 15 s.

The pressure–composition–temperature curves (P – C – T) of the alloys were measured by a Suzuki-2SDWIN PCT system using the Sievert's method. Before the P – C – T measurement, the samples were pumped at 473 K for 2 h, hydrogenated under 3 MPa H_2 (purity 99.999%) for 5 h at 303 K, and then evacuated at 573 K for 2 h. The activated samples were also hydrogenated at 2 MPa for 600 s and desorbed by evacuating at 298 K for 1200 s for gaseous cycles.

The particles with dimension of about 40–50 μm were used for the electrochemical test and details of preparation of the electrode pellets can be found in Ref. [18]. The electrode pellets were firstly immersed in 6 mol L^{-1} KOH aqueous solution for 1 d, charged at a current density of 105 mA g^{-1} for 4 h, followed by a rest for 10 min, then discharged at the same current density to the cutoff voltage of -0.6 V.

3 Results and Discussion

ICP results of the annealed La_2MgNi_9 , $La_{1.5}Mg_{0.5}Ni_7$ and La_4MgNi_{19} alloys are $La_{2.087}Mg_{0.913}Ni_{9.103}$, $La_{1.520}Mg_{0.480}Ni_{7.064}$ and $La_{4.076}Mg_{0.924}Ni_{19.038}$, respectively, which are close to that of the designed composition except a little excess of Ni which may be due to the loss of La and Mg during the melting and annealing processes.

3.1 Microstructure and Hydrogen Storage Performance

Metallographic microstructures of the three alloys observed by LSCM and backscattering electronic (BSE) micrographs are shown in Fig. 1. It shows that four contrasts can be detected for the La_2MgNi_9 alloy, as marked with A–D in the LSCM image and 1–4 in the BSE image (similarly hereinafter). The chemical quantitation of various contrast from EDS analysis is listed in Table 1, from which the four phases are speculated to be $(\text{La,Mg})\text{Ni}_2$, $(\text{La,Mg})\text{Ni}_3$, $(\text{La,Mg})_2\text{Ni}_7$ and LaNi_5 . Five crystal structures including CaCu_5 , MgCu_4Sn , PuNi_3 , Ce_2Ni_7 and Gd_2Co_7 types are identified in XRD pattern of the La_2MgNi_9 alloy, as shown in Fig. 2a. The structural parameters and phase contents are refined and listed in Table 2. The results are consistent with the metallographic observation that the main phase is $(\text{La,Mg})\text{Ni}_3$, then $(\text{La,Mg})\text{Ni}_2$ and $(\text{La,Mg})_2\text{Ni}_7$, but the content of LaNi_5 is rare.

In case of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ and $\text{La}_4\text{MgNi}_{19}$ alloy, metallographic and XRD characterization indicate that $(\text{La,Mg})\text{Ni}_2$ disappears, $(\text{La,Mg})_5\text{Ni}_{19}$ emerges and LaNi_5 increases compared with La_2MgNi_9 . The main phases of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ and $\text{La}_4\text{MgNi}_{19}$ alloys are $(\text{La,Mg})_2\text{Ni}_7$

and $(\text{La,Mg})_5\text{Ni}_{19}$, respectively, and the structural parameters and phase contents are also listed in Table 2.

Figure 3 shows the P – C – T curves of the alloys, and the detailed data are given in Table 3. Theoretically, hydrogenation capability increases with reduction in the B -side stoichiometry in the La-Mg-Ni-based alloys. However, the maximum hydrogen absorption content of La_2MgNi_9 is slightly lower than that of $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$. It is ascribed to existence of $(\text{La,Mg})\text{Ni}_2$ phase in La_2MgNi_9 since $(\text{La,Mg})\text{Ni}_2$ can hardly absorb and desorb hydrogen at the room temperature [8]. The three alloys have analogous hydrogen absorption plateau. But both the desorption pressure and the reversible hydrogen capacity elevate with the increase in the B -side stoichiometry of the three alloys. Reversible hydrogen capacity of La_2MgNi_9 is only 1.15 wt%, and the hysteresis effect is more evident than the other alloys.

Electrochemical discharge curves of the three alloys are displayed in Fig. S2, and the detailed data are also shown in Table 3. Discharge capacities of La_2MgNi_9 and $\text{La}_4\text{MgNi}_{19}$ are lower than $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$. The lower discharge capacity of La_2MgNi_9 is due to the weak reversible hydrogen storage capacity. Similar result has been reported in Ref. [22] where alloy with high content of AB_3 -type phase

Fig. 1 Microstructures of annealed La_2MgNi_9 **a, d**; $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ **b, e**; $\text{La}_4\text{MgNi}_{19}$ **c, f** at low **a–c**; high **d–f** magnification

Table 1 EDS results of annealed alloys corresponding to areas marked in Fig. 1

Alloy	Location	La	Mg	Ni	Ni/(La + Mg)	Phase
La ₂ MgNi ₉	1	16.15	20.69	63.16	1.71	(La,Mg)Ni ₂
	2	17.93	9.18	72.89	2.69	(La,Mg)Ni ₃
	3	19.35	5.16	76.50	3.26	(La,Mg) ₂ Ni ₇
	4	17.17	0.00	82.83	4.82	LaNi ₅
La _{1.5} Mg _{0.5} Ni ₇	1	16.31	10.32	73.01	2.63	(La,Mg)Ni ₃
	2	18.91	4.51	76.58	3.27	(La,Mg) ₂ Ni ₇
	3	17.87	0.00	83.13	4.96	LaNi ₅
	4	17.74	3.30	78.95	3.75	(La,Mg) ₅ Ni ₁₉
La ₄ MgNi ₁₉	1	18.31	4.37	77.32	3.41	(La,Mg) ₂ Ni ₇
	2	19.16	2.73	78.11	3.57	(La,Mg) ₅ Ni ₁₉
	3	17.35	0.00	82.65	4.76	LaNi ₅

Fig. 2 XRD profiles of annealed La₂MgNi₉ **a**; La_{1.5}Mg_{0.5}Ni₇ **b**; La₄MgNi₁₉ **c****Table 2** Crystal structure, cell parameters and phase content of annealed alloys

Alloy	Phase type	<i>a</i> (nm)	<i>c</i> (nm)	Content (wt%)
La ₂ MgNi ₉	MgCu ₄ Sn	0.71660	—	4.1
	PuNi ₃	0.50358	2.43612	61.4
	CaCu ₅	0.50182	0.39806	0.5
	Ce ₂ Ni ₇	0.50387	2.42605	13.6
	Gd ₂ Co ₇	0.50350	3.63793	20.4
La _{1.5} Mg _{0.5} Ni ₇	PuNi ₃	0.50339	2.42432	11.1
	Ce ₂ Ni ₇	0.50334	2.42635	32.6
	Gd ₂ Co ₇	0.50341	3.43493	21.9
	Ce ₅ Ni ₁₉	0.50319	4.84459	16.3
	Pr ₅ Co ₁₉	0.50347	3.22350	13.5
	CaCu ₅	0.50182	0.39806	4.6
	Ce ₂ Ni ₇	0.50341	2.42416	22.8
	Gd ₂ Co ₇	0.50298	3.63639	10.7
La ₄ MgNi ₁₉	Ce ₅ Ni ₁₉	0.50323	4.83377	27.5
	Pr ₅ Co ₁₉	0.50328	3.22454	15.3
	CaCu ₅	0.50212	0.39792	23.7

presents lower gaseous and electrochemical capacity. While the high content of LaNi₅ which is unsuited for the electrochemical application for the high plateau [23]

Fig. 3 *P*–*C*–*T* curves of three alloys (Abs and Des are the abbreviation for the absorption and desorption, respectively)

attributes to the lower discharge capability of La₄MgNi₁₉. After 100 electrochemical cyclings, capacity retention of La₂MgNi₉ is about 70%, which agrees well with that of the alloy with the same composition reported by Hu et al. [24]. La₄MgNi₁₉ has similar cycling stability compared with La₂MgNi₉, while La_{1.5}Mg_{0.5}Ni₇ presents higher capacity retention of 75%.

Table 3 Hydrogen storage performances of three alloys

Alloy	MGC (wt%)	RGC (wt%)	DC (mA h g ⁻¹)	S ₁₀₀ (%)
La ₂ MgNi ₉	1.594	1.15	350.8	70.3
La _{1.5} Mg _{0.5} Ni ₇	1.619	1.275	365.5	75.4
La ₄ MgNi ₁₉	1.572	1.443	332.1	70.1

MGC the maximum gaseous absorption capacity, RGC reversible gaseous capacity, DC the maximum discharge capacity, S₁₀₀ electrochemical capacity retention after 100 cycles

3.2 Overall Degradation Characteristics After Electrochemical Cycling

Firstly, overall characters of the degradation behaviors of the three alloys after 100 electrochemical cyclings were generated. From morphology and EDS results, it is clear that pulverization and corrosion have occurred (only La₂MgNi₉ alloy is presented in Fig. 4). XRD analysis shows that La(OH)₃, Mg(OH)₂ and La₂O₃ appear in the cycled

La_{1.5}Mg_{0.5}Ni₇ and La₄MgNi₁₉ alloys, as displayed in Fig. 5. It is noteworthy that corrosion products of the cycled La₂MgNi₉ are less than the other two alloys where Mg(OH)₂ is the main product. TEM observation of the cycled La₂MgNi₉ alloy shows three kinds of corrosion products including stick-, needle- and particle-like morphologies as illustrated in Fig. 6 (marked with 1, 2 and 3, respectively). Selected area electronic diffraction (SAED) and high-resolution TEM (HRTEM) identify the stick-,

Fig. 4 Morphologies of original **a**; electrochemical cycled particles at low **b**; high **c** magnification, and EDS analysis of La₂MgNi₉ alloy by cycling **d**

Fig. 5 XRD profiles of La_2MgNi_9 , $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ and $\text{La}_4\text{MgNi}_{19}$ after electrochemical cycling

needle- and particle-like products to be $\text{La}(\text{OH})_3$ combined with La_2O_3 , $\text{Mg}(\text{OH})_2$ and MgO , details are provided in the supplementary information (Figs. S3–S5). The reason why $\text{La}(\text{OH})_3$ and La_2O_3 can hardly be detected in XRD in the cycled La_2MgNi_9 alloy may be due to their low content. The results are consistent with other studies on the corrosion products of a $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ alloy [25]. $\text{Mg}(\text{OH})_2$ and MgO are close to the alloy surface but very loose. It also agrees well with the previous works that corrosion products of Mg are gel type and cannot form a solid protective layer for further corrosion [15, 16].

Furthermore, oxygen contents (Table 4) of the electrochemical cycled alloys follow the order that $\text{La}_2\text{MgNi}_9 < \text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7 < \text{La}_4\text{MgNi}_{19}$, which is coincident with that the cycled La_2MgNi_9 alloy presents much less corrosion products. This result raises question that corroded extent of the three alloys is inconsistent with the electrochemical performances that La_2MgNi_9 possesses

poor cycling stability. It also disagrees with the consideration that high Mg content is harmful to the corrosion resistance in La-Mg-Ni-based alloys [20, 26]. In order to comprehend this fact further, the intrinsic corrosion resistance of the three alloys was investigated next.

3.3 Intrinsic Anti-corrosion Properties

Because pulverization can increase the surface area and then accelerate corrosion, immersion corrosion test was adopted to avoid influence of pulverization on characterization of the intrinsic corrosion resistant. The alloy particles with the same diameter (around 40 μm) were immersed in KOH solution at 60 $^\circ\text{C}$ for 15 d. Then the morphology, phase structure and oxygen content were measured for characterization of the intrinsic corrosion behaviors. SEM micrographs and EDS analysis of the alloy particles illustrate that severe corrosion occurred after immersion, and the typical results are shown in Fig. 7. (Only La_2MgNi_9 alloy particles are given here.) Compared to the electrochemical cycled alloys, the stick-like products which have been confirmed as composites of $\text{La}(\text{OH})_3$ and La_2O_3 , are remarkable in the immersed samples which is due to aggravated corrosion at higher temperature.

XRD profiles identify that the corrosion products are mainly $\text{La}(\text{OH})_3$, but La_2O_3 cannot be detected in the immersed alloys, as shown in Fig. 8. Coincidentally, It was found from SAED that the stick-shaped phase is single-phase $\text{La}(\text{OH})_3$, as shown in Fig. S6b. Besides, $\text{Mg}(\text{OH})_2$ and MgO are also found existing in the immersed samples, and their morphologies are the same with that in the electrochemical cycled alloys (Fig. S6). However, $\text{Mg}(\text{OH})_2$ can only be detected in La_2MgNi_9 from identification of XRD, indicating that corrosion of Mg is violent in La_2MgNi_9 . Oxygen contents of the immersed alloys as listed in Table 4 indicate that severity of corrosion of the three alloys are $\text{La}_2\text{MgNi}_9 > \text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7 > \text{La}_4\text{MgNi}_{19}$.

Fig. 6 TEM images of alloy particles at **a** low; **b**, **c** high magnification of La_2MgNi_9 alloy after electrochemical cycling

Table 4 Oxygen contents and size retention of alloys

Alloy	Oxygen content after electrochemical cycling (wt%)	Oxygen content (wt%) after immersion	Size retention after gaseous cycling (%)
La ₂ MgNi ₉	2.68	4.66	84.6
La _{1.5} Mg _{0.5} Ni ₇	3.21	4.38	68.5
La ₄ MgNi ₁₉	3.62	4.14	66.5

Fig. 7 Morphologies at low **a**; high **b**; magnification and EDS spectra **c** of La₂MgNi₉ particles after immersion **Fig. 8** XRD profiles of La₂MgNi₉, La_{1.5}Mg_{0.5}Ni₇ and La₄MgNi₁₉ alloys after immersion

This trend is the same with that in Ref. [21] where oxygen contents of single-phase La₂MgNi₉, La₃MgNi₁₄ and La₄MgNi₁₉ alloys gradually increase after electrochemical cycling.

To provide detailed information of the relationship between the corrosion behaviors and phase constitution, immersion test was also applied to massive samples. (The condition is the same with that of the powder samples.) Figure 9 shows SEM-BSE micrographs of the immersed

samples. (Only La_{1.5}Mg_{0.5}Ni₇ alloy is present here.) Obviously, the corroded extent is inhomogeneous which is considered to be caused by differences in the anti-corrosion capabilities of the various phases. EDS analysis on two regions with diverse corrosion grades (as marked with 1 and 2 in Fig. 9a) shows no Mg but less O existing in region 1. While, high content of Mg and O can be detected in region 2 with more severe corroded extent. Likewise, EDS mapping indicates that the region possessing more Mg presents richer O, as shown in Fig. 10. Similar result is more evident in the as-cast alloys, which is attributed to the inhomogeneous chemical composition of the as-cast alloy, details can be seen in the supplementary information (Figs. S7 and S8).

The aforementioned results demonstrate that the Mg-rich phases are easy to be corroded in the alkaline solution. It has been well demonstrated that Mg solubility in La-Mg-Ni alloys follows the order that (La,Mg)Ni₂ > (La,Mg)Ni₃ > (La,Mg)₂Ni₇ > (La,Mg)₅Ni₁₉ > LaNi₅ [27]. Thus, the intrinsic corrosion resistances of various phases in the La-Mg-Ni system are considered to be according with the inverse trend. This result is in agreement with several works where AB₂- and AB₃-type La-Mg-Ni alloys have suffered serious corrosion after electrochemical experiments [8, 20, 21]. The tendency is also exactly identical with that the corrosion resistance is inversely proportional to the abundance of the Mg-rich phases. La₂MgNi₉ presents worse anti-corrosion capability because

Fig. 9 SEM images at low **a**; high **b**; magnification, EDS spectra of different points **c** in annealed $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ alloy after immersion

Fig. 10 EDS mapping **a**; elements La **b**; Mg **c**; O **d** distribution of annealed $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ alloy after immersion

the contents of the Mg-rich $(\text{La},\text{Mg})\text{Ni}_2$ and $(\text{La},\text{Mg})\text{Ni}_3$ are higher than the other two alloys. However, it is also puzzled that the trend of the intrinsic corrosion resistance is opposite to the overall corrosion extent of the three alloys after electrochemical cyclings. Concern to the fact that corrosion extent of the electrode alloys is also closely related to severity of pulverization during the electrochemical charge/discharge process, the pulverization properties of the alloys are carefully characterized then.

3.4 Intrinsic Anti-pulverization Properties

In order to avoid the influence of the additives in the electrochemical test on characterization of the intrinsic pulverization behavior, the alloys are gaseous hydrogenated and dehydrogenated for 30 cycles. Morphology observation indicates that remarkable pulverization has occurred and the decrease in the particle size and emergence of cracks can be seen clearly in the cycled alloys, as shown in Fig. 11. (Only La_2MgNi_9 alloy is present here.)

Then the particle sizes before and after cycling (S_b and S_a , respectively) are measured, and the size retention is calculated by S_b/S_a as displayed in Table 4. It shows that severity of pulverization for the three alloys are $\text{La}_2\text{MgNi}_9 < \text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7 < \text{La}_4\text{MgNi}_{19}$, which is just contrary to the tendency of the corrosion extent after the immersion experiment. Combined with the results of the intrinsic anti-corrosion and pulverization characterization, we can conclude that the weaker corrosion extent of La_2MgNi_9 in the electrochemical test is attributed to its better intrinsic anti-pulverization capability though the intrinsic anti-corrosion of La_2MgNi_9 is worse.

It has been well accepted that pulverization is induced by the cell volume expansion upon hydrogen absorption [11, 12]. Thus, large volume change will lead to severe pulverization. Unfortunately, exact measurement of the volume expansion in the present work is difficult due to the multi-phase microstructure. Instead, we summarize the volume changes according to other experimental works [11, 28–31] where microstructures of these alloys are all single phases to ensure the accuracy as far as possible. Based on the data as listed in Table 5, there is no regular trend for the volume changes among the various structures in La-Mg-Ni system. And, no unique relationship between the reported volume expansion data and the pulverization performances in the present work can be found.

Besides, pulverization is also believed to depend on the mechanical properties of the alloys [11, 12]. Alloys with

Fig. 11 Morphologies of the La_2MgNi_9 particles before **a, b**; after **c, d**; gaseous cycling at low **a, c**; and high **b, d** magnification

Table 5 Volume expansion of various La-Mg-Ni phases by hydrogenation in the reported works

Alloy	$\text{La}_{2.3}\text{Mg}_{0.7}\text{Ni}_9$	La_2MgNi_9	LaMg_2Ni_9	$\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$	$\text{La}_{1.63}\text{Mg}_{0.37}\text{Ni}_7$	$\text{La}_4\text{MgNi}_{19}$	LaNi_5
Type	AB_3	AB_3	AB_3	A_2B_7	A_2B_7	A_5B_{19}	AB_5
$\Delta V/V$	27.1	26.7	23	25.2	25.6	25.3	24
References	[28]	[28]	[29]	[30]	[30]	[31]	[11]

the more ductile character are more resistant to pulverization than the brittle materials. Usually, hydrogen storage alloys are hard and brittle; thus, direct measurement of the ductility is difficult. Alternatively, Vickers hardness has been used to evaluate the preference of pulverization for the hydrogen storage alloys. And, previous works have found an almost inverse relationship between Vickers hardness and the pulverization rate [11, 12, 32], suggesting the availability of Vickers hardness measurement for characterization of the anti-pulverization ability.

Figure 12 shows the microstructures after indentations of various phases in La_2MgNi_9 and $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ alloys. Evolution of Vickers hardness can be seen in Fig. 13. It

presents a linear relation between the Vickers hardness and *B*-side stoichiometry of the structures, which also agrees well with the pulverization behaviors of the alloys. Obviously, the mechanical property is an important factor affecting the anti-pulverization ability of the La-Mg-Ni phases. Under low loading in the hardness test, micro-cracks can hardly be observed in all three phases. As the test force increases, micro-cracks can be seen in all these phases, but there is no obvious difference between them. Differently, LaNi_5 is the hard phase, but hardness of $(\text{La},\text{Mg})\text{Ni}_2$ is far more lower than the other phases.

To comprehend more understanding on the crack formation of various phases, a massive sample with a polished

Fig. 12 Original optical images of La_2MgNi_9 **a, b**; $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ **c, d**; alloys, and indentation morphologies of La_2MgNi_9 **e, f**; $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ **g, h**; alloys **e, g**; **f, h** were tested under 10 and 25 **g, f**, respectively)

Fig. 13 Micro-hardness of various phases

surface was partially charged by electrochemical method, and the morphology and distribution of cracks were observed. To highlight characters of the hard and soft phases, the as-cast La_2MgNi_9 alloy was selected for the high content of LaNi_5 and $(\text{La,Mg})\text{Ni}_2$. Microstructure characteristics of the as-cast La_2MgNi_9 alloy are given in the supplementary (Figs. S9 and S10). As shown in Fig. 14, quite a number of cracks can be observed in the sample which is only charged for 10 min. Most of the cracks exist in LaNi_5 with the darkest contrast in the BSE image. One reason is that LaNi_5 is the catalytic phase that is primarily charged in the La-Mg-Ni system [33, 34]. More importantly, it is also ascribed to the brittle character of LaNi_5

which agrees well with the above result that the hard phase is easy to form crack.

It is noteworthy that cracks are often stopped in front of $(\text{La,Mg})\text{Ni}_2$. Obviously, the soft phase is more resistant to form crack and able to prevent the crack spreading. Similar result has been reported in other studies where ductile secondary phases are believed to be beneficial to the cycling stability [35]. However, our results are different from Ref. [21] that pulverization of single-phase La_2MgNi_9 , $\text{La}_3\text{MgNi}_{14}$ and $\text{La}_4\text{MgNi}_{19}$ alloys present an increasing trend which is considered to be caused by the discrete expansion/contraction of $[\text{AB}_5]$ and $[\text{AB}_2]$ subunits. This may be attributed to the multi-phase microstructure in the present work. Based on our results, hardness differences of the AB_3 -, A_2B_7 - and A_5B_{19} -type phase are small. While, LaNi_5 presents obvious brittle nature and severe pulverization of $\text{La}_4\text{MgNi}_{19}$ is attributed to the high content of LaNi_5 . As to La_2MgNi_9 , little LaNi_5 but existence of the soft $(\text{La,Mg})\text{Ni}_2$ make it more resistant to crack emergence. These findings also enlighten a way to improve the anti-pulverization ability by introducing appropriate content and distribution of soft secondary phases.

4 Conclusion

In the present study, corrosion and pulverization behaviors of three typical La-Mg-Ni alloys, La_2MgNi_9 , $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ and $\text{La}_4\text{MgNi}_{19}$ have been systematically investigated.

Fig. 14 Morphologies of as-cast La_2MgNi_9 alloy in different regions **a**, **b** after being partially charged

All the alloys present multi-phase microstructure with $(\text{La,Mg})\text{Ni}_3$, $(\text{La,Mg})_2\text{Ni}_7$ and $(\text{La,Mg})_5\text{Ni}_{19}$ as the main phase, respectively. $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ possesses better electrochemical properties among the three alloys. It is found that pulverization and corrosion with the main product $\text{La}(\text{OH})_3$, combined with La_2O_3 , $\text{Mg}(\text{OH})_2$ and MgO , have occurred after the electrochemical cycling. The overall corrosion extent of the electrochemical cycled alloys follow the order $\text{La}_2\text{MgNi}_9 < \text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7 < \text{La}_4\text{MgNi}_{19}$. Immersion test demonstrates that the Mg-rich phases are easy to be corroded in the alkaline solution. The intrinsic corrosion resistance are found to be $\text{La}_2\text{MgNi}_9 < \text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7 < \text{La}_4\text{MgNi}_{19}$, which is inversely proportional to the content of the Mg-rich phases. However, the intrinsic anti-pulverization ability just presents an inverse trend which is $\text{La}_2\text{MgNi}_9 > \text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7 > \text{La}_4\text{MgNi}_{19}$. It is found that the mechanical property is an important factor affecting the anti-pulverization ability. Vickers hardness elevates with the increase in the B-side stoichiometry of the various phases, which agrees well with the pulverization behaviors of the alloys. Furthermore, LaNi_5 with the highest hardness is found to be easy for crack formation, but the soft $(\text{La,Mg})\text{Ni}_2$ is more resistant to form crack and able to prevent the crack spreading. The weaker corrosion extent of La_2MgNi_9 in the electrochemical test is attributed to its better intrinsic anti-pulverization capability though the intrinsic anti-corrosion of La_2MgNi_9 is worse.

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