La₂MgNi_{7.5}Co_{1.5} Hydrogen Storage Alloy Prepared by the Magnetic Field Assisted Sintering

Feng Yang^{1,2}, Hong Li¹ and Jing Liu^{1,a}

¹School of Materials and Architectural Engineering, Guizhou Normal University, Guiyang 550001, China

²College of Materials, Xiamen University, Xiamen 361005, China

Abstract. La₂MgNi_{7.5}Co_{1.5} hydrogen storage alloy was prepared by magnetic field assisted sintering method. The phase structure and hydrogen absorption properties of the alloy were systematically studied by means of isothermal constant volume method, XRD, SEM, EDS and HPDSC etc. The results showed that the main phase is PuNi₃ type structure of (La, Mg) (Ni, Co)₃. The impure phase La (Ni, Co)₅ decreased firstly and increased later with the magnetic field increased. Addition of Co can improve the hydrogen absorption and desorption properties of the alloy obviously, the maximum hydrogen storage capacity reached 1.538 wt.%. The dehydrogenation DSC curve of the alloy has a multimodal characteristics. The magnetic field changed hydrogen desorption thermal behavior of (La, Mg)(Ni, Co)₃ phase significantly. The alloy after activation showed excellent hydrogen absorption and desorption kinetics performance.

1 Introduction

In hydrogen storage materials, rare earth-magnesium-nickel AB₃ alloy with mild hydrogen storage conditions, moderate platform pressure and abundant reserves of raw materials, etc. The alloys can be prepared by induction melting^[1-2], vacuum rapid quenching method^[3] and so on. However, the volatilization of magnesium is difficult to predict and control. Multiple remelting and long-time of homogenization increase process and cost. At the same time, the presence of amorphous may reduce the electrochemical capacity. Some researchers prepared the alloy by means of sintering method^[4-7] and obtained the product which has the main phase of PuNi₃ type structure. But the sintering time is longer, and need two or more intermediate alloys.

In recent years, with the gradual improvement of electromagnetic theory and the emergence of superconducting magnetic field, the magnetic field effect on the thermodynamics and kinetics of hydrogen storage alloy system has been found gradually^[8-11]. The author's research group prepared the Mg-Ni^[12] and La-Mg-Ni^[13] system hydrogen storage alloys by means of the hydrogenation combustion synthesis technology under the strong magnetic fields and found that the synthesis temperature decreased, the synthesis time shorten and the dehydriding temperature decreased significantly. The kinetics performance can be obviously improved. Accordingly, La₂MgNi_{7.5}Co_{1.5} hydrogen storage alloy has been prepared by the magnetic field assisted sintering technology (MASS) in this paper. The influences of

magnetic field on alloy phase structure and hydrogen absorption and desorption behavior were researched.

2 Experimental

Elemental powders (La<40 μm, purity>99.5%; Mg<150 μm, purity>99.5%; Ni≈2~3 μm, purity>99.5%; Co<75 μm, purity>99.5%) were weighed and mixed according to the design composition. Then, the premixed powder was pressed into Φ15 mm × (3~5) mm cylindrical sample. All mixed sample and the sampling process were carried out in the glove box (MBRAUN), which was protected by argon.

The cylindrical samples were put into a high pressure reaction kettle. After vacuumizing and filling in 0.5 MPa Ar, the reactor was placed in a strong magnetic field of 0~8 T and heated with 20°C/min through a tubular resistance furnace. The synthesis temperature and time were 1073 K and 4 h, respectively. Table 1 listed the sample numbers and process conditions of AB₃ alloy prepared by MASS method.

Table 1. The numbers and process conditions of the La₂MgNi_{7.5}Co_{1.5} alloys prepared by MASS.

Sample	Process conditions	Magnetic field / T
S0	1073 K×4h	0
S1	1073 K×4h	1
S2	1073 K×4h	2
S4	1073 K×4h	4
S8	1073 K×4h	8

^a Corresponding author: 408452347@qq.com

The phase structure was characterized by X-ray diffraction (Panalytical X'pert PRO). The tissue morphologies were observed by metallographic microscope. The pressure-composition-isotherms and kinetic properties were measured by dual-channel automatic PCT tester (SUZUKI SHOKAN CO, LTD). The thermal analysis of the hydrides was carried out by the high pressure differential scanning calorimeter (Netzsch DSC 204 HP Phoenix).

3 Results and discussion

3.1 Phase structure and morphology

Figure 1 is the X-ray diffraction diagram of $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ alloy prepared by MASS method. The figure shows that all the alloys consist of the same main phase with PuNi_3 (JCPDS 65-2135) type structure, this phase can be expressed as $(\text{La}, \text{Mg})(\text{Ni}, \text{Co})_3$. Because the Co and Co compounds were not found, it means that all the Co atoms can replace the positions of Ni. Compared with the La_2MgNi_9 without Co substituted, the alloy appeared more LaNi_5 phase (JCPDS 65-0942). With the magnetic field increases, the LaNi_5 phase decreases first and then increases and the lowest content can be found at 4 T.

The lattice parameters of $(\text{La}, \text{Mg})\text{Ni}_3$ phase can be calculated through the Jade 5 software and listed in table 2. It can be seen that the lattice parameters a -, c and cell volume V of the main phase firstly increased and then decreased with the increase of magnetic field strength, and reached the maximum value at 4 T. Because of the atomic radii of Co is greater than Ni, when Co replaces Ni, the cell will be distorted and the unit-cell volume will increase. It can be speculated that $(\text{La}, \text{Mg})\text{Ni}_3$ phase was formed first during sintering, due to the larger atomic radius of Co is difficult to occupy the location of Ni in AB_3 structure. When the magnetic field strength is not big enough, the content of Co in the AB_3 structure is relatively low and more Co existing in $\text{La}(\text{Ni}, \text{Co})_5$ phase. When the magnetic field strength reaches 4 T, the Co reached peak in $(\text{La}, \text{Mg})\text{Ni}_3$, LaNi_5 type phase almost disappeared. But when the magnetic field strength increases further (8T), the LaNi_5 phase emerges again. In order to confirm the above speculation, the cell parameters of LaNi_5 phase were calculated and listed in table 3. From the table, an obvious LaNi_5 phase appeared in the four alloys (S0, S1, S2 and S8), which the lattice parameters and the unit-cell volume were greater than the corresponding value of LaNi_5 phase in the database. Combined with the results in Table 2, it can be judged that part of Co phase replaced the Ni position in the LaNi_5 . But from tables 2 and 3, it can be seen that the lattice parameter of AB_3 phase in S8 alloy is different from that of S0 and S1 alloy, which is close to that of the S2 and S4 alloy. At the same time, the lattice parameters of LaNi_5 phase also is smaller than S0, S1 alloy, but slightly larger than that of the pure phase value. It can be deduced that the $\text{La}(\text{Ni}, \text{Co})_5$ generation mechanism without magnetic field or with a low magnetic field may be different from that with a high-intensity magnetic field. We can infer that $(\text{La}, \text{Mg})(\text{Ni}, \text{Co})_3$ phase can

decompose to form $\text{La}(\text{Ni}, \text{Co})_5$ phase under 8 T magnetic field due to the AB_3 structure becomes unstable.

Figure 1. The XRD patterns of $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ composites prepared by MASS. (a) S0; (b) S1; (c) S2; (d) S4; (e) S8.

Table 2. The lattice parameter of PuNi_3 in $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ composites prepared by MASS

Sample	$a(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$	c/a
S0	4.9793	24.3539	522.9	4.891
S1	4.9931	24.3018	524.7	4.867
S2	5.0044	24.4095	529.4	4.878
S4	5.0118	24.4108	531.0	4.871
S8	5.0044	24.3705	528.6	4.870

Table 3. The lattice parameter of LaNi_5 in $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ composites prepared by MASS

Sample	$a(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$	c/a
S0	5.028	4.004	87.7	0.796
S1	5.031	3.991	87.5	0.793
S2	5.036	3.987	87.6	0.792
S8	5.031	3.981	87.3	0.791
LaNi_5 (65-0942)	5.024	3.978	87.0	0.792

3.2. Activation properties

Figure 2 is the activation properties of $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ alloy prepared by MASS method. The figure shows that all samples but S4 can be fully activated in 2 cycles. S8 can absorb hydrogen quickly even without any activation. S4 needs four cycles to be activated. According to figure 2 and previous analysis, the poor activation performance is due to the dense structure of alloy. But the highest capacity of 1.55 wt.% can be obtained from S4, and it can absorb 90% H of the maximum capacity within 15 s after activation. In the initial 5 cycles, the capacity of S4 and S8 are increase slightly. The cycle stability of alloy was increased after partial substitution of Ni with Co^[14]. As it is known, Co is an essential element in the alloy electrode. Cobalt can reduce the volume change, strengthen the interatomic bonding force and inhibit the pulverization of alloy during the hydrogen absorption and desorption^[15-17]. As mentioned above, when the magnetic field strength is greater than 2 T, the Co content of $(\text{La}, \text{Mg})(\text{Ni}, \text{Co})_3$ main phase is higher, so the cycle stability of the three samples is also better than S0 and S1. In addition, all the samples prepared under the magnetic field can be completed saturation hydrogen-absorbing within 20 s after activation. Although the XRD results in Fig 1 show that there is only the AB_3 phase in the alloy except for a very small amount of $\text{La}(\text{Ni}, \text{Co})_5$, the A side of the alloy

may be composed of Mg-rich and Mg-depleted zone, the B side may be composed of Co-rich region and Co-depleted zone. The interfaces between them provide plenty of diffusion paths of hydrogen atoms, so the hydrogen absorption rates of the alloy is greatly improved.

Figure 2. The hydriding curves under 300 K and 4.0 MPa H₂ at different cycles for La₂MgNi_{7.5}Co_{1.5} composites prepared by MASS.

3.3 The hydrogen absorption and desorption thermodynamic properties

The PCT curve of La₂MgNi_{7.5}Co_{1.5} alloy prepared by MASS method is given in figure 3. It can be seen that S0, S1 and S8 alloys have some platform features, indicating that the hydride may be partially formed after hydrogenated. From the XRD results, the hydride should be formed by the La(Ni, Co)₅ phase. However, there is no obvious platform can be found in the whole range of PCT test for S2 and S4. It suggested that the Co adding had no obvious effect on the hydrogen absorption and desorption equilibrium pressure. Table 4 summarizes the PCT experiments results of La₂MgNi_{7.5}Co_{1.5} alloy prepared by MASS process. Because some samples have no clear platform, the hydrogen absorption and desorption pressure (P_{ab} , P_{dc}) which the hydrogen absorption amount reaches to 0.8 wt.% should be considered as 'platform pressure', hysteresis factor $H_f = \ln(P_{ab}/P_{dc})$, the hydrogen desorption rate $D_{Rate} = \text{dehydrogenating capacity } C_{dc} / \text{hydrogen absorption capacity } C_{ab}$.

It can be seen from table 4 that S4 has the minimum hysteresis coefficient (0.427) and the highest hydrogen absorption capacity (1.538 wt.%), but the amount and the rate of hydrogen desorption is low. According to the results of our previous works^[18-19], for AB₃ alloy, the solid solution phase should be obtained after hydrogen absorption^[20]. As the hydrogen desorption processes, the solid solution content of hydrogen in the alloy is

decreased, the inner stress is released and the driving force is reduced, it becomes difficult to release hydrogen. When a small amount of LaNi₅ type phase exists in the alloy, the amount of the alloy hydrogen desorption, especially the rate of hydrogen desorption had been improved obviously. The D_{Rate} of S0 even reaches to 0.998, indicating that the La(Ni, Co)₅ phase may play the role to attract and capture H atoms in the hydrogen desorption, and subsequently as a hydrogen diffusion channel to promote the hydrogen desorption thoroughly.

Figure 3. The PCT curves at 300 K for La₂MgNi_{7.5}Co_{1.5} composites prepared by MASS.

Table 4. The results of the hydrogen A/D properties of La₂MgNi_{7.5}Co_{1.5} composites prepared by MASS

No.	H _f	C _{ab} /wt.%H	C _{dc} /wt.%H	D _{Rate} /%
S0	0.568	1.386	1.383	0.998
S1	0.476	1.452	1.436	0.989
S2	0.687	1.467	1.343	0.915
S4	0.427	1.538	1.383	0.899
S8	0.495	1.485	1.376	0.927

3.4 The hydrogen desorption thermal behavior

Figure 4 shows the hydrogen desorption DSC curve of La₂MgNi_{7.5}Co_{1.5} alloy prepared by MASS method. It can be seen that the magnetic field has significant influences on the desorption thermal behavior of the alloy. Without the magnetic field, there are two obvious endothermic peaks in the vicinity of 320 and 340 K, the endothermic peak ends at about 360 K, which indicates that the hydrogen desorption process is almost complete. As noted earlier, there is a certain amount of La(Ni, Co)₅ phase exists in the S0 samples, and hydrogen desorption kinetics performance of LaNi₅ alloy is better than that of AB₃ phase. Therefore, the endothermic peak located at 320 K might correspond to the dehydrogenation of La(Ni, Co)₅ hydride. Since the presence of multi-phase structure in S0, the diffusion of hydrogen atoms is relatively easy and the hydrogen desorption temperatures is relatively low. However, since the low capacity of S0, its enthalpy (peak area) is relatively small. The peak at about 340 K may correspond to the dehydrogenation of the main phase AB₃. S1 also has two obvious endothermic peaks, which is similar to S0. But the peak located at the low temperature zone is about 15 K lower than that of S0. Similarly, this peak corresponds to the dehydrogenation of La(Ni, Co)₅ hydride, and the other one located at about 340 K may also correspond to dehydrogenation of the main phase AB₃. With the increasing of the magnetic field intensity, the dehydrogenation peak of the main phase AB₃ is gradually shifted to high temperature region.

The magnetic field had no obvious influence on the desorption thermal behavior of the $\text{La}(\text{Ni}, \text{Co})_5$ hydride phase, but it has great influence on the desorption peak of the AB_3 main phase. It can be speculated that the dehydrogenation of AB_3 is a desolventizing process of the solid solution phase, so there is no fixed reaction temperature. When the magnetic field intensity was increased to 4 T or 8 T, three endothermic peaks appeared in the dehydrogenation DSC curves. The first peak at the lowest temperature is corresponding to the dehydrogenation of $\text{La}(\text{Ni}, \text{Co})_5$ phase. The two latter peaks corresponding to dehydrogenation of $(\text{La}, \text{Mg})(\text{Ni}, \text{Co})_3$ phase. The peak located in slightly lower temperature (330~340 K) may correspond to the desolventizing of Co rich AB_3 phase, while the other one (365~370 K) may correspond to desolventizing of Co depleted AB_3 phase.

Figure 4. The DSC curve obtained by heating the hydrogenated samples under 0.1 MPa argon at a rate of 6.0 K/min for $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ composites prepared by MASS.

3.5 Hydrogen absorption and desorption kinetics properties of alloys

Figure 5a is the hydrogenation kinetics of $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ alloy after activated at 300 K and 1.0 MPa H_2 . It can be seen that S4 has the best kinetic performance, which can reach 90 percent of the maximum hydrogen absorption capacity within 20 s, and the highest amount (1.34 wt.%) within 150 s. S2 and S4 have approximate rates and capacity (1.31 wt.%). The hydrogen absorption rate and the amount of hydrogen absorption (1.13 wt.%) of S0 is the lowest. Overall, the phase composition and micro-morphology of the alloys have important influence on the hydrogenation kinetics. Among them, the major factors to affecting the activation performance is the phase interface. As mentioned above, since the second phase of S2 and S4 is less and unevenly distributed, the micro-structure is denser and lacked of diffusion path, they need more activation times. However, the kinetics performances of S2 and S4 are greatly improved after activation, which is due to the presences of a large number of cracks and fresh surface for the diffusion and adsorption of hydrogen. Another reason to affects the kinetic properties of $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ alloy may be the distribution of Co in the alloy. TaiYang et al.^[21] found that the alloy adding Co is prone to form crack during the hydrogen absorption, which increasing the reaction surface and improved the kinetic performance of the alloy. As mentioned, Co content is very low in the main phase AB_3 and mainly distributed in the $\text{La}(\text{Ni}, \text{Co})_5$ phase without or under low magnetic field. Since AB_3 is a major contribution phase during

hydrogen absorption, the catalytic effect of Co in S0 and S1 is weaker, and the hydrogen absorption kinetic performance is poor accordingly. The XRD results show that impurity phase $\text{La}(\text{Ni}, \text{Co})_5$ also exists in S8, but Co content of the main phase AB_3 is close to that of S2 and S4 alloy, so its dynamic performance is good. The results reaffirmed the above speculation 'the formation mechanism of LaNi_5 phase under no (weak) magnetic fields is different from that under strong magnetic fields'.

Figure 5. The hydriding kinetics under 300 K and 1.0 MPa H_2 for (a) $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ composites prepared by MASS; (b) Comparison of La_2MgNi_9 and $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ under 4T.

Figure 5b compared the hydrogenated kinetics of La_2MgNi_9 and $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ alloys prepared by sintering under 4 T magnetic field under 300 K and 1.0 MPa H_2 . It can be seen that the hydrogen absorption kinetics and capacity can be significantly improved by the addition of Co.

Figure 6a is the dehydriding kinetics of $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ alloy after activation under 333 K and 0.001 MPa hydrogen. The figure shows that the hydrogen desorption rate of the alloy is faster, especially at the beginning stage. Within 500 s, the hydrogen desorption content from high to low in order was $\text{S2} > \text{S4} > \text{S1} > \text{S8} > \text{S0}$. The highest hydrogen desorption content of S2 is 1.33 wt.%. The reason for the differences of the hydrogen desorption capacity of the alloy may be the phase composition of the sintered product. Figure 1 showed that all the three lower capacity alloys contain some LaNi_5 impurity phase. Although the LaNi_5 phase is also a hydrogen storage phase, its appearing will inevitably lead to the loss of the AB_3 main phase, so the capacity was decreased slightly.

Figure 6b compared the dehydriding kinetics of La_2MgNi_9 and $\text{La}_2\text{MgNi}_{7.5}\text{Co}_{1.5}$ alloys prepared by sintering under 4 T magnetic field under 300 K and 0.001 MPa H_2 . It can be seen that after adding Co in the alloy, both the dehydriding rate and capacity have been greatly improved. The addition of Co increased cell volume, thus increasing the solid solubility of hydrogen. In addition, the addition of Co increases the number of cracks in the alloy, the specific surface area and the diffusion path, then improves the dehydriding kinetics. Therefore, the hydrogen absorption and desorption kinetics of AB_3 alloy can be simultaneously improved by Co addition on the premise of maintaining or even improving the capacity.

Figure 6. The dehydrogenating kinetics under 333 K and 0.001 MPa H_2 for (a) $La_2MgNi_{7.5}Co_{1.5}$ composites prepared by MASS; (b) Comparison of La_2MgNi_9 and $La_2MgNi_{7.5}Co_{1.5}$ under 4T.

4 Conclusions

1) $La_2MgNi_{7.5}Co_{1.5}$ hydrogen storage alloys prepared by MASS have the major phase of $PuNi_3$ type $(La, Mg)Ni_3$. With the increase of magnetic field, the impure phase $La(Ni, Co)_5$ firstly decreases and then increases. After partial substitution of Ni with Co, the lattice parameters a , c and cell volume V of the $(La, Mg)Ni_3$ phase increase with the magnetic field, reach their maximum value at 4 T.

2) The addition of Co can improve the hydrogen absorption and desorption thermodynamics performance. The $(La, Mg)(Ni, Co)_3$ alloy prepared under 4 T magnetic field has the lowest hysteresis coefficient (0.427) and the highest hydrogen absorption capacity (1.538 wt.%).

3) The dehydrogenation DSC curves of the alloys have multiple peaks characteristic, which corresponding to the dehydrogenating of the $La(Ni, Co)_5$ and $(La, Mg)(Ni, Co)_3$, respectively. The magnetic field has no significant effect on the dehydrogenating thermal behavior of the $La(Ni, Co)_5$ phase, but has a strong effect on that of $(La, Mg)(Ni, Co)_3$ phase. Both the hydriding and dehydrogenating kinetics properties can be improved by the Co addition and appropriate intensity of magnetic field.

Acknowledgements

This work was financially sponsored by the National Natural Science Foundation of China (51464008, 51574096), the Science and Technology Foundation of Guizhou Province ([2017]1118, [2016]5607).

References

1. Yartys V, Denys R. Structure-properties relationship in $RE_{3-x}Mg_xNi_9H_{10-13}$ ($RE=La, Pr, Nd$) hydrides for energy storage[J]. Journal of Alloys and Compounds, 2015, 645: S412.
2. Zhang Y H, Ren H P, Cai Y, Yang T, Zhang G F, Zhao D L. Structures and electrochemical hydrogen storage performance of Si added A_2B_7 -type alloy electrodes[J]. Trans. Nonferrous Met. Soc. China, 2014, 24:406.
3. Nwakwuo C C, Holm T, Denys R V, Hu W K, Maehlen J P, Solberg J K, Yartys V A. Effect of magnesium content and quenching rate on the phase structure and composition of rapidly solidified La_2MgNi_9 metal hydride battery electrode alloy[J]. Journal of Alloys and Compounds, 2013, 555:201.
4. Zhang L, Du W K, Han S M, Li Y, Yang S Q, Zhao Y M, Wu C, Mu H Z. Study on solid solubility of Mg in $Pr_{3-x}Mg_xNi_9$ and electrochemical properties of $PuNi_3$ -type single-phase RE-Mg-Ni ($RE=La, Pr, Nd$) hydrogen storage alloys[J]. Electrochimica Acta, 2015, 173:200.
5. Dai L, Wang S, Wang L, Yu Y, Shao G J. Preparation of $ZrMn_2$ hydrogen storage alloy by electro-deoxidation in molten calcium chloride[J]. Trans. Nonferrous Met. Soc. China, 2014, 24: 2883.
6. Liu J J, Li Y, Han D, Yang S Q, Chen X C, Zhang L, Han S M. Electrochemical performance and capacity degradation mechanism of single-phase La-Mg-Ni-based hydrogen storage alloys[J]. Journal of Power Sources, 2015, 300:77.
7. Liao B, Lei Y Q, Lü G L, Chen L X, Ge H W, Pan H G. Acta Metallurgica Sinica, 2005, 41: 41.
8. Chen X R, Wang H Y, Zhu S P, Li F F, Tang Y G, Liu Z M. Effect of magnetic field on the microstructure and electrochemical performance of rapidly quenched $La_{0.1}Nd_{0.075}Mg_{0.04}Ni_{0.65}Co_{0.12}$ alloy[J]. Journal of Alloys and Compounds, 2014, 617:722-728.
9. Chen X J, Wang H Y, Wang Y Z, Chen X R, Tang Y G, Liu Z M, Xie H L. Enhanced electrochemical performance of Mg_2Ni alloy prepared by rapid quenching in magnetic field[J]. Journal of Power Sources, 2013, 238:257-264.
10. Pan C C, Yang S L, Yu R H, Shi J, Nakamura Y. Mechanism of the enhancement of discharge rate property for $Nd_{0.8}Mg_{0.2}(Ni_{0.8}Co_{0.2})_{3.8}$ hydrogen storage alloy by magnetic annealing[J]. Journal of Rare Earths, 2010, 28:286.
11. Li X Q, Li L, Hu K, Chen Z C, Qu S G, Yang C. Microstructure and magnetic properties of anisotropic Nd-Fe-B magnets prepared by spark plasma sintering and hot deformation[J]. Trans. Nonferrous Met. Soc. China, 2014, 24: 3142-3151.
12. Li Q, Lu X G, Chou K C. Int. J. Hydrogen Energy, 2007, 32: 1875
13. Chen C Y, Chen H L, Ma Y Q, Liu J. Hydrogen desorption kinetics mechanism of Mg-Ni hydride under isothermal and non-isothermal conditions[J]. Trans. Nonferrous Met. Soc. China, 2016, 26:160.
14. Hu W K, Denys R V., Nwakwuo C C, Holm T, Maehlen J P, Solberg J K, Yartys V A. Annealing effect on phase composition and electrochemical properties of the Co-free La_2MgNi_9 anode for Ni-metal hydride batteries[J]. Electrochimica Acta, 2013, 96 :27.

15. Casini J C S, Guo Z P, Liu H K, Ferreira E A, Faria R N, Takiishi H. Effect of Sn substitution for Co on microstructure and electrochemical performance of AB₅ type La_{0.7}Mg_{0.3}Al_{0.3}-Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8}(x=0-0.5) alloys[J]. Trans. Nonferrous Met. Soc. China, 2015, 25:520.
16. Liu J, Li Q, Hydriding/dehydriding behaviors of La₂Mg₁₇-10 wt.%Ni composite prepared by mechanical milling[J]. Journal of Rare Earths, 2013, 31:73.
17. Liu J. Isothermal dehydriding kinetics of Mg₂NiH₄ prepared under an external magnetic field[J]. Advanced Materials Research , 2013, 785:638.
18. Chen C Y, Yang F, Chen H L, Liu J. Hydrogen storage properties of La₂MgNi₉ alloys prepared by master alloy[J]. Journal of Functional Materials, 2015, 46:17111.