

Study of the hydrogen-induced amorphization in the $\text{LaNi}_{2.28}$ alloy

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To understand the fundamental reason leading to the poor stability of $\text{LaNi}_{2.28}$ hydrogen storage alloy, the cycling behavior of $\text{LaNi}_{2.28}$ alloy under hydrogen has been investigated. The present study describes the hydrogen-induced amorphization (HIA) of $\text{LaNi}_{2.28}$ alloy. The phase composition, microstructure and morphology of the phases are observed and analyzed using X-ray diffraction and scanning electron microscopy. The crystal structure and chemical composition of the amorphized alloy show that HIA is found in the sample at different cycles of the hydrogenation process. During the first hydrogenation cycle, the degree of HIA is indeclinable with the increased cycle. In addition, the formation processes of amorphous alloys, the occurrence of HIA and the relationship between the structure of the hydrogen-induced amorphous alloy and the stability of $\text{LaNi}_{2.28}$ are given. The conclusions can be summarized as follows: $2\text{LaNi}_{2.28} + \text{H}_2 \rightarrow \text{LaNi}_{2.28}\text{H}_x$ (amorphous) + LaNi_5H_y + LaH_2 , and amorphous $\text{LaNi}_{2.28}\text{H}_x$ and LaNi_5H_y can desorb 50% hydrogen of the absorption capacity of $\text{LaNi}_{2.28}$, and the absorption–desorption capacity is stable after the first cycle.

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1. Introduction

Because of the energy crisis and environmental issues, extensive efforts have been devoted to the development of high performance hydrogen storage alloys that can be used as the negative electrode of the nickel–metal hydride (Ni–MH) batteries in order to significantly reduce the adverse effects of consumption and dependence on fossil fuels.^{1–3} To date, the investigated hydrogen storage alloys for the negative electrode are mainly classified into the following categories: AB_5 (CaCu_5 type), AB_3 (PuNi_3 or CeNi_3 type), A_2B_7 (Ce_2Ni_7 type), AB_2 (MgCu_2 or MgZn_2 Laves phase), AB (CsCl type), Mg-based alloys and Zr-based Laves phase alloy.^{4–7} Among them, rare earth-based AB_5 -type and Zr-based Laves phase hydrogen storage alloys have been widely used in the commercial Ni–MH rechargeable battery due to their long-term cycling stability and environmental friendliness.^{8–10} However, with the rapid development of electronic devices requiring a Ni–MH rechargeable battery with higher overall performance, the limited discharge capacity of rare earth-based AB_5 -type (300 mA h g) and the difficult activation of Zr-based Laves phase alloy electrodes became the main

obstacles to the extension of their applications in the field of Ni–MH rechargeable batteries.^{11,12}

It has come to light that the deterioration of the hydrogen storage alloy capacity used as the negative electrode is mainly associated with pulverization, oxidation or corrosion of the alloy electrode during electrochemical charge–discharge cycling.^{13–15} Furthermore, it should be noted that the hydrogen-induced amorphization (HIA) also plays a crucial role in destroying the hydrogen storage capacity and cycle stability of AB_3 -type negative electrodes.^{16–19} Zhang *et al.*¹⁹ found that the AB_3 -type structure consists of one-third AB_5 and two-third AB_2 subunits, forming an alternating stacking structure. In the LaNi_3 crystal structure, its LaNi_2 subunits absorb hydrogen, resulting in the formation of an amorphous phase of LaNi_2H_x , while its LaNi_5 subunits transfer to the crystalline phase of LaNi_5H_x , which leads to crack down of the LaNi_3 crystal structure, and decreases the cycle stability of the corresponding alloy. The detailed reaction process may be described as: $3\text{LaNi}_3 \rightarrow \text{LaNi}_2\text{H}_x$ (amorphous) + $\text{LaNi}_5\text{H}_y \rightarrow 3/5\text{LaH}_2 + 2/5\text{LaNi}_5\text{H}_2$. Similar to the structure of AB_3 -type alloy, A_2B_7 -type alloy consists of both half AB_5 and AB_2 subunits, while A_5B_{19} -type alloy consists of three-fifth AB_5 and two-fifth AB_2 subunits. It was determined that the structural stability of the AB_2 subunits determines the hydrogen storage properties of AB_3 -, A_2B_7 - and A_5B_{19} -type alloys. With increase in the atomic proportion of the component element B among AB_3 -, A_2B_7 - and A_5B_{19} -type alloy, the content of AB_2 subunits would decline resulting in improving in the cycle stability, but decrease in the theoretical hydrogen storage and electrochemical capacity. To date, HIA has been discovered in a

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large numbers of intermetallics, including A_3B , A_2B , AB , AB_2 , AB_3 , and A_2B_7 -type alloy.^{16–23} $LaNi_{2.28}$ (La_7Ni_{16}) alloy contains less Ni as compared with $LaNi_3$ alloy, which indicates that $LaNi_{2.28}$ alloy could be a promising candidate as the negative electrode of Ni–MH rechargeable batteries due to its high theoretical hydrogen storage capacity. Therefore, it is necessary to investigate the mechanism generating HIA in $LaNi_{2.28}$ alloy during the absorption–desorption cycle process and the effects of HIA on the hydrogen storage capacity of $LaNi_{2.28}$ alloy. Unfortunately, to date, the systematic investigation of HIA in $LaNi_{2.28}$ alloy has not been conducted.^{24–27}

In order to obtain a better understanding of the underlying mechanism of why and how to avoid or lessen the HIA in $LaNi_{2.28}$ alloy to improve the cycling stability of hydrogen storage alloys as the negative electrode material, in this work the HIA process in $LaNi_{2.28}$ alloy evolving during cycling under hydrogen, as well as the relationship between HIA and the microstructure of $LaNi_{2.28}$ alloy, were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS), pressure-composition-temperature (PCT) measurement and transmission electron microscopy (TEM).

2. Experimental

Alloy ingots with nominal composition $LaNi_{2.28}$ were prepared by arc-melting mixtures of pure La (99.9 mass%) and Ni (99.9 mass%) in high purity argon atmosphere. To ensure the homogeneity of the prepared alloy, the alloy ingots were turned over and re-melted at least three times. According to the phase diagram of La–Ni binary alloy, the annealing treatment was set at 700 °C in a bid to obtain the maximum quantity of $LaNi_{2.28}$ phases. Consequently, the alloy samples sealed inside the quartz tubes were annealed at 700 °C for 24 h in a high-purity argon atmosphere. After completing the holding time at 700 °C, the annealed quartz tubes were immediately quenched in ice water to achieve relatively larger cooling speed resulting in more the tetragonal $LaNi_{2.28}$ phases. To achieve fine powders from the annealed alloy samples, the annealed alloys were used to conduct the mechanical ball milling using a high-energy Spex mill (QM-3B) at the rate of 1200 rpm for 30 min. About 1.5 g of the annealed alloy sample was loaded into the stainless milling vial with a ball to powder weight ratio of 20 : 1 in a high-purity argon-filled glovebox (H_2O : <10 ppm; O_2 : <10 ppm). Then, the alloy samples were mechanically ground into the powders with an average 35 μm diameter. Herein, it should be noted that the steel vial should rest for 5 min after every milling 10 min during the milling process in order to prevent increase in the temperature inside the steel vial.

X-ray diffraction (XRD) measurements were performed to characterize the amorphous nature and phase composition of the annealed $LaNi_{2.28}$ alloys using a Rigaku D/Max diffractometer with Cu K α radiation ($\lambda = 1.5406 \times 10^{-10}$ m). The morphologies of as annealed samples were observed using a Cambridge S360 model scanning electron microscope (SEM) coupled with energy-dispersive spectrometer (EDS). The hydriding/dehydriding properties of the $LaNi_{2.28}$ alloy samples were measured using a

pressure-composition-temperature (PCT) apparatus (Beijing Nonferrous Metal Research Institute, China). The details of the apparatus are given in previous reports.^{28,29} Typically, 0.5 g powder sample was loaded into the vessel, then the measuring system was pumped to a hard vacuum, and then the sample was heated up to 120 °C at a 6 °C min^{−1} heating rate under a pressure of 0.1 atm. After the completion of the first absorption process, the sample was subjected to re-hydrogenation at 120 °C under 3.5 MPa hydrogen pressure. Subsequently, the rehydrogenated sample was dehydrogenated at 120 °C under 0.1 MPa pressure to complete one cycle. The variation of phase composition with cycling process was examined by XRD and transmission electron microscopy (TEM).

3. Results and discussion

3.1 Structural characteristics

Fig. 1 shows the XRD pattern of $LaNi_{2.28}$ alloy annealed at 700 °C for 24 h. As can be seen in Fig. 1, the annealed sample mainly consists of $LaNi_{2.28}$ phase, but still contains traces $LaNi_3$ second phase. In order to further prove the phase composition of the annealed $LaNi_{2.28}$ alloy, Fig. 2a exhibits the back-scattered SEM image of the annealed $LaNi_{2.28}$ alloys annealed at 700 °C for 24 h. It is obvious that the overall image is divided into two regions corresponding to grey and black region. From EDS measurements for these two regions, it can be concluded that the grey region corresponds to the $LaNi_{2.28}$ phase and the black region should be $LaNi_3$, as shown in Fig. 2b and c. By analyzing the phase diagram of La–Ni alloy,³⁰ it seems that the $LaNi_2$ phase could be obtained by the peritectic reaction under equilibrium solidification, while in practice it is difficult to obtain the single $LaNi_2$ phase. Moreover, Klimyenko *et al.*³¹ found that La and Ni atoms are easier to be formed into a $LaNi_{2.28}$ phase when the atomic ratio between La and Ni is 1 : 2, which is mainly because the atomic radius ratio between La and Ni (1.506) is relatively higher than the ideal atomic radius ratio of the Laves phase (1.225). Therefore, it is easier to form a $LaNi_{2.28}$ phase when the

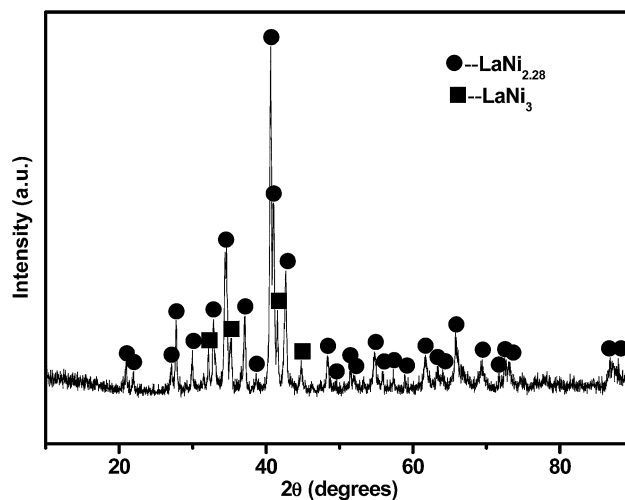


Fig. 1 XRD pattern of $LaNi_{2.28}$ alloy annealed at 700 °C for 24 h.

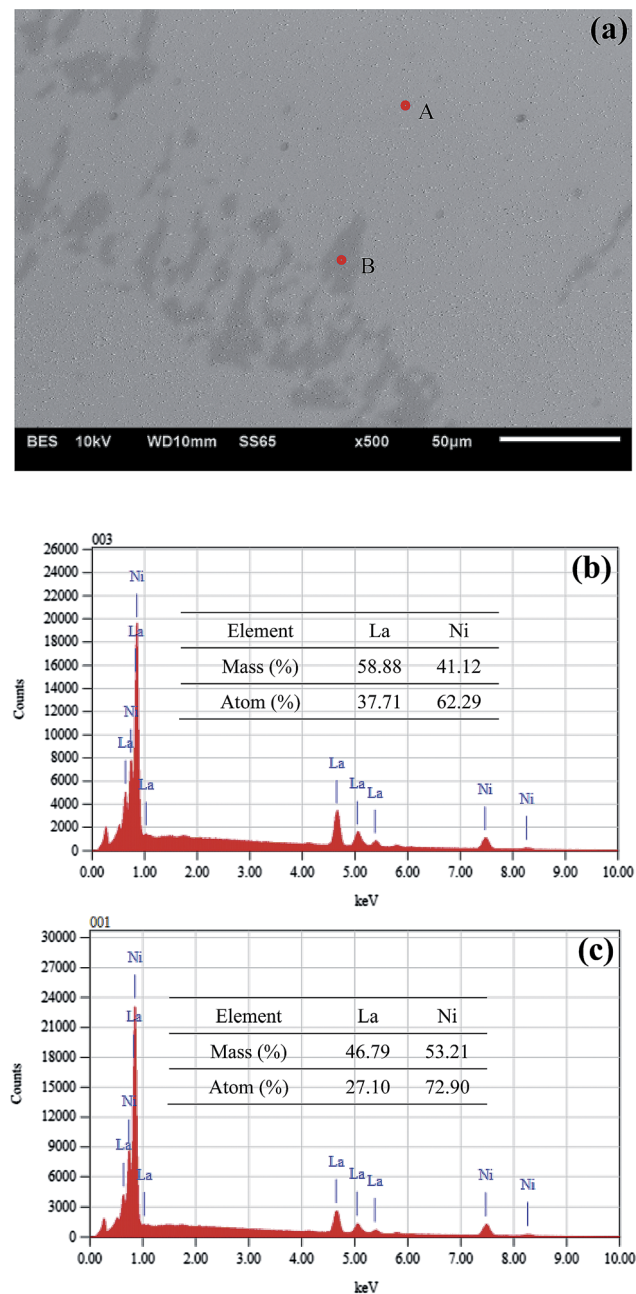


Fig. 2 (a) Back-scattered SEM image of the annealed LaNi_{2.28} alloys annealed at 700 °C for 24 h; energy dispersive spectroscopy (EDS) results of the (b) grey region A and (c) black region B.

atomic ratio between La and Ni is 1 : 2, which explains why more LaNi_{2.28} phases appear in Fig. 1.

3.2 Hydrogen absorption-desorption properties

A previous report on LaNi₂ found that the LaNi₂ alloy could achieve the equilibrium compound, corresponding to LaNi₂-H₂ when the LaNi₂ alloy occurs the absorption-desorption cycle.³² However, so far there is no detailed theory that has been established between absorption-desorption cycle and LaNi_{2.28} alloy. Herein, the hydrogenation properties of LaNi_{2.28} alloy were investigated to understand the effects of HIA on the

hydrogenation properties of LaNi_{2.28} alloy. Fig. 3a shows the hydrogen absorption curves of the as annealed LaNi_{2.28} alloy at 120 °C under a hydrogen pressure of 3.5 MPa without any activation process. As shown in Fig. 3, the as annealed LaNi_{2.28} alloy can absorb 1.6 wt% hydrogen within 0.5 h in the above-mentioned absorption condition. Compared with the traditional LaNi₃ alloy,^{16–18} the LaNi_{2.28} alloy exhibits higher hydrogen absorption behavior at relatively low temperatures (≤ 150 °C). However, the cyclic stability of LaNi_{2.28} alloy is very poor as compared with other hydrogen storage alloys. It is necessary to explore the reason for the poor cyclic stability. The desorption kinetics of LaNi_{2.28} was measured at 120 °C at an initial hydrogen pressure of 3.5 MPa without any activation process. As can be seen in Fig. 3b, the LaNi_{2.28} alloy shows very sluggish hydrogen desorption kinetics. The LaNi_{2.28} only desorbed about 1.0 wt% of hydrogen at 120 °C within 1 h, indicating that the desorption kinetics of LaNi_{2.28} are worse than its absorption kinetics.

Fig. 4 shows the isothermal absorption-desorption curves of LaNi_{2.28} alloy from the first to fourth cycle at 120 °C. Before measuring the second cycle, the sample was dehydrogenated at 120 °C for 0.5 h. It should be noted that 1.6 wt% hydrogen remains inside the alloy sample after the first absorption process. The sloping plateau appears and the hydrogen absorption clearly decreases in the second absorption-desorption process, suggesting that the isothermal absorption-desorption curves of the second cycle is remarkably different from the first one. There is a distinct decrease in hydrogen absorption during the absorption-desorption cycle of LaNi_{2.28} alloy, indicating the formation of amorphous hydrides during the cycling process.

3.3 Structural characteristics after hydriding/dehydriding

In order to understand the change of the structure and morphology of LaNi_{2.28} alloy after absorption-desorption cycles, the as-annealed alloys after hydriding/dehydriding were observed by SEM, and the results are shown in Fig. 5. By comparing SEM images of Fig. 5a–d, it can be observed that the change of granule sizes of the alloy samples is not obvious. This

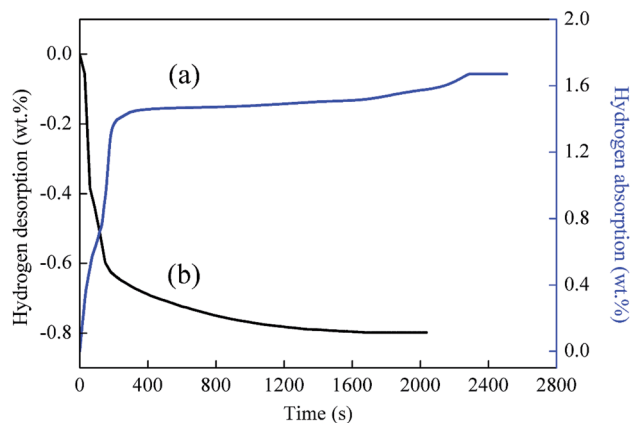


Fig. 3 First hydrogen absorption-desorption curves of LaNi_{2.28} at 120 °C under a hydrogen pressure of 3.5 MPa: (a) hydrogen absorption and (b) hydrogen desorption.

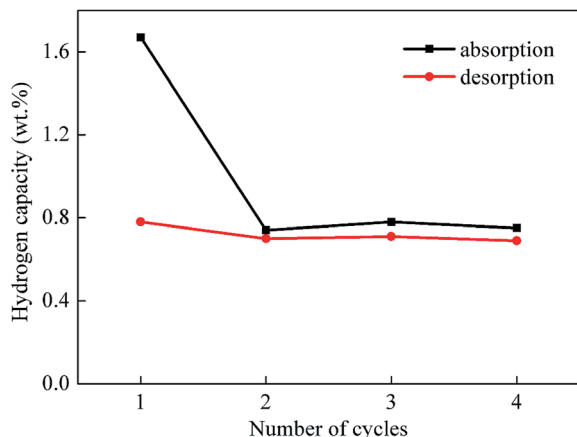


Fig. 4 The hydrogen capacity of pre-annealed $\text{LaNi}_{2.28}$ alloy during four hydriding/dehydriding cycles at 120 °C.

result shows that the pulverization basically occur in the process of hydriding/dehydriding, indicating that the HIA of the $\text{LaNi}_{2.28}$ alloy is the main reason, leading to be more difficult on the alloy hydrogenation. The formation of amorphous hydrides inside the $\text{LaNi}_{2.28}$ alloy impedes the diffusion of hydrogen atoms and decreases the dynamic property in the process of hydrogen absorption and desorption.³³ Therefore, it can be concluded that the most important approach to enhance the lifecycle of the La-Ni system ($\text{LaNi}_{2.28}$ -type) hydrogen storage electrode alloys is to improve their anti-amorphization.

Fig. 6a shows the XRD pattern of as-annealed alloy after the first absorption. Compared with Fig. 1, the $\text{LaNi}_{2.28}$ and LaNi_3 phases disappear, and the main phases are LaNi_5H_y and LaH_2 . Moreover, a small amount of LaNi_5 can also be observed, and the diffraction peaks are broadened accordingly. Combined with the TEM analysis (Fig. 7), it can be observed that a few amorphous phases are formed. Moreover, the SAED diffraction rings can be indexed with crystal planes of (111) for LaNi_5H_y , (111) for LaNi_5 and (101) for LaH_2 , which is in good agreement with XRD analysis. Fig. 6b–d show the XRD patterns of the alloy after the first, fourth and tenth cycles, respectively. There are no diffraction peaks observed in Fig. 6b–d, indicating that the detected alloy exists in the form of amorphous state. Combined with the TEM analysis (Fig. 7b–d), it can be concluded that the major phases are amorphous states and that minor crystal phases, corresponding to LaNi_5 and LaH_2 can be seen, which can be verified by SAED analysis.

It can be seen from Fig. 6a and 7a that only partial amorphous phases can be found after absorption. A disproportionation reaction occurred between $\text{LaNi}_{2.28}$ and LaNi_3 after LaH_2 and LaNi_5 formation. The major phases exist in the form of amorphous states after the first absorption, while the minor phases are LaH_2 and LaNi_5 crystalline phases. To our best knowledge, the above mentioned results are not reported in the literature; moreover, this phenomenon is not consistent with the process of HIA, but it could be related to the process of sample preparation. The first absorption was conducted at 120 °C under 3.5 MPa hydrogen pressure, whereas the XRD and TEM measurements were performed after the sample was

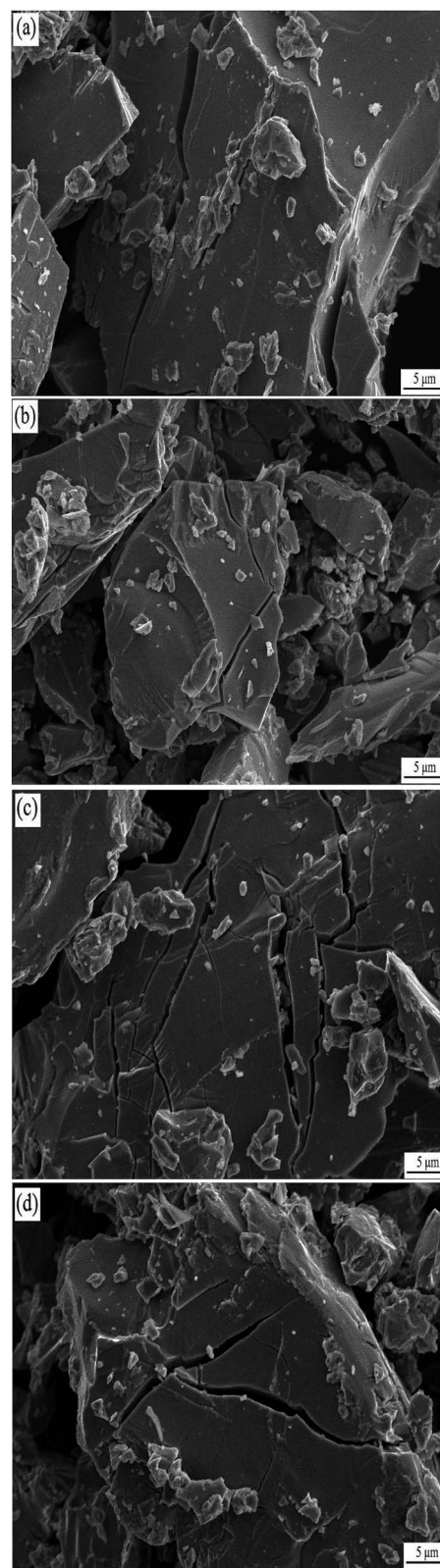


Fig. 5 SEM images of as-cast and hydriding/dehydriding of the microstructure: (a) as-cast; (b) 1 hydriding/dehydriding cycle; (c) four hydrogen hydriding/dehydriding cycles and (d) ten hydriding/dehydriding cycles.

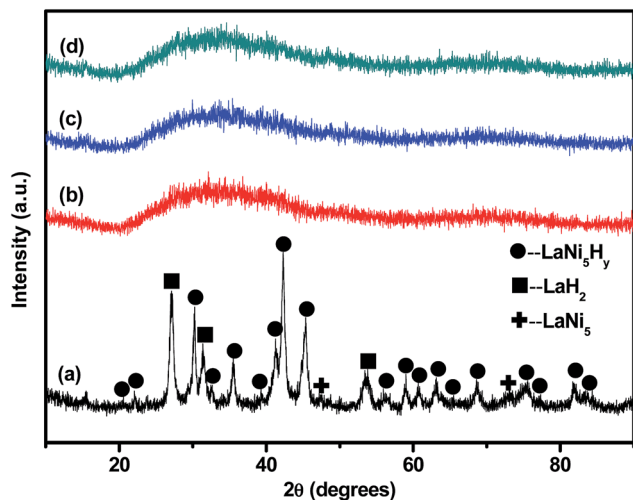


Fig. 6 XRD patterns of the pre-annealed $\text{LaNi}_{2.28}$ alloy cycled under 3.5 MPa H_2 after (a) 1 hydrogen absorption cycle; (b) 1 hydrogen desorption cycle; (c) 4 hydrogen desorption cycles and (d) 10 hydrogen desorption cycles.

cooled in an electric furnace from 120 °C to room temperature; *i.e.*, the sample was in amorphous state after the first absorption, but the crystallization process for the sample results from cooling in the electric furnace. For the samples after the first cycle, the XRD measurement was performed after the sample was cooled in air from 120 °C to room temperature. It can be seen from Fig. 4 and 5 that the absorption capacity is about 1.6 wt% for the first absorption, but the desorption capacity is only 0.8 wt% for the first desorption, which indicates that a disproportionation reaction occurs during the absorption process after LaH_2 and LaNi_5H_6 formation, according to the reaction formula (1). As a support for above, the precipitation of LaH_2 and LaNi_5H_2 from $\text{LaNi}_{2.28}\text{H}_x$ was also observed by Chung and Lee.³⁴ According to Fig. 7, after the first, fourth and tenth cycles at 120 °C, the SADP of LaNi_5 is pronounced. LaH_2 is very stable and can not desorb hydrogen at 120 °C, resulting in a decreased desorption capacity. According to the reaction formula (1), if all $\text{La}_7\text{Ni}_{16}$ ($\text{LaNi}_{2.28}$) participated in the disproportionation reaction, the desorption capacity of the formed LaNi_5H_6 would be 71.6% of the total absorption capacity; however, the actual desorption capacity is 50% of the total absorption capacity, which indicates that the disproportionation reaction is incomplete. After the absorption, amorphous $\text{LaNi}_{2.28}$, LaNi_5H_6 and LaH_2 are formed as shown in the reaction formula (2). The absorption and desorption capacities are 0.8 wt% from the second to fourth cycle, indicating that the amount of LaH_2 is stable after the first cycle and the disproportionation reaction is completed during the first cycle.

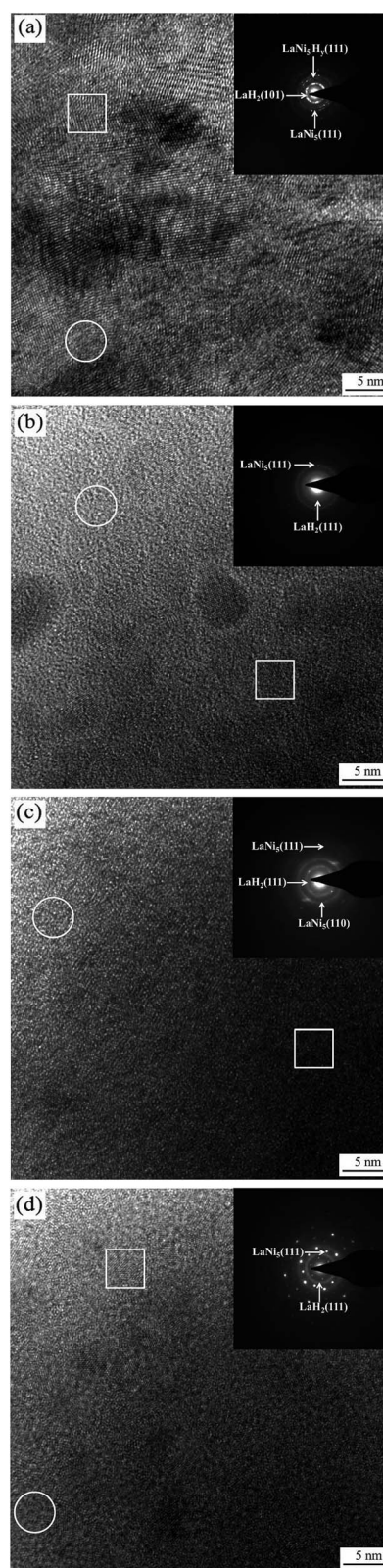
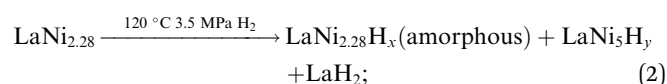
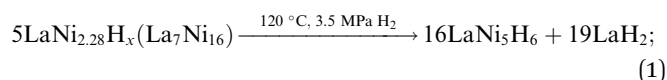


Fig. 7 TEM images and selected area diffraction patterns of pre-annealed $\text{LaNi}_{2.28}$ alloy after (a) 1 hydrogen absorption cycle; (b) 1 hydrogen desorption cycle; (c) 4 hydrogen desorption cycles and (d) 10 hydrogen desorption cycles. The circle and rectangle region in (a)–(d) show the crystalline and amorphous region, respectively; The insets in (a)–(d) show the selected area electron diffraction (SAED) patterns.

4. Conclusions

In the present work, the hydrogen storage behavior of inter-metallic $\text{LaNi}_{2.28}$ is systematically studied after absorption-desorption cycling under hydrogen gas, during which they undergo a degree of amorphization. As a result we can conclude the following.

The hydrogen-induced amorphization (HIA) is mainly responsible for the poor reversibility of the $\text{LaNi}_{2.28}$ alloy, and it mainly occurs after the first cycle. With an increase in the number of cycles, the degree of HIA does not increase. For the $\text{LaNi}_{2.28}$ alloy, the hydrogen absorption-desorption of its $\text{LaNi}_{2.28}$ phase causes the local lattice to become a disordered one, leading to the amorphous phase formation. At the same time, the LaNi_5H_x crystallites formed by the LaNi_5 subunit start to precipitate. Combining the TEM measurements in Fig. 7 with the XRD results in Fig. 6 describes what occurred in the $\text{LaNi}_{2.28}$ alloy: after the first absorption, amorphous $\text{LaNi}_{2.28}\text{H}_x$ formed, and it formed LaNi_5H_y and LaH_2 by the disproportionation reaction; amorphous $\text{LaNi}_{2.28}\text{H}_x$ and LaNi_5H_y can desorb 50% hydrogen of the absorption capacity of $\text{LaNi}_{2.28}$; and the absorption-desorption capacity is stable after the first cycle.

Acknowledgements

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