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Hydrogen induced amorphization behaviors of multiphase $\text{La}_{0.8}\text{Mg}_{0.2}\text{Ni}_{3.5}$ alloy

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ABSTRACT

Structural changes in multiphase $\text{La}_{0.8}\text{Mg}_{0.2}\text{Ni}_{3.5}$ alloy during hydrogen absorption/desorption cycles were studied in this work. XRD and TEM characterizations confirm that transformation from crystallinity to amorphous viz. hydrogen induced amorphization (HIA) of both $(\text{La},\text{Mg})_2\text{Ni}_7$ and $(\text{La},\text{Mg})_5\text{Ni}_{19}$ phases has occurred after 100 repeated cycles. In addition, P–C–T plateau is found to become slope and narrow, indicating that degradation of the hydrogen storage capacity comes with partial amorphization in the cyclic process. In order to comprehend the mechanism of HIA in the La–Mg–Ni compounds, hydrogenation processes from low to high hydrogen pressure at various temperatures were adopted and the structural evolution was investigated. Two kinds of crystalline La–Mg–Ni based hydrides are found to present successively, but transformation to amorphous subsequently takes place with the hydrogen concentration increased. Structural changes of the alloy are almost the same and no disproportion of the La–Mg–Ni phases is detected when hydrogenated at both the room and elevated temperatures. However, amorphization of the La–Mg–Ni phases becomes more severe as the charging temperature decreased. HIA of the La–Mg–Ni phases is thus considered to be non-thermally activated, which is launched directly by distortion of the lattice with hydrogen concentration increased. Furthermore, it is established that HIA of $(\text{La},\text{Mg})_2\text{Ni}_7$ phase is more liable to occur but hard to recrystallize compared with that of $(\text{La},\text{Mg})_5\text{Ni}_{19}$ compound. The structural stability towards HIA of various compounds in the multiphase $\text{La}_{0.8}\text{Mg}_{0.2}\text{Ni}_{3.5}$ alloy is then believed to be as follows: $\text{LaNi}_5 > (\text{La},\text{Mg})_5\text{Ni}_{19} > (\text{La},\text{Mg})_2\text{Ni}_7$.

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Introduction

As a negative electrode material of Ni–MH secondary battery, superlattice RE–(Mg/Ca)–Ni (RE: rare earth) hydrogen storage

alloys have been actively studied because of their excellent hydrogen storage properties compared with the traditional AB_5 -type alloys [1–3]. However, those alloys still need improvements especially the stability during long-term cycles to meet the practical application. It has been well known that

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capacity degradation of the metal hydrides is closely related to the structural changes during the absorption/desorption cycles. In binary RE-Ni alloys, LaNi_3 and La_2Ni_7 are reported to subject to hydrogen-induced amorphization (HIA) i.e. transformation from crystalline compounds to amorphous hydrides in repeated hydrogenation cycles [4,5]. HIA has been firstly studied as a potential method of preparation for the amorphous alloys, it is also in close relationship with degradation of the hydrogen storage properties. For example, no discharge potential plateau was observed during the electrochemical discharging process in a LaNi_3 alloy [6]. Similarly, the reversible discharge capacity of $\text{La}_5\text{Ni}_{19}$ is only 50 mAh g^{-1} which is much lower than the theoretical value of the gas–solid capacity [7].

It has been well described that AB_3 , A_2B_7 and A_5B_{19} -type layered structures could be treated as composed of CaCu_5 -type ($[\text{AB}_5]$) and MgZn_2 -type ($[\text{A}_2\text{B}_4]$) units stacking along the *c*-axis [8,9]. Structural studies on hydrides of the LaNi_3 and La_2Ni_7 compounds indicate that hydrogen atoms only enter $[\text{A}_2\text{B}_4]$ slabs and the borders of $[\text{A}_2\text{B}_4]$ and $[\text{AB}_5]$ slabs, but not into $[\text{AB}_5]$ slabs [10–12]. Thus, anisotropic volume expansion especially anomalous extension along the *c*-axis is introduced by hydrogen absorption, which is considered to be the major reason resulting in HIA. Though substitution of Mg for RE is reported to be able to stabilize the crystal structure, PuNi_3 -type $\text{La}_{3-x}\text{Mg}_x\text{Ni}_9$ compounds where *x* below 0.7 still suffer HIA as studied by Denys [13]. Besides, partial amorphization of Ce_2Ni_7 -type La–Mg–Ni–Co phase has also been reported by Zhang [14]. However, detailed study on amorphization by hydrogen charging in the ternary RE–Mg–Ni based compounds is still scarce. In the present work, structural changes of multiphase $\text{La}_{0.8}\text{Mg}_{0.2}\text{Ni}_{3.5}$ alloy within 100 absorption/desorption cycles as well as a gradual hydrogenation process are investigated systematically. The mechanism of HIA of the superlattice La–Mg–Ni phases is discussed on the basis of the experimental data.

Experimental procedures

The $\text{La}_{0.8}\text{Mg}_{0.2}\text{Ni}_{3.5}$ alloy was prepared by induction levitation melting in a water-cooled copper crucible under argon atmosphere. La–Ni master alloy was firstly melted three times using raw metals, then Mg was adopted and remelted twice for homogeneity. Appropriate excess of Mg was added in order to compensate for the evaporative loss of Mg during melting. Then, the as-cast alloy was annealed at 1173 K for 6 h in vacuum.

Composition of the ingot was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) using a ThermoFisher iCAP-6300 system. Metallographic characterization of the annealed alloy was performed by means of an Olympus OLS4000 laser scanning confocal microscope (LSCM). For observation of the LSCM, sample was fine polished and then etched using a mixed etchant (including water, ethanol, acetic acid, picric acid, nitric acid and hydrochloric acid) at 343 K. Microstructure of the alloy was also observed in the unetched sample by a FEI Qanta 400 scanning electron microscopy (SEM) in backscatter electron mode (BSE). The chemical composition of various phases in

the alloy was studied by energy dispersive spectroscopy (EDS) equipped in the SEM. ZAF corrections were used to acquire the precise chemical quantitation of different phases from the EDS data. Powder diffraction of the alloy was collected by a Bruker-D8 Advance X-ray diffractometer (XRD) with $\text{Cu K}\alpha_1$ radiation. The measured XRD pattern was refined by Bruker-Topas 4.2 program based on the Rietveld method. Selected area electron diffraction (SAED) and EDS were applied by means of a JEOL-2100 transmission electron microscopy (TEM) to examine the crystallographic and chemical information. TEM samples were firstly crushed the bulk into fine powder, and then ultrasonic dispersion was performed in ethanol for 1800 s. Several drops of the mixed liquid were laid on a carbon membrane support on the copper grid, and dried in a vacuum oven. Thermal analysis of the cycled alloy was studied by differential scanning calorimetric (DSC) and thermal gravimetric (TG) techniques measured using a NETZSCH STA449F3 thermal analyzer at heating rate of 10 K/min in the argon atmosphere.

Gas-solid cycling and P-C-T isotherm measurement were carried out by a Suzuki -2SDWIN PCT system (Sievert's type). For the first P-C-T analysis, sample was activated as follow: evacuated at 473 K for 7200 s (2 h), placed to 298 K, hydrogenated under 1 MPa H_2 (Purity 99.999%) pressure for 1800 s (0.5 h), evacuated at 473 K for 7200 s (2 h) again. Each cycle consists of absorption at 2 MPa for 600 s and desorption by evacuating at 298 K for 1200 s.

Results and discussion

Microstructure of the $\text{La}_{0.8}\text{Mg}_{0.2}\text{Ni}_{3.5}$ alloy

ICP result from the annealed ingot is $\text{La}_{0.826}\text{Mg}_{0.174}\text{Ni}_{3.468}$ which is close to that of the designed composition. A little deficit of Mg may be due to loss of Mg in the annealing process.

The color micrographs, BSE image and EDS profiles of the annealed $\text{La}_{0.8}\text{Mg}_{0.2}\text{Ni}_{3.5}$ alloy are displayed in Fig. 1. It is evidently that three phases present in both the LSCM and BSE images. The chemical compositions of various phases obtained from the quantitative EDS data are listed in Table 1. The Ni/(La + Mg) ratio of phase “B” which dominates in the multiphase alloy is 3.4. It is close to that of the A_2B_7 -type phase (Ni/(La + Mg) = 3.5). Though phase “C” presents the similar contrast with “B” in the BSE mode, it is significantly different as displayed in the LSCM picture. The atomic ratio of Ni/(La + Mg) in domain “C” is near to 3.7 which is resemble to both A_5B_{19} -type and A_6B_{24} -type phase. In addition, Mg content of domain “C” is lower than that in domain “B”. Ni/(La + Mg) ratio of phase “A” is nearly 5, and no Mg is detected here, which is in agreement with the fact that the La atoms cannot be substituted by Mg in the $[\text{AB}_5]$ unit. Therefore, it is identified to be LaNi_5 phase.

XRD pattern of the annealed $\text{La}_{0.8}\text{Mg}_{0.2}\text{Ni}_{3.5}$ alloy is shown in Fig. 2. Four phases including LaNi_5 (CaCu_5 -type), $(\text{La,Mg})_2\text{Ni}_7$ (Ce_2Ni_7 -type), $(\text{La,Mg})_5\text{Ni}_{19}$ ($\text{Ce}_5\text{Co}_{19}$ -type) and $(\text{La,Mg})_5\text{Ni}_{19}$ ($\text{Pr}_5\text{Co}_{19}$ -type) phase are identified in this alloy. Thus, phase B and C in Fig. 1 can be determined to be $(\text{La,Mg})_2\text{Ni}_7$ and $(\text{La,Mg})_5\text{Ni}_{19}$ phase respectively. The $\text{Ce}_5\text{Co}_{19}$ -type and $\text{Pr}_5\text{Co}_{19}$ -type phase cannot be separated in the BSE and

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