

Short communication

Thermodynamical properties of La–Ni–T (T = Mg, Bi and Sb) hydrogen storage systems

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Abstract

The hydrogen absorption properties of LaNi_{4.8}T_{0.2} (T = Mg, Bi and Sb) alloys are reported. The effects of the substitution of Ni in the LaNi₅ compound with Mg, Bi and Sb are investigated. The ability of alloys to absorb hydrogen is characterized by the pressure–composition (*p–c*) isotherms. The *p–c* isotherms allow the determining thermodynamic parameters enthalpy (ΔH^{des}) and entropy (ΔS^{des}) of the dehydrogenation processes. The calculated ΔH^{des} and ΔS^{des} data helps to explain the decrease of hydrogen equilibrium pressure in alloys doped with Al, Mg and Bi and its increase in the Sb-doped LaNi₅ compound. Generally, partial substitution of Ni in LaNi₅ compound with Mg, Bi and Sb cause insignificant changes of hydrogen storage capacity compared to the hydrogen content in the initial LaNi₅H₆ hydride phase. However, it is worth to stress that, in the case of LaNi_{4.8}Bi_{0.2}, a small increase of H/f.u. up to 6.8 is observed. The obtained results in these investigations indicate that the LaNi_{4.8}T_{0.2} (T = Al, Mg and Bi) alloys can be very attractive materials dedicated for negative electrodes in Ni/MH batteries.

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1. Introduction

The hydrogen storage alloys for the purpose of this application should exhibit a high hydrogen capacity, moderate hydride stability and, preferably, constant equilibrium H₂ pressure during the phase conversion from α -MH solid solution to MH β hydride phase. A relatively small sorption–desorption hysteresis is also desired. Information about the above-mentioned properties is usually inferred from the pressure–composition (*p–c*) isotherms.

A very important parameter characterizing the alloy as a proper hydrogen absorber for various specific applications is the heat of hydride formation. Hong [1] has stated that the heat of alloy–hydride formation should be between –40 and –15 kJ mol^{–1}. In case the heat of formation is more positive than –15 kJ mol^{–1}, the metal hydride is not stable enough. On the other hand, the hydrides that are too stable make discharging too difficult.

Among others, an intermetallic compound of the general formula LaNi₅ has been extensively investigated as possible hydrogen storage material [2–4]. To improve the hydrogen storage capacity, the stability of the hydride phase, or the alloy corrosion resistance, both La and Ni have been replaced by other elements: La by Ce, Pr, Nd or by Mishmetal (Mm) [5–7]; and Ni by Mn, Zn, Cr, Fe, Co, Cu or even by Al and Sn [8–11].

Much attention has been focused on LaNi_{5–x}Al_x compounds for their potential application as negative electrodes in the nickel–metal hydride (Ni/MH) batteries [12–14]. LaNi_{5–x}Al_x is also considered to be a very useful material for H₂ storage because of its low plateau pressure and resistance to impurities in hydrogen gas [12]. It was also found that the partial replacement of Ni in LaNi₅ by a small amount of Al resulted in a prominent increase of the cycle lifetime without causing much decrease in hydrogen absorption capacity [15].

The aim of this study was to evaluate the effect of partial substitution of Ni for Mg, Bi, and Sb on the hydrogen absorption ability. The enthalpy and the entropy of hydride formation have been determined from the temperature dependence of the hydrogen desorption pressure by using the van't Hoff relation [6,8].

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2. Experiment

Three $\text{LaNi}_{4.8}\text{T}_{0.2}$ alloys (with $\text{T} = \text{Mg}, \text{Bi}$ and Sb) were prepared by arc melting of stoichiometric amounts of the pure metals (99.9 wt.%) in an argon atmosphere. The ingots were homogenized in quartz ampoules under vacuum at 670 K for 336 h. The powder X-ray diffraction (XRD) patterns of the alloys were obtained by using a STOE powder diffractometer. Lattice parameters were calculated using the Rietveld analysis and are presented in Table 1s (see Supplementary paragraph).

The hydrides were synthesized and the p – c isotherms were measured using a Sieverts-type apparatus with an operating volume of 5 cm^3 adapted for measurements in the temperature range of 290–800 K in the H_2 gas pressures up to 10 MPa. The hydrogenation of the alloys was carried out using the pure hydrogen gas obtained from LaNi_5H_6 hydrogen storage. The amount of absorbed hydrogen was determined by hydrogen pressure change in the reactor chamber. Allowance for the coefficient of hydrogen compressibility made it possible to calculate the hydrogen concentration in the sample with an accuracy of $\pm 0.02 \text{ H/f.u.}$ The H_2 pressure in the reactor chamber has been determined with an accuracy of $\pm 10^{-4} \text{ MPa}$ whereas temperature in it has been kept on the constant level with the accuracy of $\pm 0.2 \text{ K}$. In order to secure a state of thermodynamic equilibrium in the reactor, the p – c – t measurements were preceded by five hydrogenation/dehydrogenation cycles for each sample. The p – c isotherms were determined for temperatures of 293, 313, 333 and 353 K by desorption of H_2 gas from the synthesized hydrides.

3. Results and discussion

The X-ray diffraction patterns of the studied samples appear to be similar to each other and they have corresponded to single phase material with the CaCu_5 crystal structure. Lattice parameters (a and c), together with the calculated unit cell volumes for the uncharged samples, are presented in Supplementary data paragraph. The values of the lattice parameters and the unit cell volumes indicate that partial substitution of Ni for Al, Mg, Bi, and Sb does not change these parameters as much as compared with those for pure LaNi_5 compound [6].

In Fig. 1 the p – c isotherms for hydrogen desorption in $\text{LaNi}_{4.8}\text{Mg}_{0.2}$ are presented. The p – c data for the other com-

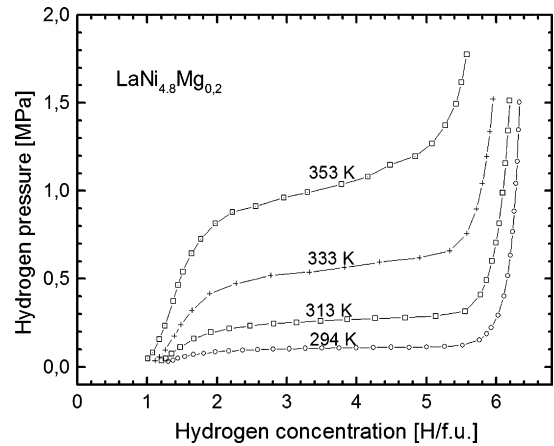


Fig. 1. p – c isotherms of hydrogen desorption from $\text{LaNi}_{4.8}\text{Mg}_{0.2}$ hydride.

pound one can find in Supplementary data paragraph. The p – c curves show a plateau range which is followed by a sharp rise corresponding to the formation of the defined hydride phases. The experimental values of H_2 equilibrium pressure taken in the middle of the plateau region (for hydrogen content equal to $\text{H/f.u.} = 3$) for individual p – c curve at four different temperatures are listed in Table 1. First of all, the partial substitution of Ni with Mg, Bi, and Sb in the LaNi_5 compound changes the related plateau pressures. As we can see from the results and data, the equilibrium pressure of hydrogen distinctly decreases in the pseudobinary compounds doped with Al, Mg, and Bi and increases in those doped with Sb compared to the equilibrium pressure registered in the initial LaNi_5 hydride. These observations are in line with enthalpy values calculated from the van't Hoff's relationship:

$$\ln \left(\frac{p_{\text{eq}}}{p_0} \right) = \frac{\Delta H^{\text{des}}}{RT} + \frac{\Delta S^{\text{des}}}{R} \quad (1)$$

where ΔH^{des} and ΔS^{des} are, respectively, the enthalpy and entropy of the desorption of 1 mol of hydrogen gas from the hydride phase. R is the gas constant, p_0 is the standard coefficient (0.101325 MPa). The dependence of $\ln(p_{\text{eq}}/p_0)$ versus $1/T$ is displayed in Fig. 2, whereas the calculated ΔH^{des} and ΔS^{des} thermodynamic functions of the slope and intercepts, respectively, of the least-squares line are collected in Table 1.

From the data in Table 1, it appears that the enthalpies of hydrogen desorption for the Al, Mg, and Bi derivate

Table 1

Equilibrium pressure of hydrogen desorption determined from the p – c isotherm's plateau at several temperatures for hydrogen content equal to $\text{H/f.u.} = 3$

Alloys	p_{eq} (MPa)				ΔH^{des} (kJ mol ⁻¹ H ₂)	ΔS^{des} (J kmol ⁻¹ H ₂)
	293 K	313 K	333 K	353 K		
LaNi_5^{a}	0.158	0.337	0.689	–	–30.6	107.3
$\text{LaNi}_{4.8}\text{Al}_{0.2}^{\text{b}}$	0.043	0.11	0.234	0.458	–32.6	104.5
$\text{LaNi}_{4.8}\text{Mg}_{0.2}$	0.11	0.27	0.57	1.07	–31.9	110.0
$\text{LaNi}_{4.8}\text{Bi}_{0.2}$	0.126	0.31	0.62	1.21	–33.5	115.2
$\text{LaNi}_{4.8}\text{Sb}_{0.2}$	0.354	0.814	1.60	2.68	–29.1	110.5

The enthalpy and entropy of hydride phase formation calculated from van't Hoff equation.

^a Ref. [8].

^b Ref. [16].

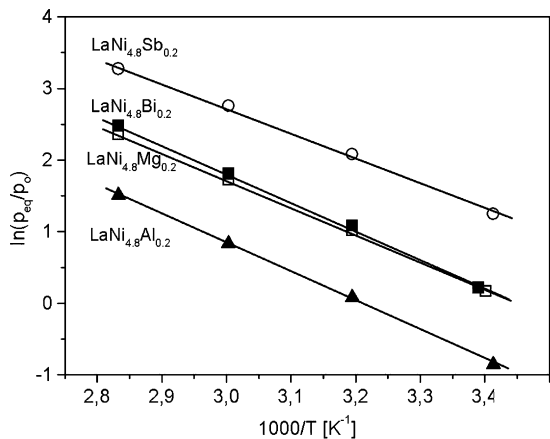


Fig. 2. van't Hoff dependence for the studied $\text{LaNi}_{4.8}\text{T}_{0.2}$ ($\text{T} = \text{Al, Mg, Bi}$ and Sb) hydride phases.

hydrides are higher than for a pure LaNi_5H_6 compound ($\Delta H^{\text{des}} = -30.6 \text{ kJ mol}^{-1}$) [7]). These values indicate that the compounds doped with Al, Mg, and Bi make their hydrides phases much more stable. The increase of the absolute value of ΔH^{des} in an average of about 11.5% for $\text{LaNi}_{4.8}\text{Al}_{0.2}\text{H}_{4.5}$ causes a decrease of equilibrium pressure at room temperature—about three times the decrease (and vice versa) for about 10% of the absolute value of ΔH^{des} in $\text{LaNi}_{4.8}\text{Sb}_{0.2}\text{H}_{4.5}$ hydride and increases the p_{eq} about three times compared to its value in LaNi_5H_6 [6,8]. This dramatic effect of aluminium and antimony on the vapour pressure is not only of scientific interest but could be profitably exploited for a variety of engineering applications, e.g. heat pumps and refrigerators where a series of hydrides with differential vapour pressure are required.

The reduction of the equilibrium hydrogen pressure by partly substituting Ni with Al, Mg, and Bi occurs without significant reduction in its hydrogen capacity. The hydrogen capacity of $\text{LaNi}_{4.8}\text{Mg}_{0.2}$ was observed to be about 6, whereas $\text{LaNi}_{4.8}\text{Bi}_{0.2}$ was to be 6.8 hydrogen atoms per formula unit at room temperature (under hydrogen pressure equal of 0.2 MPa). These results (still relatively high hydrogen capacity and low equilibrium hydrogen pressure) make both hydrides more attractive as potential materials for MH battery electrodes than the initial LaNi_5H_6 .

The Sb-substituted alloy shows lower concentration of absorbed hydrogen (H/f.u. about 4.5) and a relatively high vapour pressure that indicates that the substitution of Ni by Sb significantly diminishes the stability of the hydride. This stability is determined by a low absolute value of the enthalpy of dehydrogenation, which we have found for this compound.

4. Conclusion

Partial substitution of Ni for Al, Mg, and Bi does not greatly change the hydrogen capacity of these systems as compared with the original LaNi_5H_6 . However, it causes significant changes in their equilibrium hydrogen pressures, which makes them very interesting materials to be used as negative MH electrodes in the Ni/MH batteries. The electrode potential and electrochemical corrosion characteristic measurements are currently under investigation in our lab. Furthermore, note that the substitution of 0.2 Ni atoms for 4 Ni atoms in the formula unit by Bi causes an increase in hydrogen content for about 13%. This indicates that $\text{LaNi}_{4.8}\text{Bi}_{0.2}$ hydride can be also considered as a good hydrogen storage material in engineering applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2007.12.018.

References

- [1] K. Hong, (Gambler) US Patent 5,006,328 (1991).
- [2] S. Seta, H. Uchida, J. Alloys Compd. 231 (1995) 448–453.
- [3] H. Uchida, M. Sato, O. Moriwaki, J. Alloys Compd. 253/254 (1997) 235–237.
- [4] P. Termsuksawad, S. Niyomsoan, A.A.B. Mishra, D.L. Olson, Z. Gavra, V.I. Kaydanov, Mat. Sci. Eng. B. 117 (2005) 45–51.
- [5] J. Chen, S.X. Dou, H.K. Liu, J. Power Sources 63 (1996) 267–270.
- [6] J.G. Willems, Philips J. Res. 39 (1984) 1–94.
- [7] M. Jurczyk, W. Rajewski, W. Majchrzycki, G. Wójcik, J. Alloys Compd. 290 (1999) 262–266.
- [8] B. Rożdżyńska-Kiełbik, W. Iwasieczko, H. Drulis, V.V. Pavlyuk, H. Bala, J. Alloys Compd. 298 (2000) 237–243.
- [9] M. Lacroche, A. Percheron-Guegan, Y. Chabre, J. Bouet, J. Pannetier, E. Ressouche, J. Alloys Compd. 231 (1995) 537–545.
- [10] S. Luo, W. Luo, J.D. Clewley, T.B. Flanagan, L. Wade, J. Alloys Compd. 231 (1995) 467–472.
- [11] M. Geng, J. Han, D.O. Northwood, Int. J. Hydrogen Energy 22 (1997) 531–535.
- [12] J.W. Oh, C.Y. Kim, K.S. Nahm, K.S. Sim, J. Alloys Compd. 2278 (1998) 270–276.
- [13] J. Jurczyk, J. Alloys Compd. 307 (2000) 279–282.
- [14] R.J. Zhang, Y.M. Wang, M.Q. Lu, D.S. Xu, K. Yang, Acta Mater. 53 (2005) 3445–3452.
- [15] Y. Nakamura, H. Nakamura, S. Fujitani, I. Yonezu, J. Alloys Compd. 210 (1994) 299–303.
- [16] K. Giza, W. Iwasieczko, V.V. Pavlyuk, H. Bala, H. Drulis, L. Adamczyk, J. Alloys Compd. 429 (2007) 352–356.