Crystal structure and hydrogen storage properties of $(La,Ce)Ni_{5-x}M_x$ (M = Al, Fe, or Co) alloys

Wan-liang Mi[1], Zhao-sen Liu[1,2], Toru Kimura[2], Atsunori Kamegawa[2], and Hai-liang Wang[1]

1) School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

2) Research Center for Environmentally Friendly Materials Engineering (Muroran MATERIA), Muroran Institute of Technology, Muroran 0508585, Japan

Abstract: The effects of partial substitution of La by Ce and Ni by Al, Fe, or Co in LaNi$_5$-based alloys on hydrogen storage performance were systematically studied. All samples were prepared using vacuum arc melting in an argon atmosphere. The results showed that for La-Ni$_{5-x}$M$_x$ (M = Al, Fe, or Co) alloys, the lattice constants and unit cell volumes increased with an increasing amount of Al and Fe. On the other hand, these parameters decreased upon partial substitution of La by Ce. In addition, the lattice constant remained almost constant in the La$_{0.6}$Ce$_{0.4}$Ni$_{5-x}$Co$_x$ alloys regardless of the value of *x* (*x* = 0.3, 0.6, or 0.9), as Ce might enhance the homogeneity of the CaCu$_5$-type phase in Co-containing alloys. The hydrogen storage properties of the alloys were investigated using pressure, composition, and temperature isotherms. The experimental results showed that the plateau pressure decreased with an increasing content of Al, Fe, or Co, but it increased with Ce addition. Furthermore, the plateau pressures of all Co-containing alloys were almost identical upon substitution with Ce. Finally, the enthalpy (ΔH) and entropy (ΔS) values for all alloys were calculated using van't Hoff plots. The relationship between the lattice parameters and enthalpy changes for hydrogenation will be discussed.

Keywords: metal hydride; LaNi$_5$; hydrogen storage alloys; partial substitution; P–C–T curves; thermodynamics

1. Introduction

Hydrogen has been widely studied as a clean energy medium due to its abundance and non-polluting properties. Suitable methods to store hydrogen play an important role for hydrogen applications. One method under consideration is using metal hydrides because of their safety advantages and low volume requirements [1–3].

The AB$_5$-type alloys with a CaCu$_5$ structure are considered one of the most ideal hydrogen storage alloys because the techniques for their industrial production have been established and are widely used for applications such as negative electrodes in Ni-MH batteries and hydrogen storage tanks. LaNi$_5$ has been widely researched as a typical AB$_5$-type alloy with good cycle and easy activation properties. For example, the partial substitution of La or Ni is proposed to cut costs and modify the hydrogen absorption-desorption equilibrium pressure. The substitution of La by the relatively inexpensive metal Ce caused a striking in-crease in the hydrogen equilibrium pressure [4]. The partial substitution of Ni by various metals (Al, Mg, Fe, Co, Cu, Sn, Mn, or Cr) has also been studied extensively [5–7]. The substitution of Ni by Al in LaNi$_5$ dramatically lowered the decomposition pressure without impairing the kinetics or hydrogen-carrying capacity [8–9]. The substitution with Cu, likewise, could reduce the hydrogen dissociation pressure and its production costs. In addition, the substitution with Cr increased the cell volume and reduced the plateau pressure, whereas the substitution with Mg could increase the discharge capacity of the alloy [10–12]. Fe-containing alloys that exhibit better hydrogenation characteristics than the parent LaNi$_5$ alloy have also been studied [13]. Although substitution on one side of the unit cell has been studied well, the effects of different amounts of combined substitution on the hydrogen storage properties have not been systematically studied. Combined substitution is a viable way to optimize the proportion of elements in the alloy and control the hydrogen equilibrium pressure to ensure that it remains

🌱 Springer

within a proper range.

In this study, La was substituted with Ce and Ni with Al, Fe, and Co in three different elemental ratios. The aim was to investigate the effects of partial substitution and elemental proportions on hydrogenation properties, especially the enthalpy and entropy of the different compositions. The results were analyzed using van't Hoff plots.

2. Experimental

All alloys used in this study were prepared by vacuum arc melting on a water-cooled copper hearth under a purified argon atmosphere. The purities of the raw metals were as follows: La (99.9%), Ce (99.9%), Al (99.99%), Fe (99.9%), and Co (99.3%). Each alloy ingot was melted and turned over four times in the arc chamber to ensure homogeneity. The obtained ingots were heat-treated at 1273 K for 24 h under an argon atmosphere. The crystal structure and phases of the samples were determined by X-ray diffraction (XRD, Rigaku Corp. SmartLab) using Cu-K$_\alpha$ radiation. The pressure, composition, and temperature isotherms (P–C–T) were measured with a Sieverts-type apparatus. The enthalpy (ΔH) and entropy (ΔS) values were calculated from the desorption plateau pressures using van't Hoff plots with the following equation [14]:

$$\ln(\frac{P_{eq}}{P^0}) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (1)$$

where R, T, P^0, and P_{eq} are the ideal gas constant, experimental temperature, standard pressure, and equilibrium plateau pressure, respectively.

3. Results and discussion

3.1. Character of hydrogen storage alloys

The XRD patterns of LaNi$_{5-x}$Co$_x$ and La$_{0.6}$Ce$_{0.4}$Ni$_{5-x}$Co$_x$ alloys (where x = 0.3, 0.6, or 0.9) are shown in Fig. 1. All the alloys had a hexagonal CaCu$_5$-type structure as their main phase. Other phases were generated, such as the LaNi$_3$ phase shown in Fig. 1, but the content was very low and did not affect the experimental results. The lattice parameters, a and c, as well as the unit cell volume of each alloy are shown in Fig. 2. The values for lattice parameter, a, and the unit cell volume increased with an increasing amount of the substitute elements Al, Fe, and Co in the B location in the AB$_5$ structure. The larger radius of these elements compared to Ni may be the reason (Al (143 pm), Fe (126 pm), Co (125 pm), and Ni (124 pm)). Moreover, the rate of increase for the Al case was significantly higher than that for Fe and Co. Therefore, the lattice parameter increments are proportional

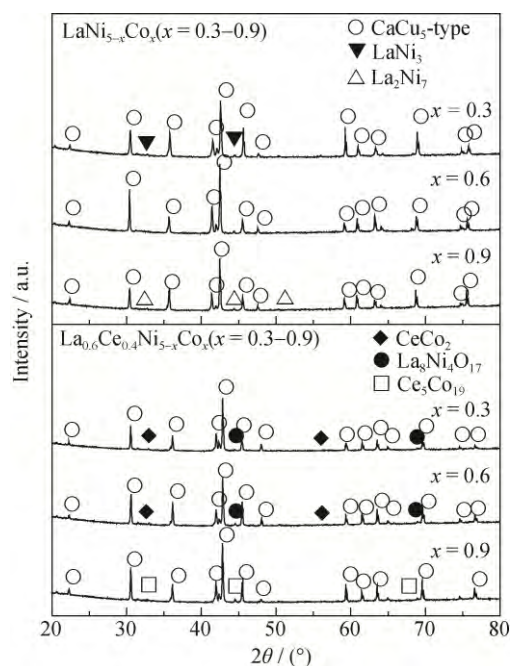to the constituent atomic radius based on geometric considerations.

Fig. 1. X-ray diffraction (XRD) patterns of LaNi$_{5-x}$Co$_x$ and La$_{0.6}$Ce$_{0.4}$Ni$_{5-x}$Co$_x$ (x = 0.3, 0.6, and 0.9) alloys.

Upon replacing part of the La with Ce, the lattice parameter, a, and unit cell volume decreased markedly, likely because the atomic radius of Ce (181.8 pm) is smaller than that of La (187 pm). In addition, it was reported previously that Ce forms a close-packed face-centered cubic structure, which is a less dense hexagonal structure [15]. Valøen *et al.* [4] reported that the lattice parameter, c, increased due to Ce substitution in LaNi$_5$. The reason for this phenomenon may be related to the maintenance of proper atomic distances between the A and B atoms in the AB$_5$ alloy. When the lattice parameter, a, decreases, the lattice parameter, c, must increase. The more the lattice parameter, a, decreases, the greater the lattice parameter, c, must increase [4].

3.2. P–C–T performance of hydrogen storage alloys

The hydrogen storage properties were measured using the Sieverts method in the pressure range from 0.001 to 10 MPa at four different temperatures from 233 to 413 K. The hydrogen desorption curves for LaNi$_{4.7}$M$_{0.3}$ (M = Al, Fe, or Co) and La$_{0.6}$Ce$_{0.4}$Ni$_{4.7}$M$_{0.3}$ (M = Al, Fe, or Co) alloys measured at 313 K are shown in Fig. 3. For comparison, the basic LaNi$_5$ was also characterized. The equilibrium hydrogen pressures were considerably changed by the substitutions of La by Ce and Ni by M. The substitution of Ce led to an increase in plateau pressure due to the smaller atomic ra-

dius of Ce than that of La. Ce forms a less dense hexagonal structure, and this was mentioned above as a possible reason for this trend [15]. The plateau pressure decreased upon substituting metals at the B location in the unit cell (Al, Fe,

Co). Furthermore, the plateau pressure decreased more rapidly upon adding Al. The difference between Al and Ni is greater than that between Fe, Co and Ni, which likely could explain above results.
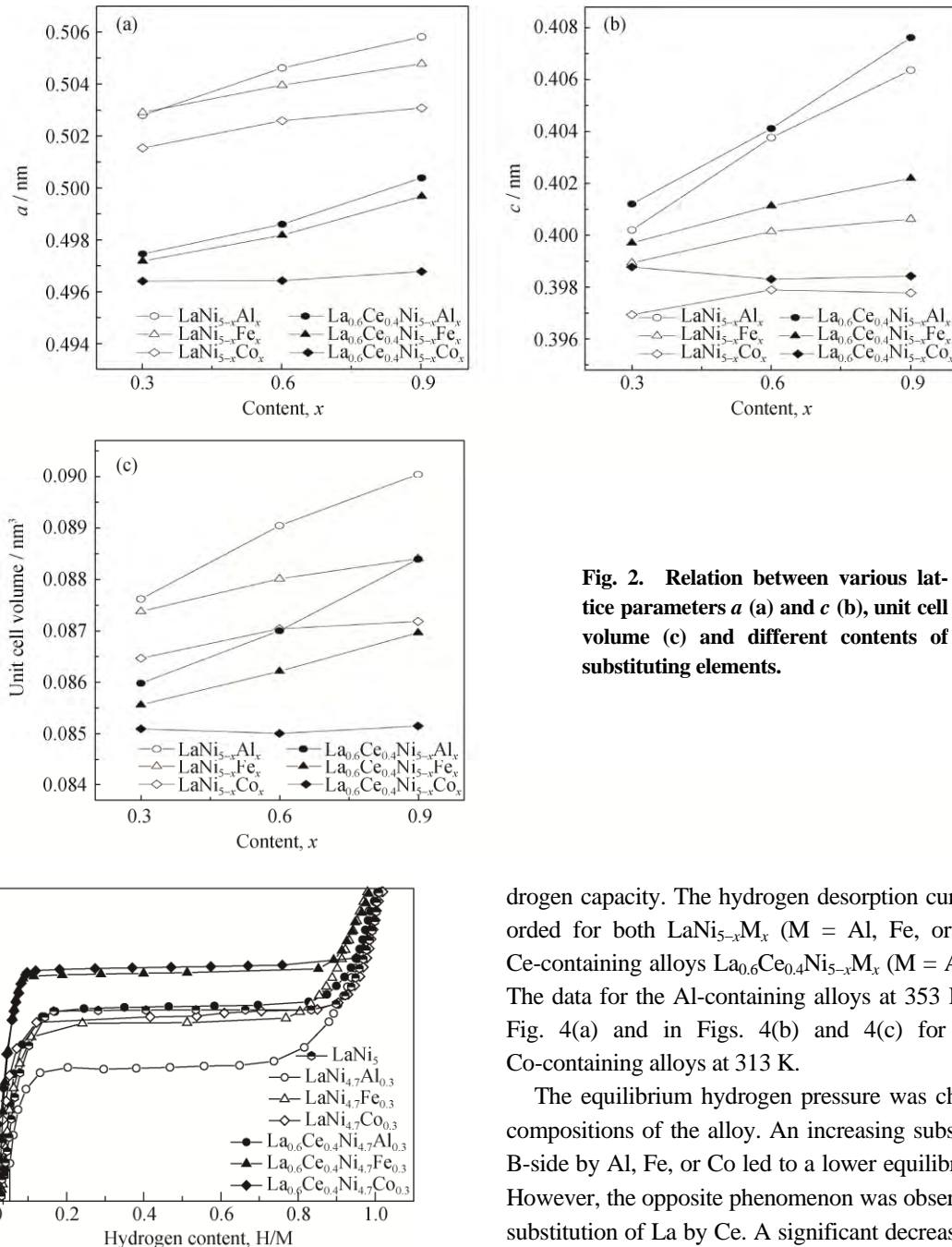

Fig. 2. Relation between various lattice parameters *a* (a) and *c* (b), unit cell volume (c) and different contents of substituting elements.

Fig. 3. P–C–T desorption curves for LaNi$_{4.7}$M$_{0.3}$ and La$_{0.6}$Ce$_{0.4}$Ni$_{4.7}$M$_{0.3}$ alloys at 313 K.

The combined effects of A and B-side substitution (A is the metal on the left side of hydrogen storage alloy, while B is the right side metal) in LaNi$_5$-type alloys were also investigated to determine the impact on plateau pressure and hy-

drogen capacity. The hydrogen desorption curves were recorded for both LaNi$_{5-x}$M$_x$ (M = Al, Fe, or Co) and the Ce-containing alloys La$_{0.6}$Ce$_{0.4}$Ni$_{5-x}$M$_x$ (M = Al, Fe, or Co). The data for the Al-containing alloys at 353 K is shown in Fig. 4(a) and in Figs. 4(b) and 4(c) for the Fe- and Co-containing alloys at 313 K.

The equilibrium hydrogen pressure was changed by the compositions of the alloy. An increasing substitution at the B-side by Al, Fe, or Co led to a lower equilibrium pressure. However, the opposite phenomenon was observed by partial substitution of La by Ce. A significant decrease of both plateau pressure and hydrogen capacity were observed for Al-containing alloys, which was attributed to great differences between the lattice parameters at different Al contents.

In the Fe- and Co-containing alloys, on the other hand, the plateau pressure decreased only slightly with an increasing amount of Fe and Co. Simultaneously, no significant loss of hydrogen capacity was observed upon increas-

ing the Fe and Co content. These results indicate that the substitution both A- and B-side elements can control the plateau pressure within the desired range. In addition, it was

found that the curves of LaNi$_{5-x}$Co$_x$ alloys had two plateau regions, and this phenomenon was more obvious as the Co content increased.
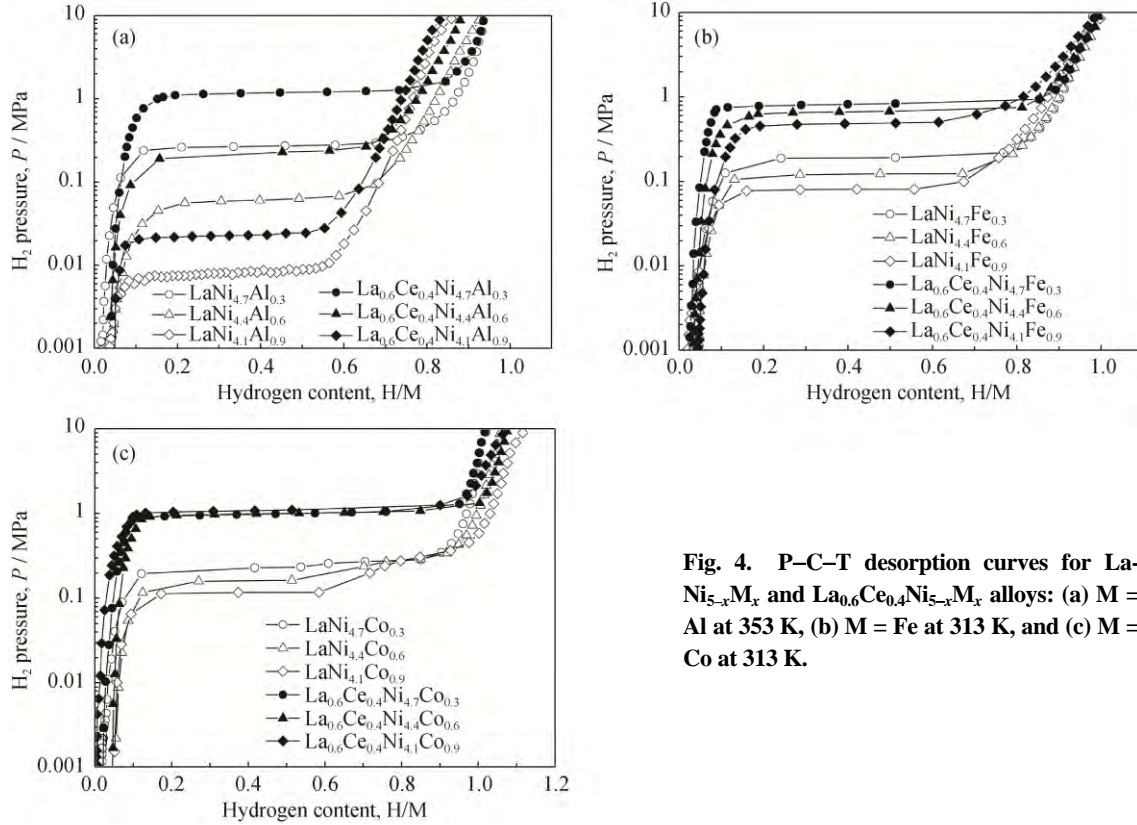

Fig. 4. P−C−T desorption curves for La-Ni$_{5-x}$M$_x$ and La$_{0.6}$Ce$_{0.4}$Ni$_{5-x}$M$_x$ alloys: (a) M = Al at 353 K, (b) M = Fe at 313 K, and (c) M = Co at 313 K.

It has been reported that the activation energies for phase transformations from β phase to γ phase are higher than for α phase to β phase, and that the substitution of Co increases the activation energies for both phase transformations [16]. It has also been found that the equilibrium pressure of the phase transformations from α phase to β phase is strongly reduced as the Co content increases [17]. The plateau pressures for the La$_{0.6}$Ce$_{0.4}$Ni$_{5-x}$Co$_x$ alloys, however, were extremely close, and the above-mentioned double plateau phenomenon caused by Co in the LaNi$_{5-x}$Co$_x$ alloys was eliminated after Ce was added. The plateau regions of the Ce-containing alloys were flatter than those of the alloys without Ce. This is an attractive trend for the development of hydrogen storage systems for various applications. In practical applications, when storing hydrogen, a flatter equilibrium pressure is better for controlling the hydrogen pressure of the hydrogen storage tank and is, therefore, conducive to the stability of the system. The latter phenomenon was also confirmed to exist at different temperatures (273, 293, 313, and 333 K), as shown in Fig. 5.

The addition of appropriate amounts of Ce might have enhanced the homogeneity of the CaCu$_5$-type phase in the

Co-containing alloys. In Fig. 2, the lattice parameter, *a*, and unit cell volume curves for La$_{0.6}$Ce$_{0.4}$Ni$_{5-x}$Co$_x$, are compared to those for LaNi$_{5-x}$Co$_x$. The curves are nearly flat, which confirms the above analysis.
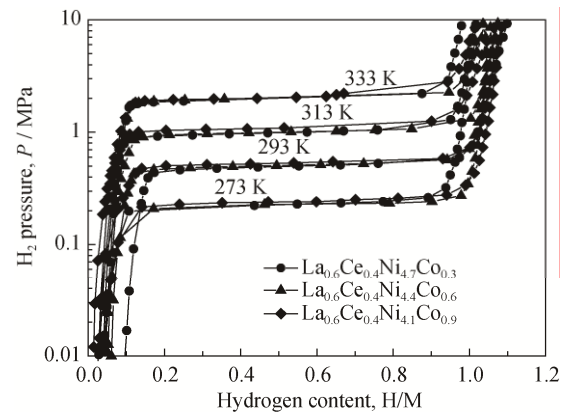

Fig. 5. P−C−T desorption curves for La$_{0.6}$Ce$_{0.4}$Ni$_{5-x}$Co$_x$ (*x* = 0.3, 0.6, and 0.9) at 273K, 293K, 313K, and 333K.

3.3. Lattice parameter analysis of hydrogen storage alloys

To investigate the relationship between the hydrogen equilibrium pressures and lattice constants of alloys, Figs.

6(a) and 6(b) present the plateau pressure as a function of lattice parameter, a, and the unit cell volume, respectively. A relatively linear character can be observed for the relationship between the equilibrium pressure and lattice parameter, a. The greater the lattice parameter, a, the lower the equilibrium pressure. A downward trend can also be ob-

served for the relationship between the equilibrium pressure and unit cell volume, However, as opposed to the relationship with lattice parameter a, no clear linear correlation exists for the lattice parameter c. This is likely because the parameters c and a changed in opposite directions upon Ce addition, as shown in Fig. 2.
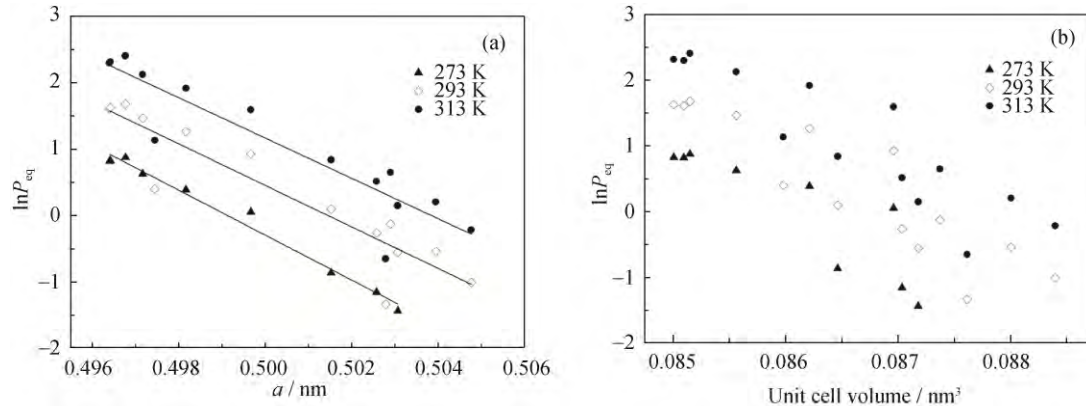

Fig. 6.   Relation between the hydrogen equilibrium pressure and lattice parameter a (a) and the unit cell volume (b).

The van't Hoff plots for $LaNi_{5-x}M_x$ (M = Al, Fe, or Co) and $La_{0.6}Ce_{0.4}Ni_{5-x}M_x$ (M = Al, Fe, or Co) are shown in Fig. 7. The enthalpy and entropy values were calculated by the slopes and y-intercepts of the function diagram, respectively.

It was found that the plots of Al-containing alloys had relatively larger slopes, which indicates that the enthalpy was higher than for the Fe- and Co-containing alloys. The enthalpy also increased significantly when the Al content increased, whereas increases in the Fe or Co content did not make a great difference. When Ce was added, the slopes became smaller, which indicated that the substitution of La by Ce reduced the enthalpy.

The relationships between ΔH and different lattice parameters are summarized in Fig. 8, which includes all alloys measured in this study. Downward trends can be observed for both parameter, a, and unit cell volume. However, the

correlation between the enthalpy and unit cell volume is more linear than the correlation between the enthalpy and lattice parameter, a.
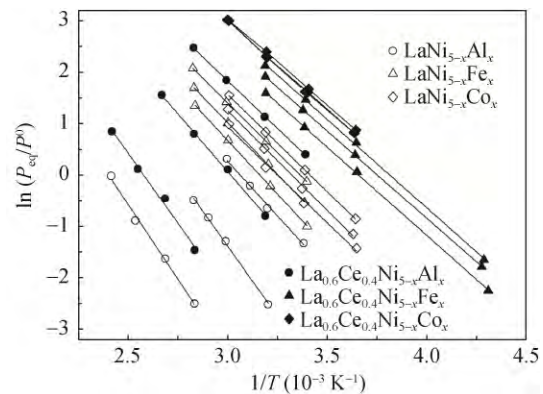

Fig. 7.   The van't Hoff plots for $LaNi_{5-x}M_x$ and $La_{0.6}Ce_{0.4}Ni_{5-x}M_x$ (M = Al, Fe, Co and x = 0.3, 0.6, and 0.9 respectively).
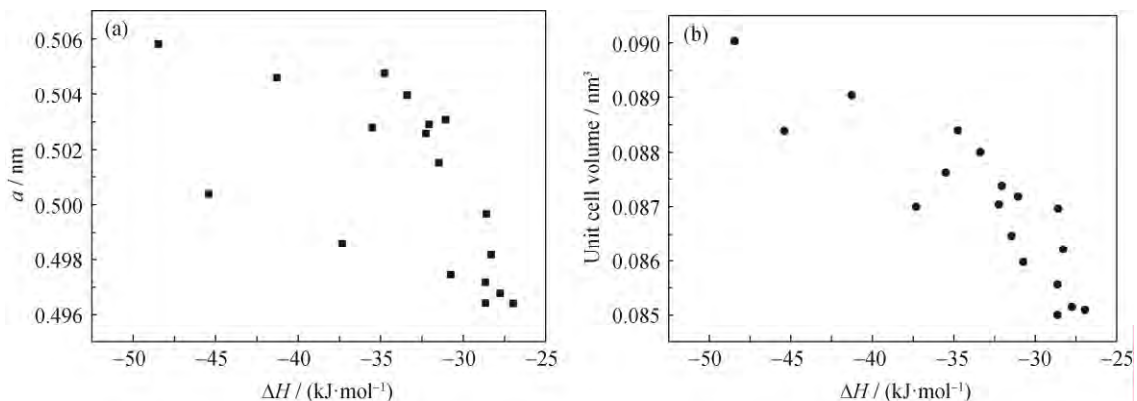

Fig. 8.   Relationship between ΔH of the alloys and (a) lattice parameter a and (b) the unit cell volume.

4. Conclusions

The combined effects of substitution at both the A and B unit cell locations in LaNi$_5$-based alloys were investigated systematically, where La was substituted by Ce and Ni by Al, Fe, or Co. The XRD profiles and lattice parameters of the alloys indicated that all alloys crystallized in a hexagonal CaCu$_5$ structure. The partial substitution with Al resulted in the most significant impact on the lattice parameters.

The P–C–T curves showed that partial substitution of La by Ce raised the equilibrium pressure without decreasing the hydrogen capacity, whereas partial substitution of Ni by Al, Fe, or Co reduced the hydrogen equilibrium pressure. This decrease was greater when increasing the amount of substitution. Al, in particular, caused the most significant decrease in the hydrogen capacity and equilibrium pressure.

In addition, the partial substitution of La by Ce (final ratio of 3 to 2) stabilized the crystal lattice parameters of the Co-containing alloys, which resulted in almost identical equilibrium pressures even when the Co content was increased. This study may serve as a good reference for the optimization of alloy compositions.

Acknowledgements

References

[1] L. Schlapbach and A. Züttel, Hydrogen-storage materials for mobile applications, *Nature*, 414(2001), No. 6861, p. 353.

[2] Y.F. Ding, C.E. Wen, P. Hodgson, and Y.C. Li, Effects of alloying elements on the corrosion behavior and biocompatibility of biodegradable magnesium alloys: a review, *J. Mater. Chem. B*, 2(2014), No. 14, p. 1912.

[3] X.W. Yang, Y.F. Zhu, J.G. Zhang, Y. Zhang, Y.N. Liu, H.J. Lin, T.M. Wang, and L.Q. Li, Effect of partial substitution of Ti for Al on the phase structure and electrochemical hydrogen storage properties of Mg$_3$AlNi$_2$ alloy, *J. Alloys Compd.*, 746(2018), p. 421.

[4] L.O. Valøen, A. Zaluska, L. Zaluski, H. Tanaka, N. Kuriyama, J.O. Ström-Olsen, and R. Tunold, Structure and related properties of (La,Ce,Nd,Pr)Ni$_5$ alloys, *J. Alloys Compd.*, 306(2000), No. 1-2, p. 235.

[5] M.P.S. Kumar, W.L. Zhang, K. Petrov, A.A. Rostami, S. Srinivasan, G.D. Adzic, J.R. Johnson, J.J. Reilly, and H.S. Lim, Effect of Ce, CO and Sn substitution on gas phase and electrochemcal hydriding/dehydriding properties of LaNi$_5$, *J. Electrochem. Soc.*, 142(1995), No. 10, p. 3424.

[6] M.H. Mendelsohn, D.M. Gruen, and A.E. Dwight, The effect on hydrogen decomposition pressures of group IIIa and IVa element substitutions for Ni in LaNi alloys, *Mater. Res. Bull.*, 13(1978), No. 11, p. 1221.

[7] T. Vogt, J.J. Reilly, J.R. Johnson, G.D. Adzic, and J. McBreen, Crystal structure of nonstoichiometric La(Ni,Sn)$_{5+x}$ alloys and their properties as metal hydride electrodes, *Electrochem. Solid-State Lett.*, 2(1999), No. 3, p. 111.

[8] M.H. Mendelsohn, D.M. Gruen, and A.E. Dwight, LaNi$_{5-x}$Al$_x$ is a versatile alloy system for metal hydride applications, *Nature*, 269(1977), No. 5623, p. 45.

[9] M.H. Mendelsohn, D.M. Gruen, and A.E. Dwight, The effect of aluminum additions on the structural and hydrogen absorption properties of AB$_5$ alloys with particular reference to the LaNi$_{5-x}$Al$_x$ ternary alloy system, *J. Less-Common Met.*, 63(1979), No. 2, p. 193.

[10] F. Pourarian and W.E. Wallace, Hydrogen storage in CeNi$_{5-x}$Cu$_x$, *J. Less-Common Met.*, 87(1982), No. 2, p. 275.

[11] R.K. Jain, A. Jain, S. Agarwal, N.P. Lalla, V. Ganesan, D.M. Phase, and I.P. Jain, Characterization and hydrogenation of CeNi$_{5-x}$Cr$_x$ (x = 0, 1, 2) alloys, *J. Alloys Compd.*, 430(2007), No. 1-2, p. 165.

[12] A.B. Aybar and M. Anik, Direct synthesis of La–Mg–Ni–Co type hydrogen storage alloys from oxide mixtures, *J. Energy Chem.*, 26(2017), No. 4, p. 719.

[13] S.K. Pandey, A. Srivastava, and O.N. Srivastava, Improvement in hydrogen storage capacity in LaNi$_5$ through substitution of Ni by Fe, *Int. J. Hydrogen Energy*, 32(2007), No. 13, p. 2461.

[14] G. Walker, *Solid-state Hydrogen Storage: Materials and Chemistry*, Woodhead Publishing Ltd., Cambridge, 2008.

[15] G.H. Aylward and T.J.V. Findlay, *SI Chemical Data*, J. Wiley & Sons, Ltd., New York, 1973.

[16] K. Asano, Y. Yamazaki, and Y. Iijima, Hydriding and dehydriding processes of LaNi$_{5-x}$Co$_x$ (x = 0–2) alloys under hydrogen pressure of 1−5 MPa, *Intermetallics*, 11(2003), No. 9, p. 911.

[17] H.H. Van Mal, K.H.J. Buschow, and F.A. Kuijpers, Hydrogen absorption and magnetic properties of LaCo$_{5x}$Ni$_{5-5x}$ compounds, *J. Less-Common Met.*, 32(1973), No. 2, p. 289.