Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Hydrogen interaction with alloys of $NdNi_{5-x}Al_x$ system

S.V. Mitrokhin*, A.A. Tepanov, V.N. Verbetsky

Chemistry Department, Lomonosov Moscow State University, 1/3 Leninskie Gory, Moscow 119991, Russian Federation

ARTICLE INFO

Article history:
Received 19 October 2016
Received in revised form
6 May 2017
Accepted 14 May 2017
Available online 2 June 2017

Keywords:
Metal hydrides
Thermodynamics
PCT diagram
Modelling

ABSTRACT

The study of hydrogen interaction with $NdNi_{5-x}Al_x$ alloys ($0 \leq x \leq 1$) and the refinement of thermodynamic parameters of hydriding reactions were performed in this work. The enthalpies and entropies of desorption reactions were calculated from the PCT-isotherms data and using our phenomenological model. Obtained results were compared with the literature data. The comparison of our experimental and calculated data proves the validity of the proposed model for prognosis of hydrogen absorption properties of alloys.

Introduction

The solution of practical tasks in the field of metal-hydride technology and the design of power plants including hydrogen storage and purification units is closely connected with the search for such compositions of hydrogen storage alloys which strictly meet the requirements of the input and output hydrogen pressure at the preset temperatures. It is well known that the hydrogen absorption–desorption pressure values can be tuned by alloying other metals to the basic compositions such as $LaNi_5$. However, for more accurate relevance to preset values of pressure at particular temperature, the number of alloying metals can reach five, which results in a considerable increase of the experimental work of proportioning compositions which fit best of all the input and output parameters. In case of only one alloying component it is rather easy to consider its impact on the alteration of hydrogen absorption–desorption parameters. For multicomponent compositions such an evaluation is a very complicated task because the change of concentration of one component results in the change of concentrations of all other components of alloy. Several calculation models of phase equilibrium in metal-hydrogen systems (e.g. Refs. [1–5]) have been proposed up to now. A good comparison of some of these models may be found elsewhere [6,7]. Although all the models give sufficiently correct predictions and descriptions of PC-isotherms for particular alloy compositions they do not allow optimization of compositions to fit the pressure–temperature criteria.

Earlier we proposed a phenomenological model [8] of calculation and selection of alloy compositions, which possess the preset values of equilibrium hydrogen pressure at given temperature. It is known that according to Vegard law in a set of solid solutions cell parameters are linearly dependent on component concentrations [9]. Taking into account that the stability of hydride phases (i.e. the enthalpy of hydriding reaction) increase with increasing alloy cell parameters [10],

* *Corresponding author.*
E-mail address: mitrokhin@hydride.chem.msu.ru (S.V. Mitrokhin).
http://dx.doi.org/10.1016/j.ijhydene.2017.05.098

and that the hydriding reaction pressure and temperature can be determined from the enthalpy and entropy of this reaction using van't Hoff equation, it is possible to assume the existence of dependence between component concentrations and thermodynamic parameters. Similar to classic Vegard law for real solid solutions there exist positive and negative deviations from linearity. Since the $f(c_1 \ldots c_n)$ plot should be a continuous function, then the full second power polynomial is enough for their mathematical description. The polynomial coefficients can be determined from the sets of experimental enthalpy and entropy values of hydriding–dehydriding reactions for studied alloys with the same crystal structure. In order to augment the precision of these calculations it is extremely important to secure maximal compliance of thermodynamic parameters to real alloy compositions during database compilation.

While preparation of such databases for multicomponent compositions of $CaCu_5$ structure type we came across the fact, that for $NdNi_5$ compound the literature data on cell parameters differ greatly (Table 1).

Table 1 – Literature crystal data for $NdNi_5$.

a (Å)	c (Å)	c/a	V (Å^3)	Ref.
4.9500	3.9820	0.804	84.50	[11]
4.9730	4.0124	0.807	85.94	[12]
4.9410	3.9590	0.801	83.70	[13]
4.9550	3.9730	0.802	84.48	[14]
4.9540	3.9780	0.803	84.55	[15]
4.9200	3.9500	0.803	82.81	[16]
4.9470	3.9780	0.804	84.31	[17]
4.9480	3.9770	0.804	84.32	[18]
4.9260	3.9570	0.803	83.15	[19]
4.9560	3.9760	0.802	84.57	[20]
4.9480	3.9770	0.804	84.32	[21]
4.9499	3.9754	0.803	84.35	[22]

A considerable discrepancy also exists in literature data on equilibrium hydrogen desorption pressures for the $NdNi_5$–H_2 system (Fig. 1).

As well, we noticed the results of study of $NdNi_{5-x}Al_x$–H_2 system [13]. Abnormally high values of reaction entropy were obtained for solid solution compositions ($0 \leq x \leq 1$) having $CaCu_5$ structure. It is known [26] that almost for all absorption–desorption reactions in metal-hydrogen systems the value of reaction entropy amount roughly to 130 J/K mole because it is mainly determined by the entropy of the change from molecular hydrogen gas to dissolved solid hydrogen. Furthermore according to literature data for related $LaNi_{5-x}M_x$–H_2 systems (M = Al, Fe, Mn) reaction entropy has a tendency to decrease with increasing M content.

The aim of this work was the investigation of hydrogen interaction with $NdNi_{5-x}Al_x$ alloys ($0 \leq x \leq 1$) and refinement of thermodynamic parameters of hydriding reactions.

Material and methods

Starting alloys were prepared from pure metals (99.9% or higher) in arc furnace with tungsten nonexpendable electrode in high purity argon atmosphere (1.2 atm). Evaporation losses were less than 0.1%. Obtained alloys were annealed in vacuum at 850 °C for 240 h.

Phase composition of alloys was determined by X-ray analysis (DRON-3, CuKα). Chemical composition was analysed by EMPA (SEM LEO EVO 50 XPV). PC-isotherms were measured in high pressure device, described earlier [27].

Calculations of thermodynamic parameters using proposed model were performed by solving of a quadratic equations system in regard to equation coefficients:

$$F(x) = Y_0 + \sum A_i x_i + \sum B_{ij} x_i x_j \quad (j \geq i)$$

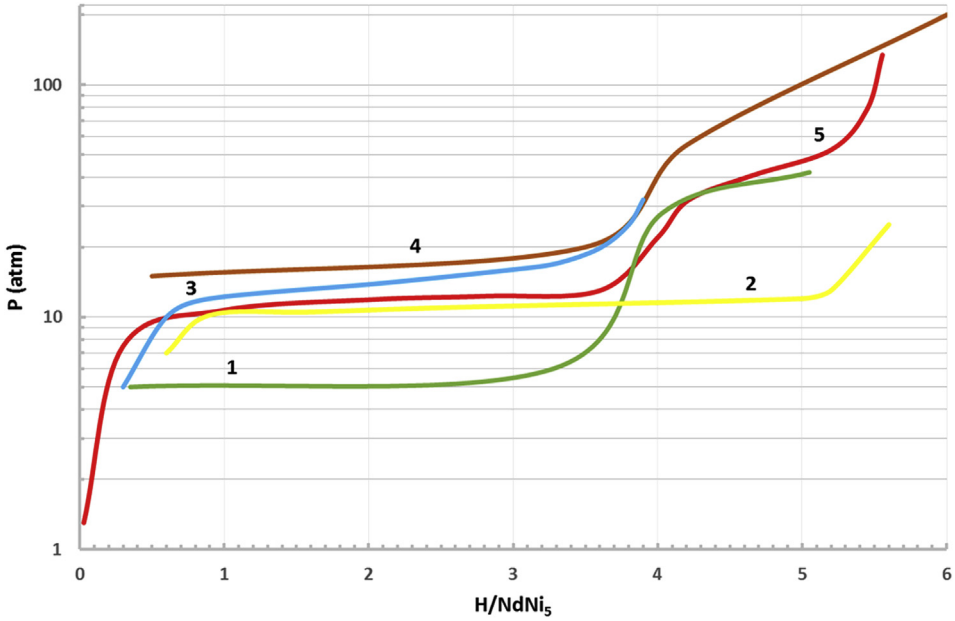

Fig. 1 – Desorption isotherms for $NdNi_5$–H_2 system at 293 K: 1 – [23], 2 – [24], 3 – [25], 4 – [22], 5 – this work.

Table 2 – X-ray characteristics of $NdNi_{5-x}Al_x$ alloys.

Alloy	a (Å)	c (Å)	c/a	V (Å^3)
$NdNi_5$	4.9545(5)	3.9747(6)	0.802	84.50(1)
$NdNi_{4.75}Al_{0.25}$	4.9815(4)	3.9889(5)	0.801	85.72(1)
$NdNi_{4.5}Al_{0.5}$	4.9745(6)	4.0139(7)	0.807	86.02(2)
$NdNi_{4.25}Al_{0.75}$	4.9693(3)	4.0267(4)	0.810	86.11(1)
$NdNi_4Al$	4.9691(5)	4.0339(6)	0.812	86.26(1)

Table 3 – EPMA data for $NdNi_{5-x}Al_x$ alloys.

Alloy	Nd (at.%)	Al (at.%)	Ni (at.%)	Calculated composition
$NdNi_5$	16.64	–	83.36	$NdNi_5$
$NdNi_{4.75}Al_{0.25}$	16.15	4.24	79.61	$Nd_{0.97}Ni_{4.78}Al_{0.25}$
$NdNi_{4.5}Al_{0.5}$	16.46	8.14	75.40	$Nd_{0.99}Ni_{4.52}Al_{0.49}$
$NdNi_{4.25}Al_{0.75}$	16.29	11.71	72.00	$Nd_{0.98}Ni_{4.32}Al_{0.7}$
$NdNi_4Al$	16.38	15.57	68.05	$Nd_{0.98}Ni_{4.08}Al_{0.94}$

where $F(x)$ – enthalpy or entropy of reaction, x – alloy component content, Y_0, A and B – equation coefficients.

The number of equations minimally required for the solution is determined by formula: $N = 2i + (i^2 - i)/2$, where i = [(number of components in alloy) – 1]. In our case the database, which includes 8 components (La, Ce, Nd, Fe, Al, Mn, Sn, Ni), requires at least 35 equations, i.e. 35 sets of enthalpy, entropy and component concentrations. Certainly, this database must not include the data for those compositions for which evaluations are calculated. After the calculation of polynome coefficients it is possible to calculate the theoretical values of enthalpy, entropy and equilibrium pressures at given temperatures for particular compositions, or to choose theoretical compositions satisfying predetermined range of pressure values at particular temperature.

Results and discussion

According to X-ray data (Table 2) all studied initial alloys were of $CaCu_5$ structure type. For $NdNi_5$ our data agree best of all with results of Refs. [11,15,20].

All alloys were single phase samples. This was also confirmed by SEM data. Five points-averaged alloy compositions according to EPMA are shown in Table 3.

As can be seen, the increasing Al content results in natural expansion of unit cell volume. This should result in the increase of the hydride stability and decrease of the equilibrium pressure values. Hydrogen desorption isotherms for $NdNi_{5-x}Al_x$–H_2 systems are shown in Fig. 2. Actually the stability of hydrides increases for alloys with greater Al content.

For $x = 0$ and $x = 0.25$ isotherms show two well defined plateaux of $\beta \leftrightarrow \alpha$ and $\gamma \leftrightarrow \beta$ transformations. Further increase of Al content results in degeneration of upper $\gamma \leftrightarrow \beta$ plateau, although the full hydrogen capacity at high pressure decreases slightly from 5.5 H/AB$_5$ for $x = 0$ to 4.9 H/AB$_5$ for $x = 1$.

PCT-isotherms were measured for all alloys at temperatures 293, 313, 333 and 353 K. From the values of equilibrium pressure at specified temperatures the values of enthalpies and entropies of desorption reactions were calculated using a' Hoff equation. Obtained results are summarised in Fig. 3 and Table 4 together with the results of Ref. [13] and our model calculations.

As follows from Fig. 3 and Table 4 the enthalpy of reaction trends to increase with increasing Al content for experimental as well as calculated and literature data. However our calculated values agree well with our experimental, while those obtained in Ref. [13] for the same x are about 13 kJ/moleH_2 greater. In case of entropy the differences between our and literature results become more dramatic. While the calculated entropy values pass through a small maximum for $x \approx 0.3$, the

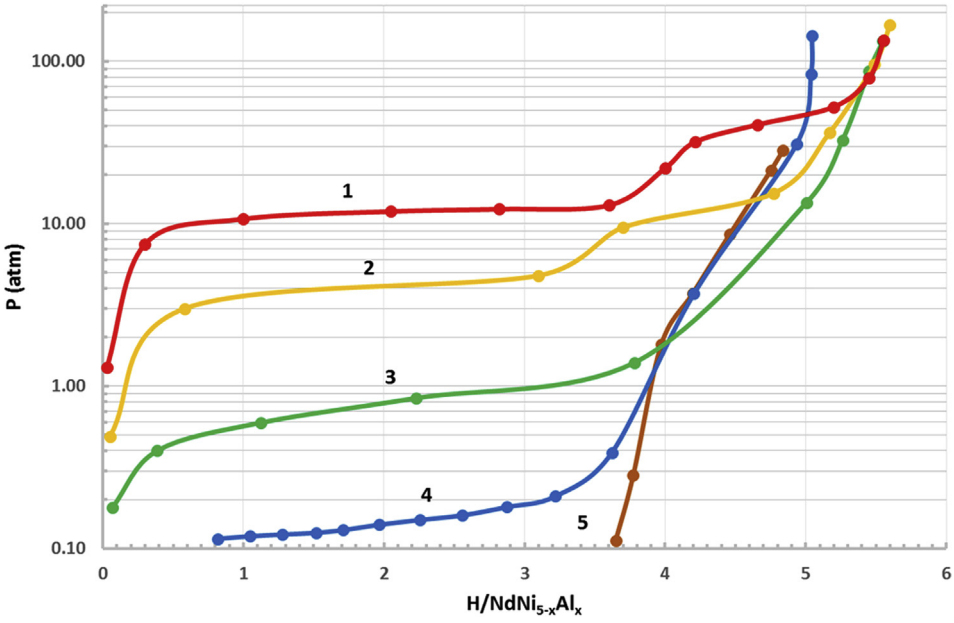

Fig. 2 – Desorption isotherms for $NdNi_{5-x}Al_x$–H_2 systems at 293 K: 1 – $NdNi_5$, 2 – $NdNi_{4.75}Al_{0.25}$, 3 – $NdNi_{4.5}Al_{0.5}$, 4 – $NdNi_{4.25}Al_{0.75}$, 5 – $NdNi_4Al$.

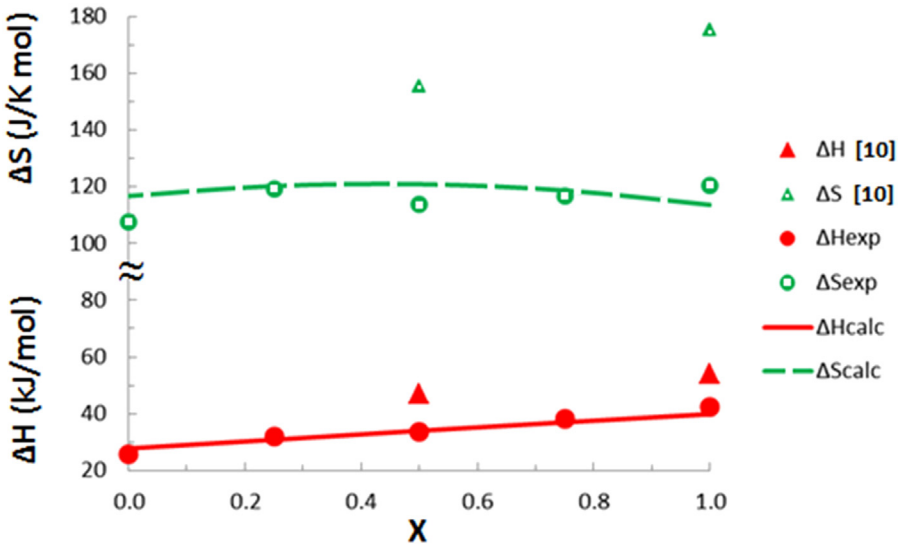

Fig. 3 – Comparison of experimental, calculated and literature values of enthalpies and entropies of hydriding reactions in $NdNi_{5-x}Al_x$–H_2 systems.

Table 4 – Thermodynamic parameters for $NdNi_{5-x}Al_x$–H_2 systems.

Alloy	ΔH (kJ/mole H_2)			ΔS (J/K mole H_2)		
	Calc	Exp	[13]	Calc	Exp	[13]
$NdNi_5$	27.8	25.6(3)		116.8	107.4(7)	
$NdNi_{4.75}Al_{0.25}$	30.9	31.8(2)		120.3	119.2(5)	
$NdNi_{4.5}Al_{0.5}$	34.1	33.7(5)	47.0	120.9	113.7(8)	154.9
$NdNi_{4.25}Al_{0.75}$	37.0	38.2(3)		118.7	116.7(7)	
$NdNi_4Al$	39.9	42.5(3)	54.1	113.6	120.4(6)	174.7

experimental values follow this trend and both do not exceed 130 J/K moleH_2, the literature values are much greater with an obvious trend to increase with increasing Al content.

Conclusions

The comparison of our experimental and calculated data proves the validity of the proposed model for prognosis of hydrogen absorption properties of alloys.

Acknowledgements

The authors are grateful to E. Movlaev for practical help in the high pressure experiments.

REFERENCES

[1] Bjurström H, Suda S, Lewis D. Numerical expression for the P–C–T properties of metal hydrides. J Less Common Met 1987;130:365–70.
[2] Zhou ZQ, Zhang JL, Ge JS, Feng F, Dai ZM. Mathematical modelling of the PCT curve of hydrogen storage alloys. Int J Hydrogen Energy 1994;19(3):269–73.
[3] Fang SS, Zhou ZQ, Zhang JL, Yao MY, Feng F, Northwood DO. Two mathematical models for the hydrogen storage properties of AB_2 type alloys. J Alloys Compd 1999;293–295:10–3.
[4] Lototskyy MV. New model of phase equilibria in metal-hydrogen systems: features and software. Int J Hydrogen Energy 2016;41:2739–61.
[5] Ledovskikh AV, Danilov DL, Vliex M, Notten PHL. Modeling and experimental verification of the thermodynamic properties of hydrogen storage materials. Int J Hydrogen Energy 2016;41:3901–18.
[6] Sharma Vinod Kumar, Anil Kumar E, Prakash Maiya M, Srinivasa Murthy S. Experimental and theoretical studies on static and dynamic pressure concentration isotherms of $MmNi_{5-x}Al_x$ (x = 0, 0.3, 0.5 and 0.8) hydrides. Int J Hydrogen Energy 2014;39:18940–51.
[7] Payá J, Linder M, Laurien E, Corberán JM. Mathematical models for the P–C–T characterization of hydrogen absorbing alloys. J Alloys Compd 2009;484:190–5.
[8] Verbetsky VN, Mitrokhin SV. Intermetallic hydrides – synthesis, properties and application for hydrogen storage. Int Sci J Altern Energy Ecol 2005;10:41–61.
[9] Vegard L. Bildung von Mischkristallen durch Berührung fester Phasen. Z Phys 1921;5:393–5.
[10] Lundin CE, Lynch FE, Magee CB. A correlation between the interstitial hole sizes in intermetallic compounds and the thermodynamic properties of the hydrides formed from those compounds. J Less Common Met 1977;56:19–37.
[11] Che G-C, Yu Y-D, Liang J-K. A study on the phase diagrams of pseudo-binary systems $LaNi_5$–$NdNi_5$ ($CeNi_5$) and their hydrogen absorption characteristics. Acta Phys Sin 1984;33:770–8.
[12] Zeng LM, Franzen HF. Single-crystal structure investigation of NdNi and $NdNi_5$. J Alloys Compd 2000;311:226–7.
[13] Bobet J-L, Pechev S, Chevalier B, Darriet B. Structural and hydrogen sorption studies of $NdNi_{5-x}Al_x$ and $GdNi_{5-x}Al_x$. J Alloys Compd 1998;267:136–41.
[14] Chuang YC, Wu CH, Jiao F. Investigation of the structure and phase equilibria of $Nd(Co_{1-x}M_x)_5$ compounds (M = Ni, Cu, Al). J Less Common Met 1987;133(2):215–23.
[15] Che GC, Liang JK, Yu YD. Studies of phase relations between mischmetal (Mm) and $MmNi_5$ together with their hydrogen absorption properties. Jinshu Xuebao 1986;22(5):B206–11.

[16] Kalychak YM, Oniskovets BD, Bodak OI. The Nd–Mn–Ni system. Sov Non-Ferrous Met Res 1983;11:227–30.
[17] Rykhal RM, Zarechnyuk OS. Isothermal section at 600 °C of neodymium–nickel–aluminium ternary systems in the range of 0–33.3 at.% of neodymium. Dopov Akad Nauk Ukr SSR (Ser. A) 1979:1057–9.
[18] Bayanov AP. Enthalpies of formation of compounds of the rare earth elements, calculated on the basis of their crystal chemistry. Inorg Mater 1973;9:858–61.
[19] Virkar AV, Raman A. Crystal structure of AB_3 and A_2B_7 rare earth–nickel phases. J Less Common Met 1969;18:59–66.
[20] Dwight AE. Factors controlling the occurrence of Laves phases and AB_5 compounds among transition elements. Trans Am Soc Met 1961;53:479–500.
[21] Wernick JH, Geller S. Transition element–rare earth compounds with Cu_5Ca structure. Acta Crystallogr 1959;12:662–5.
[22] Senoh H, Takeichi N, Takeshita T, Tanaka H, Kiyobayashi T, Kuriyama N. Hydrogenation properties of RNi_5 (R: rare earth) intermetallic compounds with multi pressure plateaux. Mater Trans 2003;44(9):1663–6.
[23] Young K, Huang B, Ouchi T. Studies of Co, Al, and Mn substitutions in $NdNi_5$ metal hydride alloys. J Alloys Compd 2012;543:90–8.
[24] Uchida H, Tada M, Huang YC. The influence of cerium, praseodymium, neodymium and samarium on hydrogen absorption in $LaNi_5$ alloys. J Less Common Met 1982;88:81–7.
[25] Takaguchi Y, Tanaka K. Hydriding–dehydriding characteristics of $NdNi_5$ and effects of Sn-substitution. J Alloys Compd 2000;297:73–80.
[26] Züttel A, Wenger P, Rentsch S, Sudan P, Mauron Ph, Emmenegger Ch. $LiBH_4$ a new hydrogen storage material. J Power Sources 2003;118:1–7.
[27] Mitrokhin S, Zotov T, Movlaev E, Verbetsky V. Synthesis and properties of AB_5-type hydrides at elevated pressures. J Alloys Compd 2007;446–447:603–5.