Development of Rare Earth Hydrogen Storage Alloys: Correlation Between Structure, Stability, and Hydrating Properties

ZHAO Shuang   LIN Qin   CHEN Ning   YE Wen   MA Li

Applied Science School, USTB, Beijing 100083, China

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Abstract: The structure of β-LaNi$_x$H$_x$ is mentioned. Special emphasis is laid on the influence of substitutions with metallic elements on the thermodynamic properties of the rare-earth-nickel hydrogen storage alloys. The models of the heat of hydride formation are studied attentively. The relation between the stability and the heat of formation of intermetallic compounds including with other physical properties is discussed. The relations between hydriding properties and the geometric and electronic structure of the intermetallic compounds are presented.

Key words: rare earth, hydrogen storage alloys, hydride

Since the appearance of hydrogen storage alloys in late sixties, through the joint efforts of scientists and technical persons all over the world, both the alloys and the applications have been developing rapidly. The rare-earth-nickel alloys are as a whole very suitable. The most important property is that their pressure characteristics can be modified by making suitable element substitutions to meet specific demands. The hydrogen absorption properties of these alloys are deeply dependent on the constituent metals. It has been found that these substitutions induce a large change in both the stability and the capacity of the related hydrides. Different models are established to explain these characteristics through the properties of the intermetallic compounds. They show the role played by geometric, thermodynamic and electronic properties.

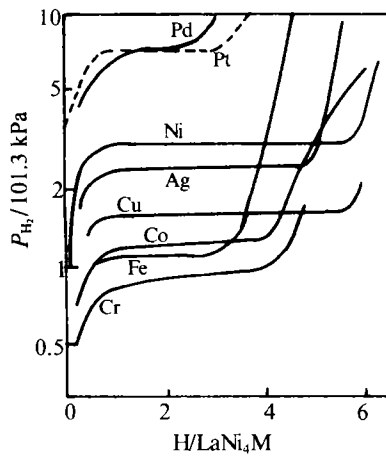## 1 Thermodynmics and Models

1.1 Thermodynamic properties

For REM$_5$-H systems, with RE fixed and M varied (M=Ni, Co, Fe, and Cr), the desorption pressures of hydrides vary from high to low in the order of Ni, Co, Fe, and Cr. And when RE=La, Ce, Pr, Nd, Sm, Gd or Th, the desorption pressures of the hydrides of RENi$_5$ and RECo$_5$ increase with the atomic number of RE except for Ce, which is exceptionally unstable, hence gives a high desorption pressure as can be seen in table 1.

On partly substituting either RE or M in REM$_5$, the thermodynamic properties of the hydrides usually change quite noticeably. For LaNi$_5$, on substituting a transitional element (Pd, Pt, Ag, Cu, Fe, Co, Cr, Mn etc.) partly for Ni, the desorption pressure of all hydrides decreases except those with Pt and Pd as shown in Fig. 1. The stability of the hydrides decreases in the order of Ag, Cu, Co, Fe and Cr. Vacancies of Ni atoms in intermetallics have the same effect as element substitutions On substituting a rare earth element for La, the decomposition pressures of their hydrides increase with the atomic number of the substituting element (see Fig. 2). The substituted CeNi$_5$ is of special interest for applications. The desorption pressure of the hydride of CeNi$_5$ is high and its pressure hysteresis is very large (Pa=24 MPa, Pd=4.8 MPa at 20°C) hence it is not good for applications. On partly substituting Al, Mn, or Cu for Ni, the isotherms are depressed and the pressure hysteresis diminishes greatly. This is also a very effective way of improving the properties of the hydrides of Ce-rich alloys.

The mischmetal-nickel alloys are much cheaper in price than LaNi$_5$. The contents of mischmetals vary. The mischmetals with high La and lower Ce contents are more suitable for practical uses[4~6]. Ce rich mischmetal-nickel alloys should be generally modified by element substitution. When Al, B, Cu, Mn, Si, Ti, or Ca substitutes partly for Ni the desorption pressures generally decrease. For substitution of mischemetal, Ca is most effective[7] (see Fig. 3). On

## Table 1 Thermodynamics properties of REM5-hydrogen system

Compound	Hydrogen content(H/AB$_5$)	Plateau pressure/× 101.3kPa	ΔH° / (kJ · mol^{-1})	ΔS° / J·(K · mol)$^{-1}$	Ref.
LaNi$_5$	6	1.5	−31.1	109.2	[1,2]
CeNi$_5$	6	48.6	−14.1	80.2	[1,2]
PrNi$_5$	6.4	12.2	−30.6	−	[1,2]
NdNi$_5$	6.2	20.3	−29.4	−	[1,2]
SmNi$_5$	1.6	60.8	−26.9	126	[1,2]
GdNi$_5$	2.9	121.6	−25.2	126	[1,2]
ThNi$_5$	0.05	no plateau	−	−	[1,2]
YNi$_5$	4	12	−	−	[3]
CaNi$_5$	5	0.5	−	−	[3]
LaCo$_5$	4.3	0.04	−45.4	128.1	[2,4]
CeCo$_5$	3	2.0	−39.1	136.9	[2,4]
PrCo$_5$	3.8	0.52	−38.6	126.4	[2,4]
NdCo$_5$	2.7	0.72	−42.8	−	[2,4]
SmCo$_5$	3	3.34	−32.8	121.8	[2,4]
GdCo$_5$	2.8	24.32	−	−	[2,4]
ThCo$_5$	2.3	48.64	−	−	[2,4]

Fig. 1 Hydrogen desorption isotherms for LaNi$_5$ and LaN$_4$M systems at 40℃ [2]
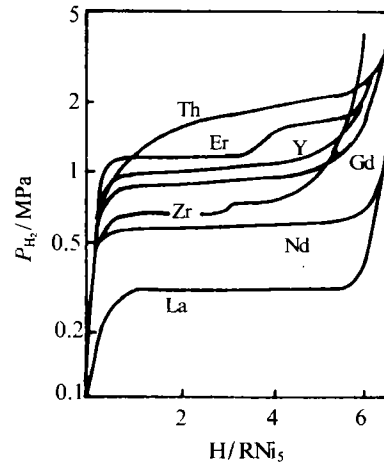
Fig. 2 Desorption isotherms for LaNi$_5$ and La$_{0.8}$R$_{0.2}$Ni$_5$-H systems at 40℃ [2]

substituting Al, B, Cr, Mn, Si, Ti, Zn, V,Cu, Fe, or Co for Ni partly in MnNi$_5$, the desorption pressures decrease for all substitutions except B. The effects of Mn and Al are most pronounced, as shown in Fig. 4. Generally, on element substitution, the desorption isotherms of the hydrides become more slanted and hydrogen storage capacities decrease. In this respect the effects of B, Si and Al are large while the effects of Co, Cu, Cr and Mn are small. The overall effect of substituting Mn for Ni is the best.

1.2 Models of the enthalpy of hydride formation and stability

The knowledge of ΔH is of great importance for practical applications of metal-hydrogen systems
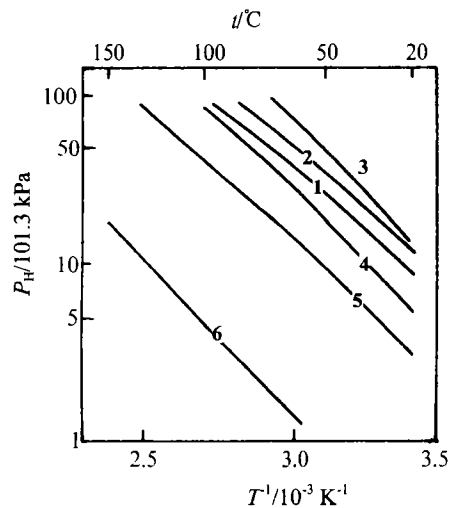
Fig. 3 The temperature-hydrogen desportion pressure relation for Mn$_{1-x}$Ca$_x$Ni$_5$-H systems[7]
1: MnNi$_5$; 2: Mn$_{0.9}$Ca$_{0.1}$Ni$_5$; 3: Mn$_{0.75}$Ca$_{0.25}$Ni$_5$; 4: Mn$_{0.5}$Ca$_{0.5}$Ni$_5$; 5: Mn$_{0.25}$Ca$_{0.75}$Ni$_5$; 6: CaNi$_5$

concerning energy storage since the dissociation pressure for two-phase metal hydrides is related to ΔH via the Vant' Hoff relation where ΔS is for the entropy change and is nearly constant. Investigations about models of enthalpy of formation of metal hydride have been reported by many authors. Some empirical
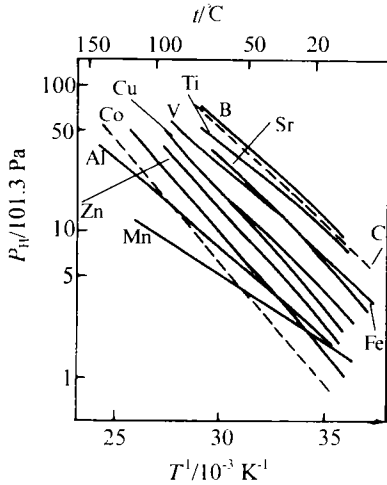

Fig. 4 The temperature-hydrogen desorption pressure
relations for $MnNi_{5-y}B_y$-H systems (y=0.5, B ≡ B,
Ti, Si, V, Cr, Zn, Al, Mn; y=2.5, B ≡ Co; y=1.0,
B ≡ Fe, Cu)[7]

models was first established. These empirical rule is significant for alloy design.

The atomic-cell model is the most representative in most semiempirical models of the enthlpy. Miedema[8,9] demonstrated in the model that the model could approximate to the enthalpy of formation of 1 g atom of a binary alloy of two transition metals by the following equation:

$$\Delta H = f(c)Pe\left\{ -(\Delta\phi^*)^2 + (\frac{Q}{Pe})(\Delta n_{ws})^2\right\} \quad (1)$$

where P and Q are constants for the system, c is the atomic fraction of one of the components, e is the electronic charge, arises from the difference in electronega-

tivity of the components and is nearly the same as the work function and n_{ws} is the difference in the density of electrons at the boundary of the Wigner-Seitz cells. For solid solutions $f(c)=c(1-c)$, but for ordered alloys Miedema tabulated empirical values. In 1980, Bouten and Miedema[10] claimed further improvement, specially for hydrides:

$$\Delta H = \frac{Pc_H V_H^{2/3} f_M^H}{n_{ws}^{-1/3}}\left[-(\Delta\phi^*)^2 + \frac{Q}{P}\{\Delta(n_{ws}^{1/3})\}^2 - \frac{R}{P}\right] \quad (2)$$

V_H is the molar volume of metallic hydrogen and equals to 1.7 cm^3, f_M^H represents the degree to which hydrogen atoms are surrounded by metal atoms M. The values from equation (1) are listed in table (2).

On the basis of above, Miedema[11] suggested the heat of ternary hydrides formation equation is written:

$$\Delta H(AB_n H_{x-y}) = \Delta H(AH_x) + \Delta H(BH_y) -$$
$$(1-F)\Delta H(AB_n) \quad (3)$$

The first two terms on the right-hand side are the contributions from the two binary hydrides. The third term is a contribution from the loss of A-B contact where F is fitted. For AB_5 type of alloys ,it contributes 90% loss of A-B bind after formatting hydrides. As $\Delta H(AB_n)$ becomes more negative, $\Delta H(AB_n H_{x+y})$ becomes less negative. This is the rule of reversed stability: the more stable is the binary compound, the less stable is its hydride.

Pasturel, et al.[12,13] have developed a model to calculate the enthalpy of hydrogen of the ternary compounds. Starting from Miedema relation (3), compounds can be expressed by

$$\Delta H_{reaction} = (1 - \frac{m}{3})\Delta H_f(AB_{n-x}C_x) - \Delta H_f(AB_n) +$$

$$\frac{m}{3}\Delta H_f(AH_3) + \frac{m(n-x)}{3}\frac{1}{n}\Delta H_f(B_nH_3) + \frac{mx}{3n}\Delta H_f(C_nH_3) \quad (4)$$

The values calculated are reported in table 2.

In attempt to find a correlation between ΔH and the

Table 2 Comparison of the formation of some intermetallics and of the heat of hydriding reaction

Compound	ΔH_f^{298}/(kJ·mol⁻¹)		$\Delta H_{reaction}$/(kJ·mol⁻¹)	
	experiment	calculated from eq.(1)	experiment	calculated from eq.(4)
LaNi₅	−158.9	−165.9	−31.7	−29.7
LaNi₄Cu	−143.1	−142.1	−33.9	−34.3
LaNi₄Fe	−129.7	−130.8	−34.3	−37.2
LaNi₄Al	−246.8	−169.7	−47.6	−49.7
LaNi₄Mn	−133.9	−131.7	−48.5	−46
LaNi₂Cu₃	−107.5	−108.7	−30.9	−38.8
LaNi₃Cu₂	−128.3	−125.4	−37.6	−36.4
LaNiCu₄	−93.3	−91.6	−30.5	−43.47
LaCu₅	−75.7	−75.2	−44.3	−47.23

smallest possible number of band-structure parameters of the host metal, Griessen, et al.[14] found the experimental values for the heat of formation of binary hydrides MH_x could be reproduced reasonably well by the following simple relation:

$$\Delta H = \frac{n_S}{2}(\alpha\Delta E + \beta) \qquad (5)$$

with $\Delta E = E_F - E_S$; $\alpha = 29.62$ kJ/eV (for 1 mol H); $\beta = -135.0$ kJ (for 1 mol H). where n_S represents the number of electrons per atom in the lowest s-like conduction band of the host metal. E_S is the energy for which the integrated density of states of the host metal is equal to $1/2n_S$ electron per atom. For ternary hydrides :

$$\Delta H(A_{yA}B_{yB}H_z) = \alpha(\frac{y_A\Delta E_A^* + y_B\Delta E_B^*}{y_A + y_B}) + \beta \qquad (6)$$

with $\Delta E_i^* = \Delta E_i + \phi_i + \phi_i^*$; ϕ_i^* is work function of alloy $A_{yA}B_{yB}$; ϕ_i is work function of pure alloy i.

After that Griessen[15] gave another local band structure model, the equation of the enthalpy of hydrogen solution in transition metals could be written:

$$\Delta H_x = a\Delta EW^{1/2}\sum_j R_j^{-4} + b \qquad (7)$$

with $a = 18.6$ kJ/mol; $b = -90$ kJ/mol; $\Delta E = E_F - E_S$; W is the width of d band; R_j is the distance between H atom and its nearest metal atom.

In addition to the models above some references indicate the relation between the heat of formation of intermetallics compounds with the stability, the stability of the hydrides also being considered to correlate with the interstitial hole size[3,16], the unit cell volume[17], the compressibility[18] or the shear modules[19], features of the band structure[14,20,21]. Although these models also have their limitations, these models are suitable for predicting trends and useful in search for new hydrogen-absorbing materials. The concept of a minimal H-H distance impose a restriction on the maximum hydrogen content of binary and ternary hydrides[22,23].

2 Structure and Hydriding Properties

2.1 Structure of hydride

The structure of β-LaNi$_5$ deuteride has been studied by numerous researchers by means of neutron diffraction on the corresponding deuterides[4,24~28]. Various structural models were proposed, differing not only in the symmetry of the structure but also in the kind and

number of interstitial sites occupied by the hydrogen atoms. The location of hydrogen in β-LaNi$_5$ sees Fig. 5. Lartige[29] reinvestigated the structure of β-LaNi$_5$D$_x$ in the range $5.0 \le x \le 6.7$ and show that the ternary deuteride undergoes a structural phase transformation owing to progressive ordering of the deuterium atoms, four types of different interstitial sites being occupied in the fully ordered hydride LaNi$_5$D$_7$. The ordering of deuterium atoms leads to a symmetry reduction and to a superstructure corresponding to a doubling of the LaNi$_5$ unit cell along the c direction. The model descriptions for preferred hydrogen (or deuterium) occupation of the interstitial holes are based on geometrical considerations[30] or on local affinities[16]. Yvon[31] showed that there is a close correspondence between the two models, which is based on the correlation between the size of the holes and the affinity of the hydrogen atoms to the metal atoms surrounding the holes.

2.2 Relation between structure and hydriding properties

(1) Plateau pressure

The atomic structures of single rare earth metals are similar, but their hydride dissociation pressure are different especially for Ce. See table 1. In order to study the relationship between the structures of RENi$_5$ and their hydrogen absorption properties, Chen N and Lin Q[32] calculated the electronic structures of RENi$_5$ using SCF-X α-WS method. A typical RE$_2$Ni$_4$ octahedral cluster was selected to represent the RENi$_5$, as shown in Fig. 6 . This cluster includes all of the three kinds of atoms (Ni$_1$, Ni$_2$ and RE), with its center position is occupied by a majority of the hydrogen atoms.

Table 3 lists the results on FH force, total energy (E_{tot}), Viril coefficient, Fermi energy level (E_f) and the

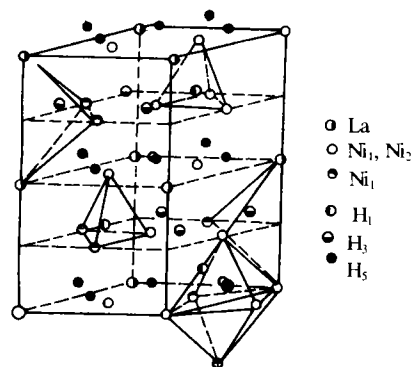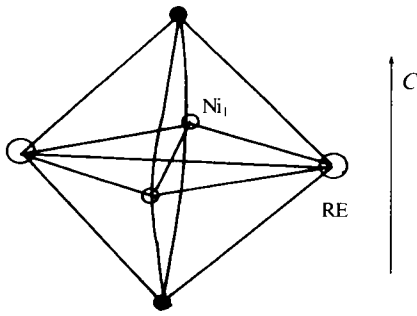Fig.5 The location of hydrogen in LaNi$_5$

Fig.6 Model for RE_2Ni_4

energy level above $E_f(E_f^+)$. The Viril coefficients of four clusters are all larger than 0.999 77. The results show that both electrons on complete shells of $5s$ and $5p$ of RE, and the electrons on uncompleted shells contribute to the coupling between RE and other atoms, which plays an important role in stabilizing the structures; The result also indicated that E_f has close relationship with the hydrogen absorption plateau pressure: the lower the energy level of E_f, the better the stability of hydride and the smaller the hydrogen absorption plateau pressure. Recently they further stud-

Table 3 Results of calculation of electronic structure in RENi system

| | E_{tot} $(R \times 10^4)$ | Viril coef. | $E_f(R_f)$ | $E_f^+(R_f)$ | Hellmann-Feynma/u | | |
					RE-RE	RE-Ni$_1$	RE-Ni$_2$
La$_2$Ni$_4$	-4.492	0.999 94	-0.318 1	-0.264 6	0.611	2.668	3.099
Ce$_2$Ni$_4$	-4.631	0.999 86	-0.176 2	-0.160 8	1.034	2.893	2.225
Pr$_2$Ni$_4$	-4.771	0.999 77	-0.228 7	-0.209 1	2.736	3.560	0.579
Nd$_2$Ni$_4$	-4.895	0.999 88	-0.246 6	-0.232 8	1.732	2.544	1.079

ied the relationship between electronic and hydriding properties when Cu partly substituted for Ni in LaNi$_5$ alloy and draw a similar conclusion[33].

(2) Hydrogen content

It is of interest to know the interaction of the hydrogen atom with their neighbor atoms in the ternary hydrides and the change in the electronic properties associated with the hydrogen content. A method based on geometrical considerations has been developed in order to predict preferred occupation of hydrogen sites and stoichiometry of hydrides[23] . It suggested the smallest radius of interstitial sphere was to be about 0.04 nm. The results indicated that the hydrogen atoms can not occupy an interstitial site with radius smaller than 0.04 nm surrounded by and kind of atoms and that the hydrogen atom occupies the particular interstitial site not only because of the stabilization due to the bond formation between the hydrogen atom and its surrounding atoms but also because the hydrogen atom prefers the interstitial sites where metal atoms are not gather densely and the electron density is low[34]. Percheron-Guegan[28] showed that the reduction in the amount of hydrogen absorbed by some pseudobinary LaNi$_{5-x}$M$_x$ compounds is associated with a reduction in the number of occupied interstitial sites. From electronic aspect, Takeshita[18] and Gschneidner[35] pointed out the important role of the 3 d electrons in the absorption capacity. Wallace[20] also suggested the amount of hydrogen is controlled by the

number of metal-hydrogen bonding states by X-ray photoelectron spectroscopy. Recently, Richter[36] and Schonfeld[37] investigated an LaNi$_5$H$_{0.08}$ single crystal by quasi-elastic neutron scattering technique and found that the hydrogen occupation in the $3f$ sites were more stabilized than in the $6m$ sites. This also supports the calculation results of electronic states for the $3f$ and $6m$ site model clusters[38] . The results suggested that various alloys are different in the charge distribution around the hydrogen sites in the host metal lattices and the LaNi$_5$ alloy with the hydrogen sites of the lower electron density appears to absorb hydrogen easily.

3 Conclusion

It is a convenient way to monitor the equilibrium pressure of the hydrides through substitutions in REM$_5$. The relation between these substitutions and hydrogen absorption characteristics needs a detailed investigation. It is the heat of formation of the intermetallics which reflects their cohesive energy. The models based on enthalpy of binary or ternary hydrides and other properties leads us to predict the stability of the hydrides easily. The relate geometric and electronic factors to hydrogen content need further study.

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