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Hydrogen-absorbing characteristics of 15 rare earth elements

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Abstract

The amounts of absorbed hydrogen and the rates of hydrogen-absorption reaction were measured for 15 rare earth elements. The cohesive energy and energy fluctuation of metal clusters were also calculated by using the extended-Hückel method. The characteristics of each rare earth element in the capacity of hydrogen absorption and the reaction rate were discussed by comparing the experimental results with the calculated ones. The major results are as follows. (i) Hydrogen/metal ratios (H/M) of rare-earth metals are nearly constant, ∼3, except for Eu and Yb; (ii) the rate of hydrogen-absorption reaction may be determined by the product of (magnitude of energy fluctuation) and (density of states); (iii) the 15 rare-earth elements would be classified into four groups: Group 1 (Ce, Pr, Nd), Group 2 (Sm, Gd, Tb, Dy, Ho, Er), Group 3 (Tm, Yb, Lu) and Group 4 (Y, La, Eu) and (iv) the rate of hydrogen-absorption reaction is remarkably promoted by pre-heating the metals before the reaction.

Keywords: Hydrogen storage materials; Metals; Gas–solid reactions; Electronic states

1. Introduction

The authors have an idea that the hydrogen-absorbing mechanism is substantially controlled by the exchange of electrons between metal and hydrogen. Several researches based on this point of view have already been reported; physical properties of 5d-transition metal hydrides were examined using total energies calculated by the band theory [1] and hydrogen absorption was studied based on the bond order between atoms calculated by the molecular orbital method [2]. To understand the rates of hydrogen-absorption and desorption and their temperature dependence, however, the authors think that cohesive energy, energy fluctuation and the density of states are important. In this work, the amounts and rates of hydrogen-absorption were measured for 15 rare earth metals including yttrium and hydrogen-absorption characteristics were discussed by using the calculated values that were obtained by the extended Hückel method.

2. Experimental

Commercial 15 metals of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Er, Tm, Yb, and Lu of 99.9% purity were used. After cutting, polishing and drying, the sample metal of 1 g was placed in a 6 mm ϕ stainless steel tube that was connected to a PCT device. The initial hydrogen pressure was 2 MPa. The absorption was conducted at 298 and 573 K; the experiment was also carried out at 276 or 400 K in some cases. The change of hydrogen gas pressure was measured continuously; a maximum duration of the reaction was 7 days. The sample was preheated in a nitrogen gas for 30 min before the absorption of hydrogen.

3. Molecular orbital calculation

The electronic states of model clusters containing 55 rare earth metal atoms were calculated by the extended Hückel method; a cluster of 87 atoms was employed only for Y or La. To examine the change of electronic state when the metal absorbs hydrogen, the calculation was also carried out for

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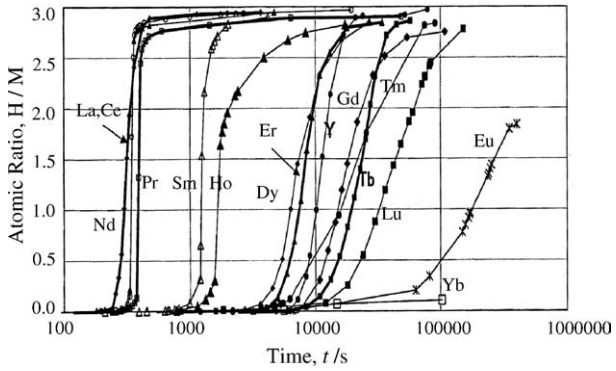

Fig. 1. Hydrogen-absorbing rate of rare earth elements at 276 K: preheating temperature is 573 K.

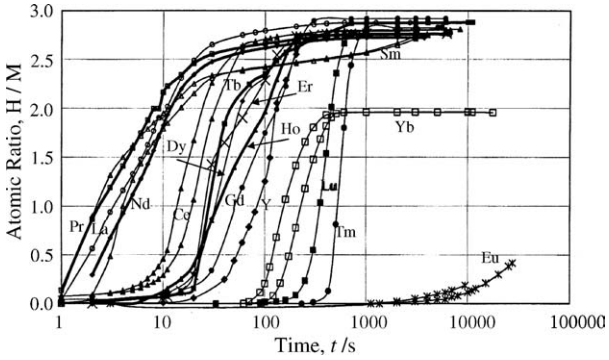

Fig. 2. Hydrogen-absorbing rate of rare earth elements at 573 K: preheating temperature is 573 K.

each atomic cluster of which rare earth atoms were replaced by hydrogen atoms. The cohesive energy was defined by the total energy of a cluster minus the sum of ionisation potentials of cluster-constituting atoms. The energy fluctuation ΔE was estimated by the following equation, with using E_n as the n-th energy level above the highest occupied molecular orbital [3].

$$(\Delta E)^2 = < (E_n - < E_n >)^2 >$$

$$< E_n > = \frac{\sum_n E_n \exp(-E_n/kT)}{\sum_n \exp(-E_n/kT)}$$

The cohesive energy and energy fluctuation may be effective for estimating the direction of change (statistic stability of materials) and the reaction rate (dynamic stability), respectively.

4. Results

4.1. Hydrogen absorption

The hydrogen absorption curves measured for 15 kinds of samples at 298 K are shown in Fig. 1. It is seen in this diagram that the maximum amounts of absorbed hydrogen converge to about three of H/M-value except for Eu and Yb, although the absorption rate varies for various metals. The absorption characteristics seem to be dispersed in four groups. Fig. 2 shows the results of hydrogen absorption at 573 K. The absorption rates increases about 100 times greater than at 298 K but the absorbed amounts of hydrogen saturate to the same value of about three (also except for Eu and Yb) as that at 298 K. The temperature dependences of hydrogen absorptions for La, Ce,

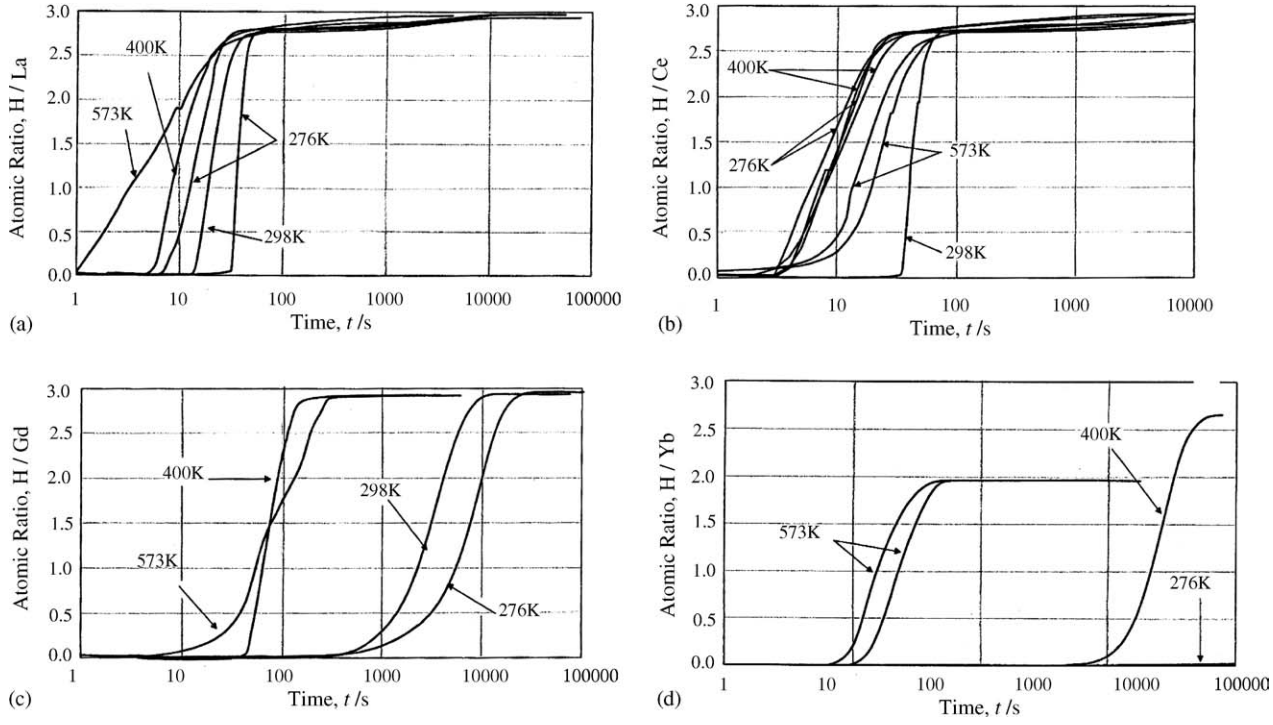

Fig. 3. Temperature dependence of hydrogen-absorbing reactions: (a) La, (b) Ce, (c) Gd and (d) Yb.

Gd and Yb are shown in Fig. 3. The temperature dependence is significant except for Ce; the shape of absorption curve becomes irregular for Gd and the saturated amount of hydrogen H/M for Yb is irregularly changed with temperature.

4.2. Molecular orbital calculation

Some examples of the calculated results are shown in Fig. 4; the upper and lower parts indicate the energy fluctuation and cohesive energy against the composition of the atomic clusters, respectively. The results show that (a) the cohesive energy decreases as going from Y to Er and increases from Tm to Lu and (b) the temperature dependence of energy fluctuation is lower for Y and decreases from La to Nd and then increases from Sm to Er and it is much higher for Tm, Yb, Lu.

5. Discussion

5.1. Rate of hydrogen absorption

The reaction rate is usually defined as the product of specific rate constant and concentration of reacting material. In the present reaction of hydrogen absorption, we think that the rate constant and the concentration of reacting material correspond to the energy fluctuation and the density of states, respectively. In this context, we can see that the temperature dependence of hydrogen absorption rate is large for the metals of La, Gd, Ho, Tm, Yb of which energy fluctuations exhibit relatively large temperature dependence.

On the other hand, the temperature dependence for Ce is small; this can be correlated with the theoretical fact that the energy fluctuation has a small temperature dependence as shown in Fig. 4(b).

Unfortunately, the reason why the reaction rates for Gd and Yb are irregularly changed with temperature remains unsolved in the present stage of study.

5.2. Grouping of elements

It is reported [4] that the hydrogen-desorption characteristics of 7 rare earth hydrides can be divided into two groups, but no reasons were presented. In this study we can try to do the following grouping for the hydrogen-absorption characteristics of 15 rare earth metals. For the electronic systems of rare earth elements, they are divided into 2 groups of sd

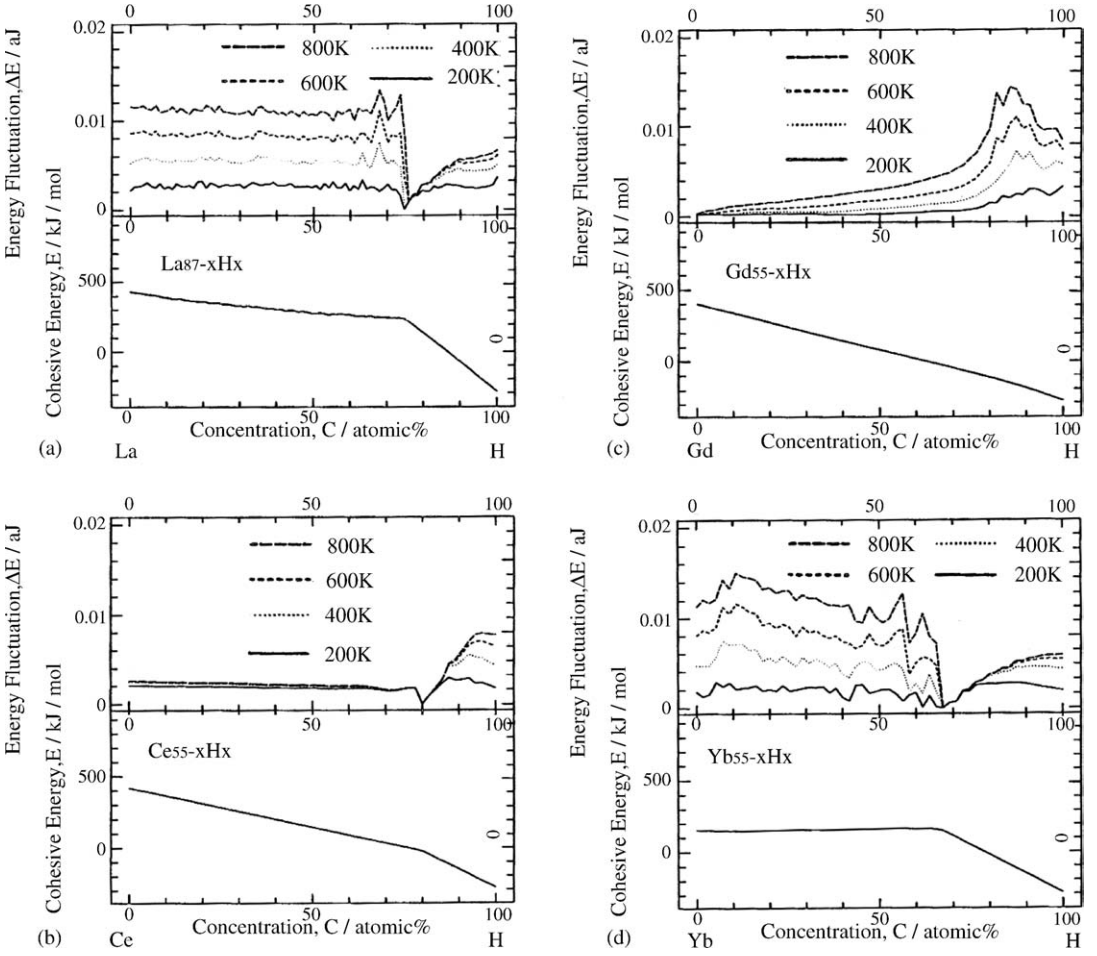

Fig. 4. Energy fluctuation and cohesive energy of RE-H systems: (a) La-H, (b) Ce-H, (c) Gd-H and (d) Yb-H.

Table 1
Grouping of rare earth elements

Element	Cohesive energy (kcal/mol)	Energy fluctuation pattern	Electronegativity	Exception	Grouping (theoretical)	Grouping (experimental)
Y	420	a	○	1[a]	1, 3 or 4	3
La	320	a′	○	1[a]	1, 3 or 4	1
Ce	90	a	○		1	1 or 2
Pr	70	a	○		1	1
Nd	60	a	○		1	1
Sm	∼0	b	○ or ●		2	l or 2
Eu	10	b	●	2[b]	2 or 4	4
Gd	30	b	●		2	2 or 3
Tb	40	b	●		2	2
Dy	50	b	●		2	2 or 3
Ho	30	b	●		2	2
Er	∼0	b	●		2	2 or 3
Tm	190	c	○		3	3
Yb	290	c	○		3	3 or 4
Lu	360	c	○		3	3

a: invariant with H concentration, a′: invariant but having large temperature dependence, b: increase with H concentration, c: decrease with H concentration, ○: less electro-negative than H (Electron is transferred to H.), ●: more electro-negative than H (electron is transferred from H).
[a] 1: sd electronic system.
[b] 2: half-filled electronic shell.

(Y and La) and sf (Ce–Lu) systems. From the results of the cohesive energy and energy fluctuation, the elements can be classified into 3 groups of Y–Nd, Sm–Er and Tm–Lu. In the sense of electro-negativity, they may also be classified into the same 3 groups. These groupings are summarized in Table 1. The following grouping may be possible: Group 1 (Ce, Pr, Nd), Group 2 (Sm, Gd, Tb, Dy, Ho, Er), Group 3 (Tm, Yb, Lu) and Group 4 (Y, La, Eu).

6. Summary

The characteristics of 15 rare earth elements in the capacity of hydrogen absorption and the reaction rate were measured and discussed by comparing with the cohesive energy and energy fluctuation calculated by using the extended Hückel method. The major results are as follows. (i) Hydrogen/metal ratios (H/M) of rare-earth metals are nearly constant, ∼3, except for Eu and Yb; (ii) the rate of hydrogen-absorption reaction may be determined by the product of (magnitude of energy fluctuation) and (density of states); (iii) the 15 rare-earth elements would be classified into four groups; Group 1 (Ce, Pr, Nd), Group 2 (Sm, Gd, Tb, Dy, Ho, Er), Group 3 (Tm, Yb, Lu) and Group 4 (Y, La, Eu); (iv) the rate of hydrogen-absorption reaction is remarkably promoted by pre-heating the metals before the reaction.

References

[1] D.A. Papaconstantopoulos, J.P. Stroch, G.D. Drew, J. Less-Common Metals 172–174 (1991) 401–410.
[2] Y. Takahashi, H. Yukawa, M. Morinaga, J. Alloys Compd. 242 (1996) 98–107.
[3] S. Yamamoto, Acta Mater. 45 (1997) 3825–3833.
[4] V.A. Yartys, O. Gutfleisch, V.V. Panasyuk, I.R. Harris, J. Alloys Compd. 253–254 (1997) 128–133.