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Hydrogen absorbing characteristics of R–M (R = La, Ce; M = Co, Rh, Ir, Ni, Pd, Pt) binary systems

J. Kadono [a,*], K. Hirano [b], S. Nishiuchi [a], R. Ariga [c], S. Yamamoto [c], T. Tanabe [c], H. Miyake [d]

[a] *Kyoto Municipal Industrial Research Institute, Shimogyo-ku, 600-8813 Kyoto, Japan*
[b] *Asahi Seiren Co Ltd., 9 Oota, Yao 581-0037, Japan*
[c] *Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*
[d] *Faculty of Engineering, Kansai University, Yamate-cho, 564-0073 Osaka, Japan*

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Abstract

The capacity, rate and reversibility of the hydrogen absorbing/desorbing reaction have been measured for the binary systems composed of rare earth metal, R (La or Ce), and transition metal, M (Co, Rh, Ir, Ni, Pd or Pt), by Sieverts' method. These experimental results were discussed by comparing with the theoretical ones; density of states, cohesive energy and energy fluctuation, which were calculated by the extended Hückel method. Major results obtained are as follows. (1) The capacity of hydrogen absorption decreases almost linearly with increasing M components in R–M systems and it is explained in terms of the density of states. (2) The rate of hydrogen-absorbing reaction in La–M systems are larger than that of Ce–M systems. The larger absorption rate corresponds to the larger energy fluctuation. (3) The reversibility of the hydrogen absorbing/desorbing reaction is closely related with the cohesive energy of these systems. When the cohesive energy of the hydrogen absorbed system is large, a reverse (i.e. desorbing) reaction hardly occurs.
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Keywords: Hydrogen storage materials; Metals; Gas–solid reactions; Electronic band structure; Electronic states

1. Introduction

The hydrogen-storage materials are requested to have the following properties: (i) the high capacity of hydrogen absorption; the material is expected to absorb hydrogen as much as possible under moderate conditions, (ii) the higher rate of hydrogen absorption; it is expected to absorb hydrogen as fast as possible, and (iii) the reversibility of hydrogen absorbing/desorbing reaction; the hydrogen-absorbed material is also expected to desorb hydrogen easily as possible. How many factors control the capacity, rate and reversibility? To understand the real nature of the hydrogen-storage phenomenon, therefore, we have to elucidate comprehensively the issues of capacity, reaction rate and reversibility. We think it indispensable for proceeding the task to examine the phenomenon based on the electronic states of the hydrogen-material systems [1,2].

Several studies have already been carried out in terms of electronic energy levels or band structures obtained by the molecular orbital method or band calculations for hydrogen-storage materials [3–8]. Despite of the calculations based on the quantum mechanics, unfortunately, they have explained the experimental results in terms of rather classical concepts such as a hole size or the number of interstitial sites in the crystal lattice of the materials. Furthermore, their approach for verification of their thinking is too narrow; the application to experimental results is limited mainly to $LaNi_5$.

We measured the amount of absorbed hydrogen, the rate of hydrogen absorption reaction and reversibility of hydrogen absorbing/desorbing reactions for the rare earth (La or Ce)–transition metal (Co, Rh, Ir, Ni, Pd or Pt) systems and calculated the three physical quantities, density of states,

* Corresponding author.
E-mail address: monmon@city.kyoto.jp (J. Kadono).

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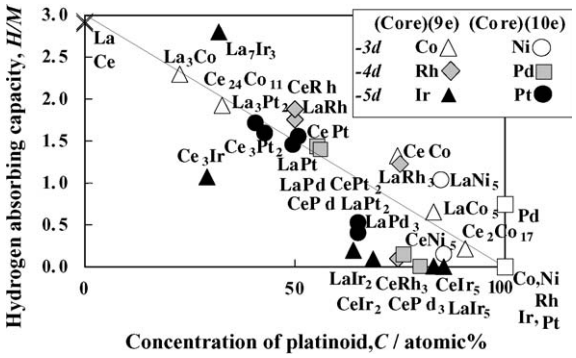

Fig. 1. Dependence of the concentration of platinoid on hydrogen absorption capacity.

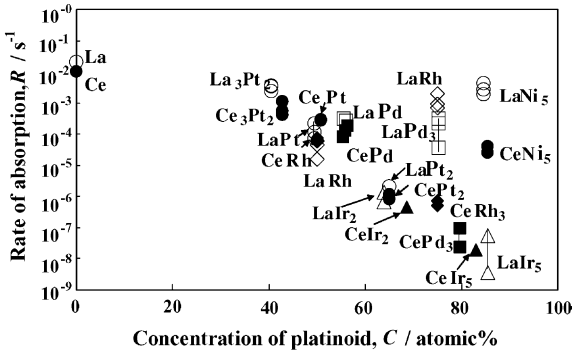

Fig. 3. Dependence of the concentration of platinoid on hydrogen absorption rate.

energy fluctuation and cohesive energy, by the molecular orbital method. We have tried to comprehensively explain the characteristics of hydrogen absorbing/desorbing reactions by comparing them with the calculated three physical quantities.

2. Experimental method

The composition of R–M alloys prepared by arc melting are as follows: La_3Co, $LaCo_5$, LaRh, $LaRh_3$, La_7Ir_3, $LaIr_2$, $LaIr_5$, $LaNi_5$, LaPd, $LaPd_3$, La_3Pt_2, LaPt, $LaPt_2$, $Ce_{24}Co_{11}$, $CeCo_3$, Ce_2Co_{17}, CeRh, $CeRh_3$, Ce_3Ir, $CeIr_2$, $CeIr_5$, $CeNi_5$, CePd, $CePd_3$, Ce_3Pt_2, CePt, $CePt_2$. The amounts of absorbed hydrogen were measured by Sieverts' method at 303 K and under 2 MPa hydrogen pressure till saturation occurs or about 2 weeks. The amounts of desorbed hydrogen were measured at 573 K. The pressure for hydrogen desorption experiment was terminated at 0.01 MPa.

3. Method of calculation

In the present work, Molecular orbital calculation was carried out by the extended Hückel method. Several reported values of orbital exponents [9–11], and ionization potentials [12–14] are used in calculation. The size of model clusters used in the present work is 55 at. for Ce and 87 at. for La and platinoid metals. These sizes are chosen so that the shape of cluster becomes spherical so as to eliminate the influences of surface on the calculated results. As mentioned above, three concepts, density of states, the energy fluctuation and the cohesive energy, are used in our models. Density of states were calculated from the obtained eigenvalues of clusters. The cohesive energy is defined as

(the total energy of a system)

−(sum of the energy of isolated constituent atoms) (1)

The zero level of energy is taken as the energy of a system when an electron is infinitely distant from an atomic core.

The energy fluctuation (ΔE) is defined as

$$\Delta E^2 = \langle (E_n - \langle E_n \rangle)^2 \rangle \quad (2)$$

where $\langle E_n \rangle = \sum E_n \exp(-E_n/kT) / \sum \exp(-E_n/kT)$ and E_n is nth eigenvalue above the highest occupied molecular orbital energy level that corresponds to the Fermi energy.

4. Results and discussion

4.1. Capacity

From the experiment in the R–M systems, as shown in Fig. 1, hydrogen-absorbing capacity shows maximum at

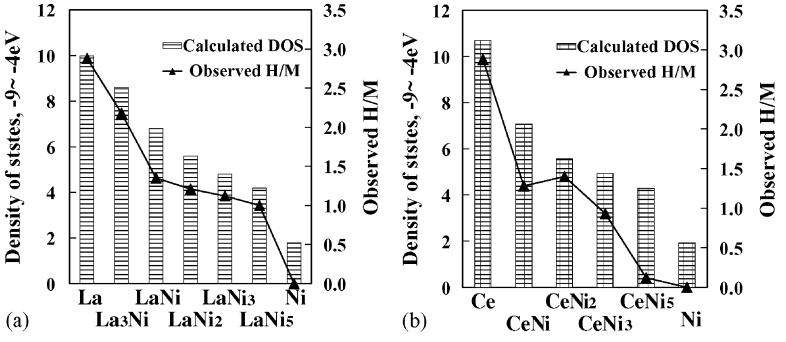

Fig. 2. Density of states and H/M ratio: (a) La–Ni, (b) Ce–Ni systems.

pure substances (La, Ce), and decreases almost linearly with increasing M components.

It can be seen from the calculation for clusters of La–H and Ce–H systems that the density of states in the energy range from −9 to −4 eV changes drastically as the hydrogen content at interstitial sites of La or Ce lattices increases.

Thus we may conclude that molecular orbitals at −9 to −4 eV are used for the interaction with hydrogen orbitals in the process of the hydrogen absorption. As shown in Fig. 2, the density of states in the energy range from −9 to −4 eV shows maximum at pure substances (La, Ce), and decreases almost linearly with increasing M components, so a good correlation can be seen between theoretical measure; the density of states and experimental measure; the capacity.

4.2. Reaction rate

If the hydrogen-absorbed state of hydrogen storage material is unstable under a certain condition of pressure and temperature, the material can not absorb hydrogen. When

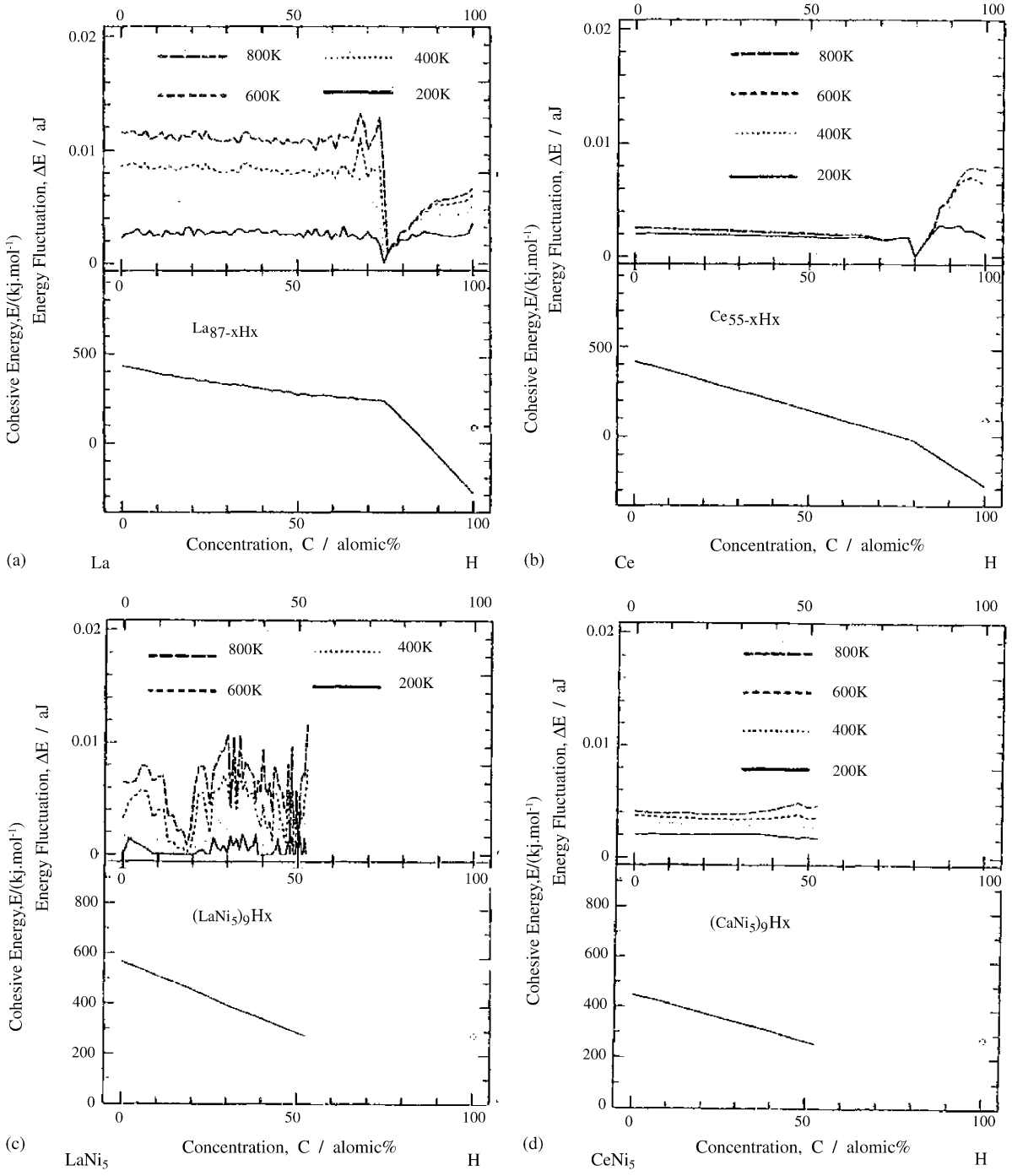

Fig. 4. Cohesive energy and energy fluctuation: (a) La–H, (b) Ce–H, (c) $LaNi_5$–H and (d) $CeNi_5$–H systems.

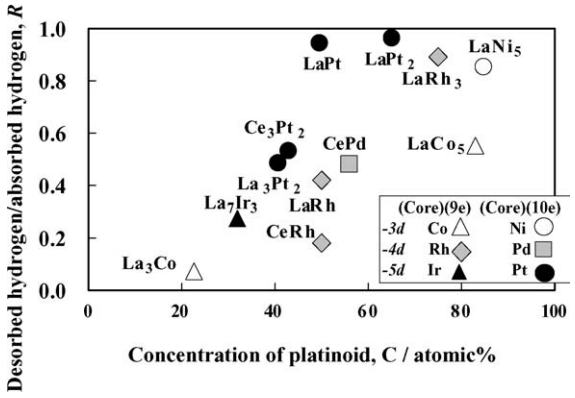

Fig. 5. Dependence of the concentration of platinoid on ratio desorbed and absorbed hydrogen.

the rate of hydrogen-absorption reaction is zero, the material can not absorb hydrogen even if the hydrogen-absorbed state is thermodynamically stable. It can be said, therefore, that the static stability and dynamic stability are both necessary to understand the reaction kinetics of hydrogen absorption/desorption. We think that the cohesive energy and the energy fluctuation correspond to the static stability and the dynamic stability, respectively [1].

The reaction rate of hydrogen-absorption is defined as the ratio 95% of the saturated H/M-value and the time necessary to arrive at the point in the work. From the experiment in R-M systems, as shown in Fig. 3, hydrogen-absorption rates in La–M systems are larger than those of Ce–M systems.

From the theory, as shown in Fig. 4, calculated energy fluctuation is larger in La and La–M systems and smaller in Ce and Ce–M systems, so a good correlation can be seen between theoretical measure; the energy fluctuation and experimental measure; the rate.

4.3. Reversibility

To examine the reversibility of the absorption/desorption reaction, the ratio of desorbed hydrogen and absorbed hydrogen is plotted in Fig. 5 against the metal concentration in R–M systems. The amount of desorbed hydrogen increases with increasing M component in R–M systems. This means that pure substances (La, Ce) absorb hydrogen easily and hardly desorb it, though La–M and Ce–M can desorb easily.

It can be said from the definition of the cohesive energy (1) that when the cohesive energy of a system is large, the hydrogen-absorbed system is very stable and therefore the reverse (hydrogen desorption) reaction hardly occurs. As shown in Fig. 5, calculated cohesive energy is large (maximum is seen at a certain chemical composition) in pure substances and is small (maximum is not seen) in both La–M and Ce–M systems, so a good correlation can be seen between theoretical measure; the cohesive energy and experimental measure; the reversibility.

4.4. $LaNi_5$

Why is $LaNi_5$ one of the most excellent hydrogen storage materials? This is because of (a) large density of states, (b) large energy fluctuation, and (c) small cohesive energy. Thus it can be said that three concepts (density of states, the energy fluctuation and the cohesive energy) are effective to comprehensively discuss the capacity, rate and reversibility of hydrogen absorption/desorption reaction.

5. Summary

For the systems of rare earth–transition metal, the capacity of hydrogen, the reaction rate and the reversibility of hydrogen absoption/desorption were measured. The density of states, cohesive energy and energy fluctuation were calculated by the extended Huckel method. The comparison of the measured and calculated results revealed that a good correlation was seen between (i) the density of states and the capacity, (ii) the energy fluctuation and reaction rate, and (iii) the cohesive energy and reversibility.

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