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Correlation between electronic structure and phase stability of metal hydrides

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Abstract

Local electronic structures around hydrogen in a small octahedral cluster are simulated by the DV-Xα molecular orbital method. It is shown that the ionicity of hydrogen in the cluster is a good indicator of the stability of hydrides, as long as the charge transfer from metal to hydrogen atoms is responsible for the hydride stability. For example, the heat of formation of pure metal dihydrides, ΔH, correlates well with the calculated ionicity of hydrogen. A similar correlation is observed in binary vanadium alloys and ternary V–Ti–Ni alloys.

Keywords: Electronic structure; Molecular orbital method; Ionicity of hydrogen; Charge transfer; Stability of hydrides

1. Introduction

Hydrogen storage alloys are an important material for the development of clean hydrogen energy systems. This is because hydrogen fuel is one of the cleanest energy resources and obtained easily by the electrolysis of water. A variety of hydrogen storage alloys have been developed, but the amount of hydrogen stored in them is still low in view of the practical application to automobiles.

Hydrogen is stored by forming hydrides in hydrogen storage alloys. Therefore, it is important to understand alloying effects on the stability of hydrides for the design of new hydrogen storage alloys. It has been reported that the hydriding properties of hydrogen storage alloys are well understood in terms of the nature of the chemical bond between atoms and also of the crystal structural evolution in the course of hydrogenation [1–7]. In addition, it has been reported that the stability of pure transition metal hydrides is evaluated by the charge transfer between metal and hydrogen atoms using the band structure calculation [8]. However, in these studies the charge transfer between atoms in the alloyed hydrides has not been elucidated in a systematic manner.

In this study, using a small model cluster for the hydrides of metals and alloys, local electronic structures around hydrogen are simulated by the DV-Xα molecular orbital method to examine the charge transfer between atoms in them. Also, the pressure–composition isotherms are measured experimentally in ternary V–Ti–Ni alloys. By comparing the present and previous experiments with the calculation, a useful parameter is proposed for treating a stability problem of those hydrides in which charge transfer occurs dominantly between metal and hydrogen atoms.

2. DV-Xα cluster method and cluster model

The DV-Xα cluster method is a molecular orbital method assuming a Hartree–Fock–Slater (HFS) approximation. With this method, local electronic structures around hydrogen can be calculated accurately. In this method, the exchange-correlation between electrons, V_{xc}, is given by the following Slater's $X\alpha$ potential

$$V_{xc} = -3\alpha\left[\frac{3}{8\pi}\rho(\mathrm{r})\right]^{1/3}$$

where $\rho(\mathrm{r})$ is the density of electrons at position r, the parameter α is fixed at 0.7 and the self-consistent charge approximation is used in the calculation. The matrix elements of Hamiltonian and the overlap integrals are calculated by a random sampling method. The molecular orbitals are constructed by a linear combination of numeri-

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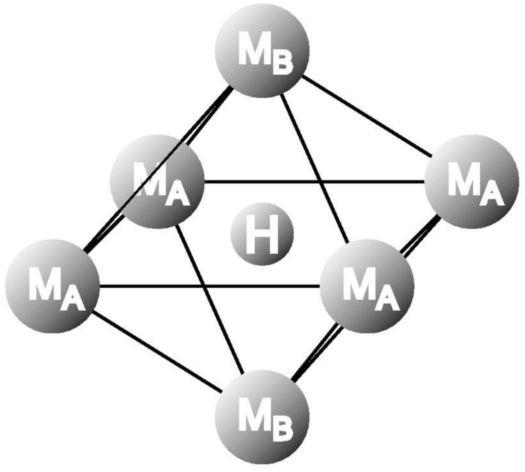
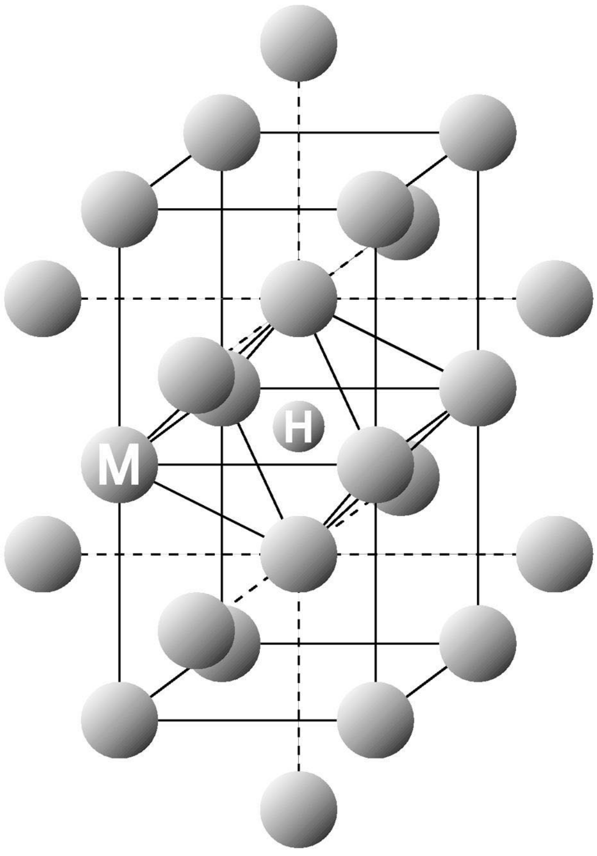
cally generated atomic orbitals (LCAO). Further explanation of the calculation method is given elsewhere [9,10].

The cluster models employed in the present calculation are shown in Fig. 1a and b. The M_6H cluster model shown in Fig. 1a is an octahedral cluster, consisting of six metal atoms (M_A and M_B) and one hydrogen atom at the center. A variety of elements are located in the M_A and M_B atomic sites to simulate the characteristics of the chemical bond in the hydrides formed in metals and alloys. Needless to say, the same metal elements are located at both the atomic sites, M_A and $M_{B,}$ for the calculation of pure metal hydrides. The interatomic distances in the cluster are set so that the metal atoms with the atomic radius of CN = 12 [11] contact with each other, as if they are rigid spheres. In any hydrides, hydrogen occupies either octahedral or tetrahedral interstitial sites irrespective of crystal structures, so the octahedral cluster model shown in Fig. 1a is one representative of such local atomic configurations around hydrogen.



(a) M_6H



(b) $M_{24}H$

Fig. 1. Cluster models employed in the calculation; (a) M_6H cluster and (b) $M_{24}H$ cluster.

Local electronic structure around hydrogen is also calculated using a larger cluster model, $M_{24}H$, as shown in Fig. 1b, to show the validity of the results obtained from a small octahedral cluster model, as shown in Fig. 1a. This cluster model is made on the basis of the b.c.c. crystal structure where one hydrogen atom is located at the octahedral site at the center. The locations of each atom in the cluster was set following the lattice parameter of pure M metal with b.c.c. crystal structure, where Ms are Sc, Ti, V, Y, Nb, Ta, La, Zr and Hf. By comparing the results between these small and large cluster models, the nature of the local chemical bond is able to be simulated approximately even in use of a small octahedral cluster in the calculation, as explained later. The calculated result of tetrahedral cluster is similar to that of octahedral cluster [12].

3. Experimental procedure

As shown in Table 1, five ternary V–Ti–Ni alloys, Nos. 1–5, are prepared to investigate the correlation between the hydriding property and the electronic structure. These alloys are arc-melted in a high purity argon gas atmosphere. The melting operation is repeated five times to increase homogeneity of the button ingot. Such as-cast ingots are pulverized by hydrogenating at 773 K in a hydrogen gas atmosphere of about 7 MPa and then by crushing mechanically. For these powder samples, the pressure–composition isotherms are measured at 333 K

Table 1
Chemical compositions of V–Ti–Ni alloys

No.	V (mol%)	Ti (mol%)	Ni (mol%)	$\overline{Io}$
1	62	20	18	−0.203
2	49	30	21	−0.205
3	55	30	15	−0.207
4	61	30	9	−0.208
5	67	30	3	−0.210

using a Sieverts-type apparatus in order to evaluate the stability of hydride formed in the alloys.

4. Results and discussion

4.1. Stability of pure metal hydrides

The ionicity of hydrogen in the cluster for pure metal hydride is evaluated by the Mulliken population analysis [9]. More negative ionicity of hydrogen means that the charge transfer occurs more largely from metal atom to hydrogen, resulting in the formation of the stronger ionic bond between them. Thus, it is supposed that the stability of hydride will increase as the ionicity of hydrogen become more negative.

In fact, as shown in Fig. 2a, the calculated ionicity of hydrogen using the M_6H cluster correlates well with the measured heat of formation, ΔH, of pure metal dihydrides, MH_2. This octahedral cluster may be small, but even in use of a larger cluster such a correlation is seen as shown in Fig. 2b and c. Here, the results shown in Fig. 2b are obtained from the calculation using the $M_{24}H$ cluster model shown in Fig. 1b. Also shown is the result for another larger cluster, $M_{19}H_{32}$, inserted in Fig. 2c, which is constructed on the basis of the CaF_2-type crystal structure of MH_2 (e.g. TiH_2, VH_2) [13]. In this cluster, hydrogen is located at the center of a tetrahedron, being different from an octahedron shown in Fig. 1a and b. Despite these differences, the results are approximately similar among these three calculations as shown in Fig. 2a–c. Thus, the trend of the chemical bonding is well reproduced using the M_6H cluster.

Table 2
List of $(Io)_M$ values for various M in the V_4M_2H cluster

M	Ionicity	M	Ionicity	M	Ionicity
Ti	−0.235	Zr	−0.244	Hf	−0.239
V	−0.200	Nb	−0.221	Ta	−0.213
Cr	−0.188	Mo	−0.192	W	−0.183
Mn	−0.181	Tc	−0.174	Re	−0.165
Fe	−0.178	Ru	−0.167	Os	−0.160
Co	−0.171	Rh	−0.163	Ir	−0.168
Ni	−0.175	Pd	−0.185	Pt	−0.187
Cu	−0.180	Ag	−0.210	Au	−0.208

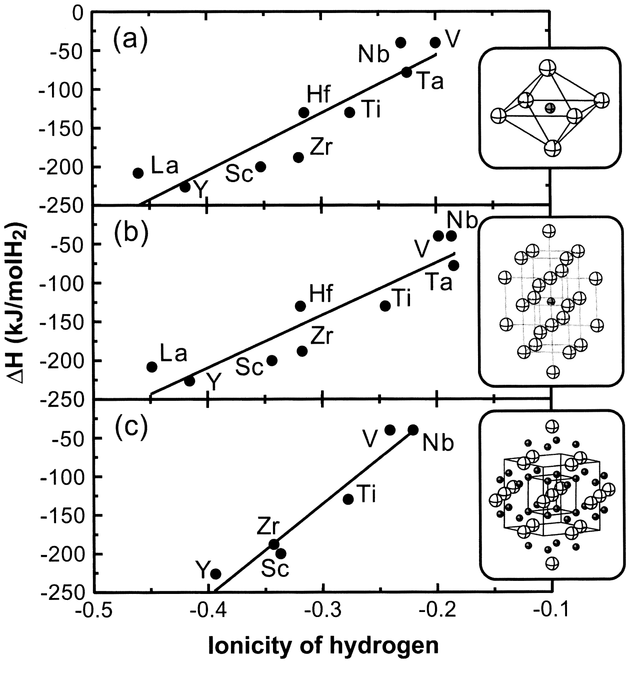


Fig. 2. Correlation between the heat of formation of pure metal dihydrides, ΔH, and the ionicity of hydrogen; (a) M_6H cluster (b) $M_{24}H$ cluster and (c) $M_{19}H_{32}$ cluster.

4.2. Stability of hydride formed in binary vanadium alloys

The present approach is applied to the stability problem of the hydride formed in binary vanadium alloys. The VH_2 hydride is formed in them by hydrogenation and the ionic interaction between hydrogen and metal atoms is responsible mainly for the stability of the hydride [5]. In order to simulate the electronic structures of the hydride in binary vanadium alloys, the calculations are performed using the octahedral cluster model, V_4M_2H. For a variety of M, the calculated values of the ionicity of hydrogen are listed in Table 2. Also, the results are plotted in Fig. 3 following the order of elements, M, in the periodic table, and compared with the plateau pressures of V-1mol%M alloys measured at 313 K by Yukawa et al. [13]. In the figure, the logarithm of the plateau pressure is plotted, since it is proportional to the ΔH at a constant temperature following the van't Hoff equation. As is evident from this figure, the ionicity of hydrogen changes with M in a similar manner as does the measured plateau pressure for V-1mol%M alloys, even though there are still small discrepancies, for example, the

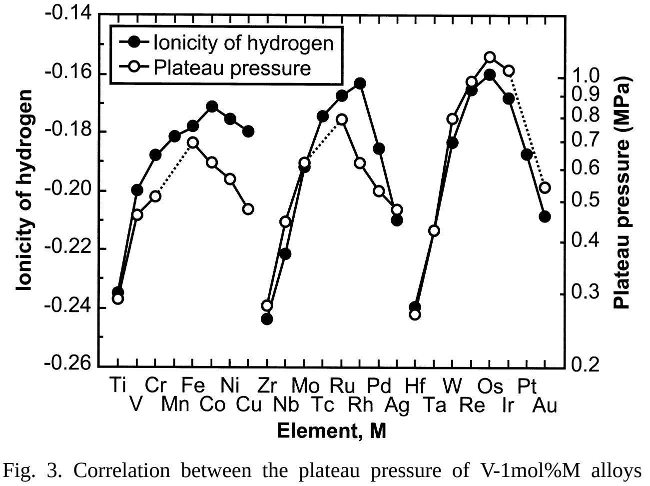


Fig. 3. Correlation between the plateau pressure of V-1mol%M alloys and the ionicity of hydrogen in the V_4M_2H cluster.

peak position is different. In addition to the ionicity of hydrogen, the chemical bond strength between V and M atoms is also taken into account, but the correlation has not been improved significantly. Thus, the ionicity of hydrogen is indeed a useful parameter to represent the stability of hydrides, as long as the stability is attributable mainly to the ionic interactions between hydrogen and the metal atoms.

4.3. Stability of hydride formed in ternary V–Ti–Ni alloys

The pressure–composition isotherms (PCT) are measured at 333 K for five ternary V–Ti–Ni alloys listed in Table 1, and the results are shown in Fig. 4. In this figure, solid symbols and open symbols denote the results measured in the hydrogen absorption and desorption process, respectively. As shown in Fig. 4, the plateau region does not appear in the No.1 alloy. On the other hand, plateau-like regions tend to appear in the other alloys, although the slope of the plateau-like region is rather steep. Here, for convenience, the pressure at the center of each plateau-like region in the desorption process is referred to as the plateau pressure. Fig. 4 shows that the plateau pressure changes in the order No. 2>No. 3>No. 4>No. 5, although the desorption curves of Nos. 4 and 5 alloys are terminated around 10^{-2} MPa.

Here, the average values of ionicity, $\overline{\mathrm{Io}}$, is defined by taking the compositional average as follows,

$$\overline{\mathrm{Io}} = \Sigma X_{\mathrm{M}} \cdot (\mathrm{Io})_{\mathrm{M}}$$

where X_{M} is the atomic fraction of component M in the alloy and $(\mathrm{Io})_{\mathrm{M}}$ is the ionicity value of M listed in Table 2. The calculated values of $\overline{\mathrm{Io}}$ for the five V–Ti–Ni alloys are listed in Table 1. Here, $\overline{\mathrm{Io}}$ is considered as a measure to show the average strength of the ionic bond between hydrogen and metal atoms. It is supposed that when $\overline{\mathrm{Io}}$ is a large negative value, the hydride is stable and the plateau pressure of hydrogen is low. In fact, the plateau pressure shown in Fig. 4 changes in the order, No. 2>No. 3≥No. 4>No. 5, which is consistent with the order of $\overline{\mathrm{Io}}$, as shown in Table 1. Also, the No. 1 alloy shows the least negative $\overline{\mathrm{Io}}$ value among all the alloys, so its hydride is considered to be most unstable, as might be expected from the PCT curve shown in Fig. 4.

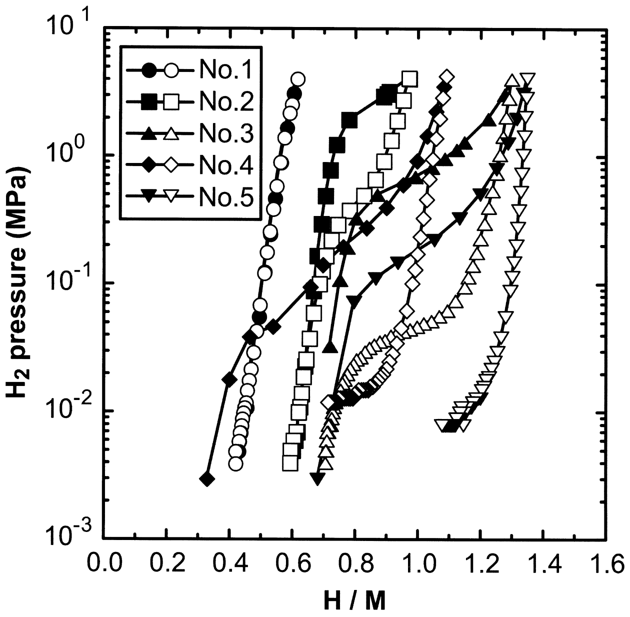


Fig. 4. Pressure–composition isotherms of V–Ti–Ni alloys measured at 333 K.

Thus, the ionicity of hydrogen is found to be a good indication to show the stability of several hydrides (e.g. VH_2) in which charge transfer occurs dominantly from metal atom (e.g. V) to hydrogen and ionic interaction is operating between them. However, in the hydrides formed in most hydrogen storage alloys, covalent interaction is operating, for example, between Ni and H atoms in $LaNi_5H_6$ [14]. The present method is not applicable to the stability problem of such hydrides.

5. Conclusion

The ionicity of hydrogen calculated by the DV-Xα molecular orbital method is a useful parameter for evaluating the stability of hydrides formed in pure transition metals or vanadium based alloys, since charge transfer is responsible for the stability of their hydrides.

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