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Roles of constituent elements and design of hydrogen storage alloys

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Abstract

The chemical interactions between atoms in hydrogen storage alloys have been investigated by the DV-Xα molecular orbital method. In view of the nature of the chemical bond between atoms, a completely different interstitial space for the hydrogen occupancy is formed in binary A–B hydrogen storage alloys, where A and B are the hydride forming and non-forming elements, respectively, as compared to the interstitial space in pure A metals. As a result, hydrogen interacts more strongly with the B element than the A element in every hydrogen storage alloy, despite the fact that the A element has a larger affinity for hydrogen than the B element in the binary metal–hydrogen system. In addition, it is shown that the A:B compositional ratio of hydrogen storage alloys is predictable using a simple equation, 2×Bo(A–B)/[Bo(A–A)+Bo(B–B)], where Bo(A–B), Bo(A–A) and Bo(B–B) are the bond orders between atoms given in the parentheses.

Keywords: Electronic structures; Hydrogen storage alloys; Hydrides; Materials design

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1. Introduction

Hydrogen storage alloys are important materials for the future development of clean hydrogen energy systems to protect the earth from pollution. Recently, we have investigated the effects of alloying on the electronic structures of typical hydrogen storage alloys such as $LaNi_5$, $ZrMn_2$, TiFe and Mg_2Ni [1–5]. It is shown that the stability of hydrides formed in these alloys can be understood in terms of the nature of the chemical bond between atoms in a small polyhedron where hydrogen is stored and also of the crystal structural evolution during hydrogenation [6,7].

In this study, the electronic structures of hydrogen storage alloys are simulated using the DV-Xα cluster method in order to clarify the roles of the constituent elements in them. For comparison, the electronic structures of metal dihydrides are calculated. In addition, the chemical composition of hydrogen storage alloys is estimated using the bond strengths between the metal atoms.

2. DV-Xα cluster method and cluster models

The DV-Xα cluster method is a molecular orbital method, assuming a Hartree–Fock–Slater (HFS) approximation. The detailed explanation of the calculation method is given elsewhere [8].

Depending on the crystal structure being investigated, appropriate cluster models are employed in the calculation. For example, a cluster model used for pure metal dihydride, AH_2, with the CaF_2-type crystal structure is shown in Fig. 1, where A represents Sc, Ti, V, Y, Zr and Nb. Every hydrogen is located at the center of a tetrahedron made of four A atoms.

3. Results and discussion

3.1. Chemical bonding state of hydrogen

Most of hydrogen storage alloys such as $LaNi_5$ (AB_5-type), $ZrMn_2$ (AB_2-type), TiFe (AB-type) and Mg_2Ni (A_2B-type) consist of hydride forming elements, A, and non-forming elements, B. From our previous calculations, hydrogen interacts more strongly with the B elements (e.g. Ni) than the A elements (e.g. La) in every hydrogen storage alloy (e.g. $LaNi_5$) [1–5]. An example of this is shown in Fig. 2: the electron density around hydrogen in $LaNi_5H_6$ is directed toward the Ni atom but not toward the La atom, indicating that the Ni–H interaction is stronger than the La–H interaction in this alloy. The reason why such a B–H interaction is operating in the hydrides formed in hydrogen storage alloys can be understood by consider-

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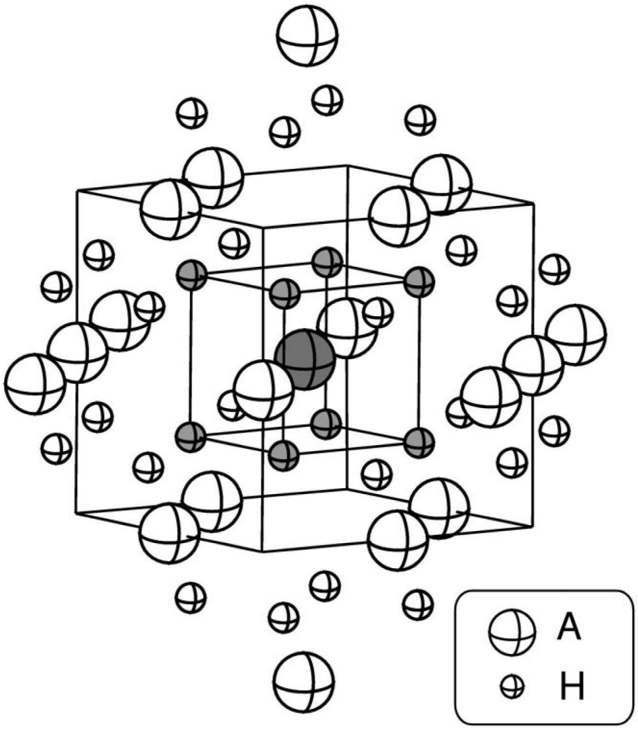

Fig. 1. Cluster model used in the calculation for AH_2 hydride with CaF_2-type crystal structure.

ing the energy band structures of electrons as explained below.

3.1.1. *Metal–hydrogen interaction in pure metal hydrides*

The energy band structures are schematically illustrated in Fig. 3(a) for pure metal hydrides such as AH_2, and (b) for hydrides formed in hydrogen storage alloys. For pure metal hydrides, the hydrogen band appears below the valence band of the A element as shown in Fig. 3(a). As the energy gap between them is relatively wide, a strong ionic interaction will be operating between the A and H atoms through the charge transfer between them. For example, for six metal dihydrides, AH_2, the electronic structures are calculated using the cluster model shown in Fig. 1. The ionicites of the central metal A atom and its surrounding H atoms (shaded atoms in Fig. 1) are shown in Fig. 4(a). The ionicity of the central A atom is always positive, whereas that of the H atom is always negative, indicating that charge transfer always takes place from the A atom to the H atom. Then, the ionicity differences, $\Delta I\text{o}(=I\text{o}(\text{A})-I\text{o}(\text{H}))$, are calculated for various A atoms and compared with the measured heat of formation of AH_2, ΔH, as shown in Fig. 4(b). Needless to say, this $\Delta I\text{o}$ represents the amount of transferred charges between the A and H atoms and hence it is a measure to show the ionic bond strength between them. Fig. 4(b) shows that there is a strong correlation between the $\Delta I\text{o}$ and the ΔH. Thus, such a strong ionic A–H interaction is characteristic of pure metal hydrides such as AH_2.

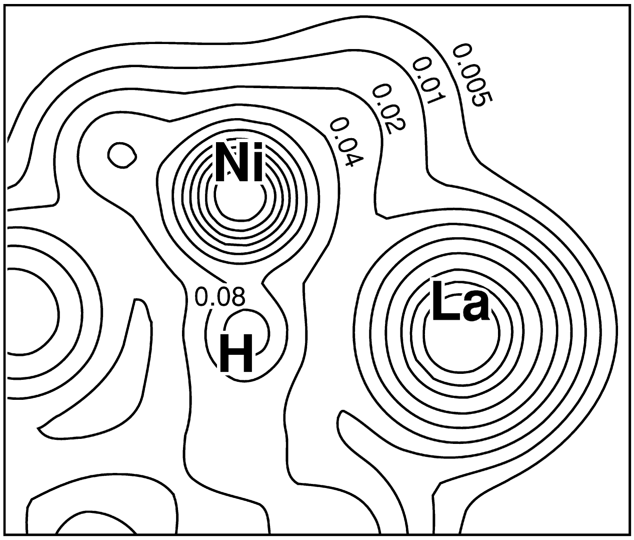

Fig. 2. Electron density distribution in $LaNi_5H_6$. The numbers indicate the numbers of electron per a.u.^{3} (1 a.u. = 0.0529 nm).

3.1.2. *Metal–hydrogen interaction in hydrogen storage alloys*

However, the situation is completely different in hydrogen storage alloys. As shown in Fig. 3(b), the valence band of B element appears just above the hydrogen band, and lies in the intermediate energy range between the two bands of hydrogen and A element. In this case, the covalent interaction is operating between B and hydrogen atoms rather than the ionic interaction. This is because, the eigen energies of the atomic orbitals of B and H are relatively close to each other, so that they are readily hybridized to form the molecular orbitals. As a result, the B–H interaction is enhanced, whereas the A–H interaction is weakened in the hydrogen storage alloys.

In addition. the B–H interatomic distance is shorter than the A–H interatomic distance, because the atomic size of B is usually smaller than A. Then, hydrogen occupies an interstitial site at the center of either distorted octahedron or tetrahedron with different edge lengths, so that the B–H interaction is strengthened, while the A–H interaction is weakened. This may be an another reason why the B–H interaction becomes stronger than the A–H interaction in hydrogen storage alloys.

Thus, in view of the chemical bond, a polyhedron made of A and B elements provides a unique interstitial space for the hydrogen occupancy in the binary A–B hydrogen storage alloy, being very different from the space in a pure A metal. According to our previous calculation [9], the B–H interaction is enhanced only when the A element exists in the neighborhood of the B element. In other words, such a unique space is not formed unless A elements are present in the alloy. In this sense, both A and B elements are essential elements in hydrogen storage alloys.

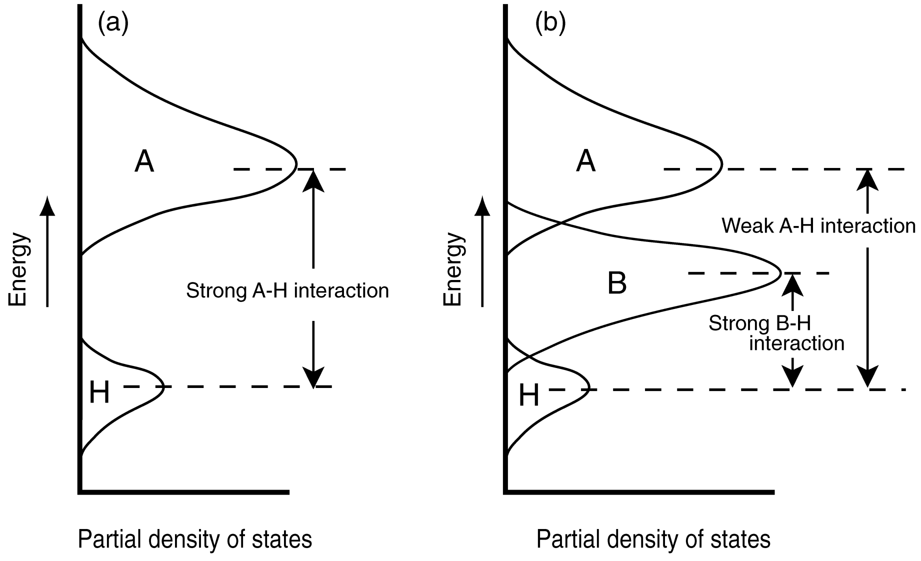

Fig. 3. Schematic illustrations of the energy band structures of (a) pure A metal hydride and (b) hydride formed in hydrogen storage alloy consisting of both A and B elements.

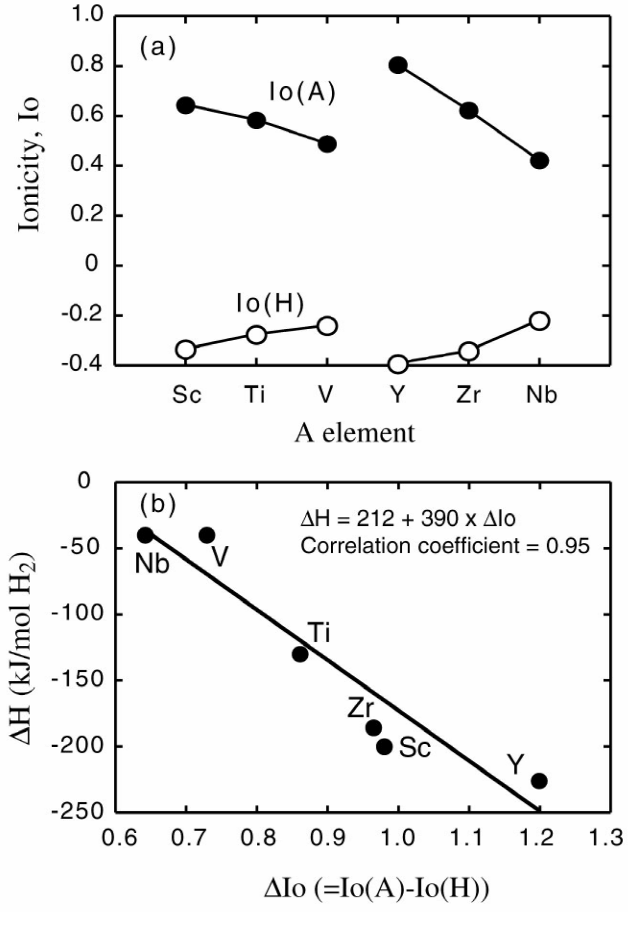

Fig. 4. (a) Ionicites of A and H atoms and (b) correlation between the ionicity difference, Δ*I*o, and the heat of formation of dihydrides, AH_2, Δ*H*.

The presence of the B–H interaction is characteristic of hydrogen storage alloys. However, this B–H (e.g. Ni–H) interaction in the hydrides formed in hydrogen storage alloys (e.g. $LaNi_5H_6$) is much weaker compared to the A–H (e.g. La–H) interaction in the pure metal hydrides, AH_2, (e.g. LaH_2), judging from the magnitude of the heat of formation for their hydrides, which is −209.2 kJ/mol H_2 for LaH_2 and −30.1 kJ/mol H_2 for $LaNi_5H_6$. The hydrogen desorption process can be activated readily because of such a B–H interaction mainly operating in hydrogen storage alloys.

3.2. Chemical composition of hydrogen storage alloys

3.2.1. Alloy cluster suitable for hydrogen storage

As explained above, the B–H bond is formed when A elements are in the neighborhood. Therefore, the effective number of B–H bonds is supposed to be large when the concentration of the A element is high in the alloy. In other words, the total amount of hydrogen absorbed in the alloy will increase with increasing A:B compositional ratio.

However, a disproportionation reaction tends to take place if the concentration of the A element is too high in the alloy. Let us explain this assuming that there are three types of tetrahedral spaces in an A–B binary alloy as shown in Fig. 5(a)–(c). Here, if the A:B compositional ratio is high, or the A–A bond is stronger than the A–B or the B–B bond, the interstitial space shown in Fig. 5(a) is dominant in the alloy. In such a case, hydrogen will interact mainly with A elements when hydrogen is introduced into the alloy, resulting in the formation of strong A–H bond and a disproportionation reaction, AB+H→AH+B, will take place easily in the alloy. Here, the

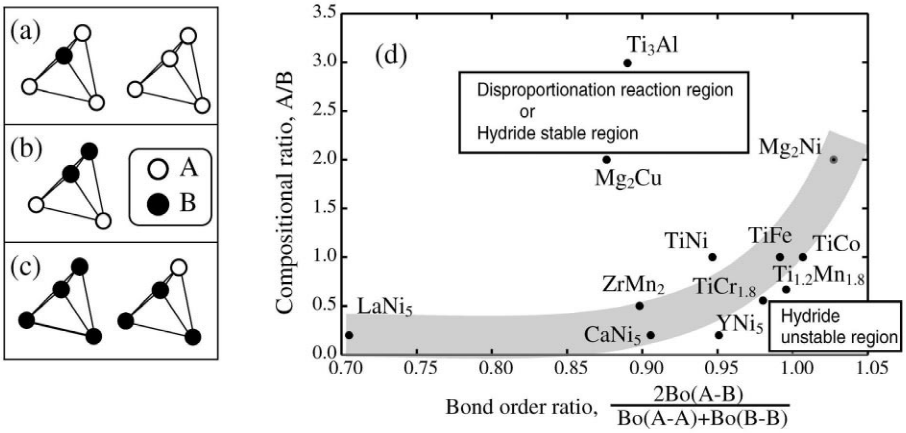

Fig. 5. (a)–(c) Three types of tetrahedral interstitial spaces and (d) correlation between the A:B compositional ratio and the bond order ratio.

hydride, AH (or AH_2), is so stable that the onset of this reaction is unlikely.

On the contrary, when the A:B compositional ratio is low, or the B–B bond is stronger than the A–A or the A–B bond, the interstitial space shown in Fig. 5(c) is dominant in the alloy. In this case, it is very difficult for hydrogen to be absorbed in the B-atom-abundant interstitial space.

Therefore, in order to absorb and release hydrogen smoothly without the onset of any disproportionation reaction, the A:B compositional ratio should be controlled in a proper manner, depending on the chemical bond strength between the A and the B atoms. The optimum cluster shown in Fig. 5(b) may be made in the alloy only when the bond order ratio, $2\times\mathrm{Bo(A–B)}/[\mathrm{Bo(A–A)}+\mathrm{Bo(B–B)}]$, takes a suitable value for a given A:B compositional ratio. Here, the bond order is a measure to show the covalent bond strength between atoms. Bo(A–B), Bo(A–A) and Bo(B–B) are the bond orders between atoms given in the parentheses.

3.2.2. Prediction of A:B compositional ratio

A series of calculations is performed to obtain the bond order ratio, $2\times\mathrm{Bo(A–B)}/[\mathrm{Bo(A–A)}+\mathrm{Bo(B–B)}]$, for various alloy systems using the tetrahedral cluster, and the result is shown in Fig. 5(d). There is a strong correlation between the A:B compositional ratio and the bond order ratio. For example, all the typical hydrogen storage alloys, $LaNi_5$, $ZrMn_2$, TiFe and Mg_2Ni, are located on a narrow band illustrated in Fig. 5(d). Here, for Mg_2Ni, the bond order ratio is high, because the Mg–Ni bond order is larger than the Mg–Mg bond order. Also, for $LaNi_5$, the bond order ratio is low, because the La–Ni bond order is smaller than that of La–La. All the alloys located in the upper region above this narrow band tend to decompose during hydrogenation and/or tend to form stable hydrides. One example is the Mg_2Cu system, in which a disproportionation reaction, $Mg_2Cu + 2\ H_2 \rightarrow 2MgH_2 + Cu$, takes place and a stable hydride, MgH_2, is formed during hydrogenation. Therefore, the region lying above the narrow band is called the disproportionation reaction region or hydride stable region. On the other hand, the alloys located in the region below this narrow band, tend to form unstable hydrides. YNi_5 is one example. Therefore, this region is called the hydride unstable region. Similar results are also obtained in the calculation using octahedral clusters [7]. Thus, the present result is independent of the clusters used for the calculations.

This method mentioned above is applied to the Mg-based alloys as shown in Fig. 6. When the compositional ratio, A:B, is fixed at 2.0, the total amount of hydrogen stored in the hydrides changes in the order, $Mg_2FeH_6 > Mg_2CoH_5 > Mg_2NiH_4 = Mg_2RuH_4 > Mg_2RhH$, so it decreases with increasing bond order ratio. In other words, hydrogenation proceeds further in an alloy that has a lower bond order ratio. This is reasonable since the alloy position moves from the hydride stable region to the hydride unstable region with increasing bond order ratio.

Once the bond order ratio is calculated, the A:B compositional ratio can be estimated using this correlation.

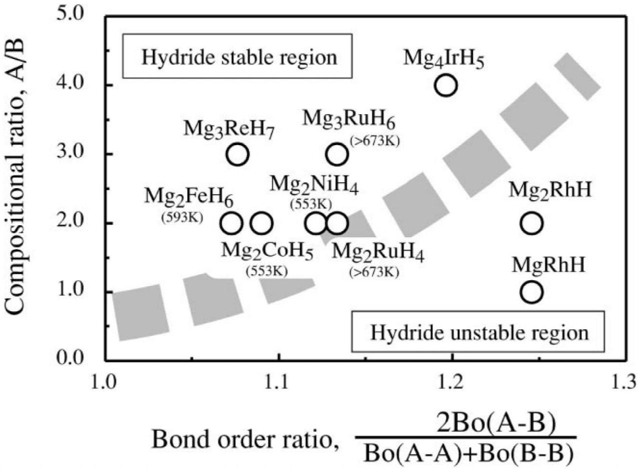

Fig. 6. Correlation between the A:B compositional ratio and the bond order ratio for Mg-based alloys.

This approach is applicable not only to ordered alloys but also to disordered alloys (e.g. Ti–Mo alloys) [10].

4. Conclusion

The chemical interaction between atoms in hydrogen storage alloys were investigated by the DV-Xα molecular orbital method. From a series of calculations of the electronic structures, the nature of the chemical bond between atoms was elucidated, and the roles of the constituent elements were clarified in hydrogen storage alloys. In addition, some criteria are shown for the design of hydrogen storage alloys.

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