Journal of Alloys and Compounds 293–295 (1999) 227–230

Chemical bond state and hydride stability of hydrogen storage alloys

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Abstract

The electronic structures for typical hydrogen storage alloys, $LaNi_5$, TiFe, $ZrMn_2$, Mg_2Ni and b.c.c.V, all containing a variety of alloying elements, M, are investigated by the DV-Xα molecular orbital method. It is shown that atomic interactions of controlling the stability of their hydrides, depend strongly on the way how crystal structural evolution takes place in the course of hydrogenation. For example, when the hydride structure is the derivative one of the starting alloy, the metal–metal interaction and its change with hydrogenation will determine the stability of the hydride. $LaNi_5$, TiFe and $ZrMn_2$ belong to this group. On the other hand, if the crystal structure of the hydride is completely different from that of the starting alloy, the importance of the metal–hydrogen interaction increases, and in case of b.c.c.V, only the metal–hydrogen interaction is responsible mainly for the relative stability of alloyed VH_2. In case of Mg_2Ni, both the metal–metal and the metal–hydrogen interactions control the stability of the hydride, Mg_2NiH_4. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Electronic structure; Hydride; Phase stability; $LaNi_5$; Mg_2Ni; TiFe; $ZrMn_2$; VH_2

1. Introduction

Hydrogen storage materials are one of key materials for the development of future clean hydrogen energy system. For a variety of materials, alloying effects have been investigated experimentally to improve the hydrogen absorption and desorption characteristics of them. However, despite such great effort, the alloying effect still remains unclear. Therefore, a new electronic approach is strongly needed to solve this problem in a fundamental manner. In this paper, the correlation between the electronic structures and the stability of the hydrides of typical hydrogen storage alloys, $LaNi_5$, $ZrMn_2$, TiFe, Mg_2Ni and b.c.c.V, are discussed in terms of the nature of the chemical bond between atoms in them. For this purpose, the DV-Xα cluster method is employed in this study.

2. DV-Xα cluster method

This is a molecular orbital calculating method based on the Hartree-Fock-Slater approximation, and a Slater's Xα potential is employed to express an exchange correlation interaction between electrons [1]. Local electronic structures around hydrogen atom can be calculated by this method even for the large size of atom cluster.

Depending on the crystal structure, appropriate cluster models are employed in the calculation. For example, a cluster model used in the calculation for the TiFe system is shown in Fig. 1. This model is constructed on the basis of the CsCl-type crystal structure of TiFe. Here, a hydrogen atom is located at the central site of the octahedron with the frame of four Ti atoms and two Fe atoms. In order to examine alloying effects on the electronic structures, one of the two Fe atoms is substituted for alloying elements, M. The bond order which is a measure of the covalent bond strength between atoms is estimated following the Mulliken population analysis [2]. Also, the ionicities of each elements in the cluster are calculated in order to get information of the charge transfer between atoms. A detailed explanation of the calculation method is given elsewhere [3,4].

3. Correlation between the electronic structures and the stability of hydrides

There have been a lot of experiments concerning the alloying effect on the hydriding properties of the alloys. When an alloying element, M, is added into the mother alloy, the chemical interaction between atoms changes in

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PII: S0925-8388(99)00424-7

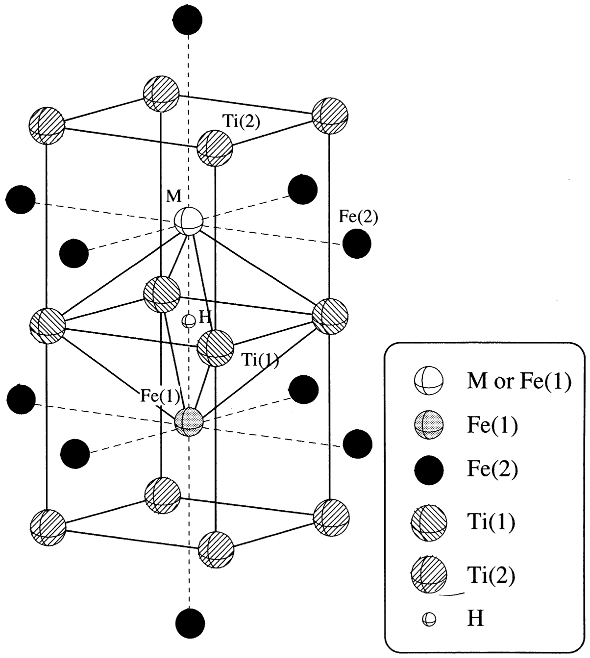

Fig. 1. Cluster model used in the calculation for the TiFe system.

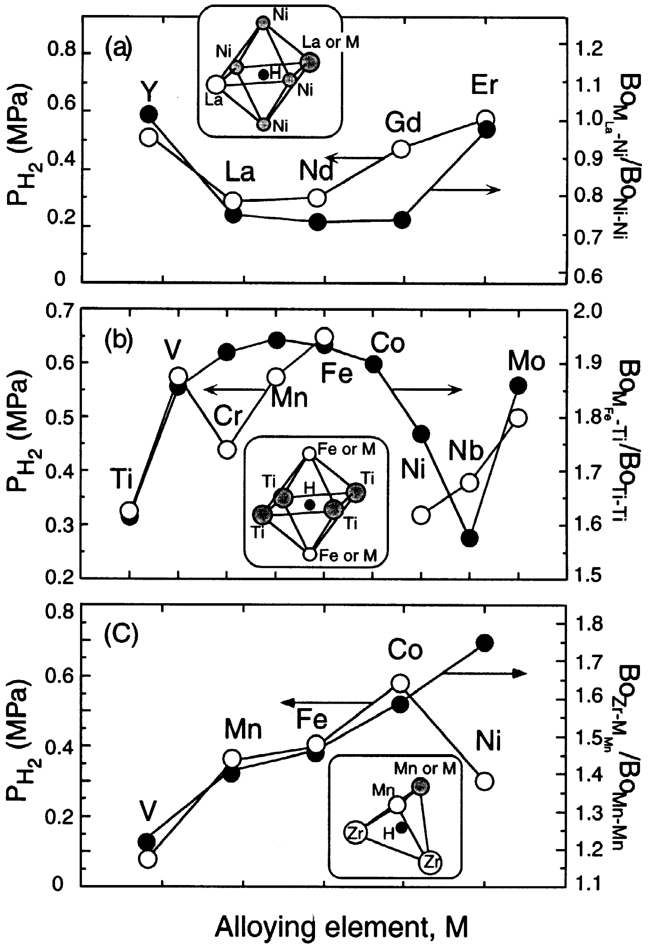

Fig. 2. Comparison between the bond order ratios and the experimental plateau pressures for (a) $LaNi_5$ system, (b) TiFe system and (c) $ZrMn_2$ system.

some ways depending on M, and hence the stability of the hydride is modified. This can be understood in terms of the chemical bond strength between atoms and also of their changes in the framework of small metal polyhedra where hydrogen atoms are located [5].

3.1. Hydrides with derivative crystal structures

First of all, it is very important to understand how crystal structural evolution takes place in the course of hydrogenation. For example, the crystal structure of $TiFeH_2$ is not substantially different from that of TiFe, since only the lattice expansion and the lattice distortion are introduced into them during hydrogenation. In other words, hydrogen atoms occupy a part of the interstitial sites in the crystal lattice and any substantial changes of the crystal structure do not occur in the course of hydrogenation except for the onset of lattice expansion and distortion in it.

Therefore, it is supposed that the easiness of the lattice expansion and distortion during hydrogenation will be important in considering the hydride stability and this will be controlled by the nature of the chemical bonds between metal atoms in the starting alloys. For example, as shown in Fig. 2(a), when a hydrogen atom is located at the center of a small metal octahedron, the hydrogen interacts strongly with the Ni atoms rather than the La atoms. So, the Ni–Ni interaction in this octahedron is reduced by the hydrogenation [6]. In such a case, lattice expansion may occur so as to recover the Ni–Ni interaction. In fact, according to the previous calculation [7], the Ni–Ni interaction is reduced by the hydrogenation, but it is recovered to some extent by introducing small expansion to the Ni atomic plane. However, such a recovery is hard to take place if the La–Ni interaction is significantly large. This is because, as is evident from the atomic arrangements in the octahedron shown in an insert of Fig. 2(a), the La–Ni interaction acts to suppress such lattice expansion on the Ni atomic plane, so that the Ni–Ni interaction never recovers. As a result, the stability of the hydride decreases with increasing La–Ni interaction and with decreasing Ni–Ni interaction. In fact, as shown in shown in Fig. 2(a), the ratios of the La–Ni bond order to the Ni–Ni bond order are approximately similar to the experimental results of the equilibrium plateau pressure of hydrogen for $La_{0.8}M_{0.2}Ni_5$ alloys.

Similar results are also obtained for TiFe (Fig. 2(b)) and $ZrMn_2$ (Fig. 2(c)), in which the hydride structures are the derivative ones of the starting alloys [8]. Thus, the metal–metal interaction on the small polyhedron and its change with alloying elements, M, will determine the stability of

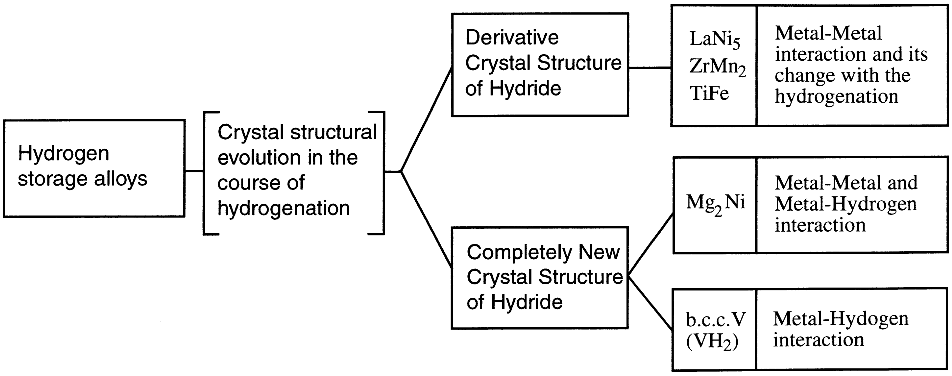

Fig. 3. Classification of hydrogen storage alloys in terms of the crystal structural evolution in the course of hydrogenation.

hydrides. This is summarized in Fig. 3 together with another case explained below.

3.2. Hydrides with completely new crystal structures

On the other hand, in case of Mg_2Ni, the hydride, Mg_2NiH_4, of having a completely different crystal structure from that of Mg_2Ni appears in the course of hydrogenation above 518 K. In this case, the importance of the metal–hydrogen interaction increases as well as the metal–metal interaction [9]. Namely, the change of the hydride stability with alloying elements, M, which are substituted for Ni atoms, is related not only to the M(Ni)–Mg interaction, but also to the M(Ni)–H interaction. Their curves resemble each other. In fact, as shown in Fig. 4, the measured enthalpy of the hydride formation in $Mg_2Ni_{0.75}M_{0.25}$, changes in an approximately similar way as does the M–Mg or the M–H interaction. It is noticed that the M–H chemical bond plays a more important role in the hydride stability in this Mg_2Ni, compared to $LaNi_5$, TiFe and $ZrMn_2$, as summarized in Fig. 3.

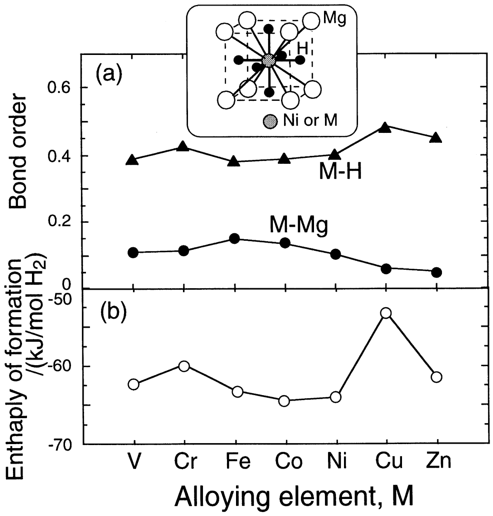

Fig. 4. Comparison between (a) the bond orders and (b) the enthalpy of formation for the hydride in Mg_2Ni system.

Also, the importance of the M–H interaction further increases in the b.c.c.V [10]. In this case, the ionicity difference between H and M atoms, $\Delta I_o(I_o[H]-I_o[M])$, which is a measure of the ionic interaction through the charge transfer between them, is responsible mainly for the relative stability of alloyed VH_2 hydride as shown in Fig. 5.

4. Conclusions

The stability of hydrides formed in $LaNi_5$, $ZrMn_2$, TiFe, Mg_2Ni and b.c.c.V solid solution is well understood in terms of the nature of the chemical bond between atoms in small polyhedra and also of the crystal structural evolution during hydrogenation.

Acknowledgements

The authors acknowledge the Computer Center, Institute for Molecular Science, Okazaki National Institute for the use of the SX-3/34R computer. This research is supported by the Grant-in-Aid for Scientific Research from the

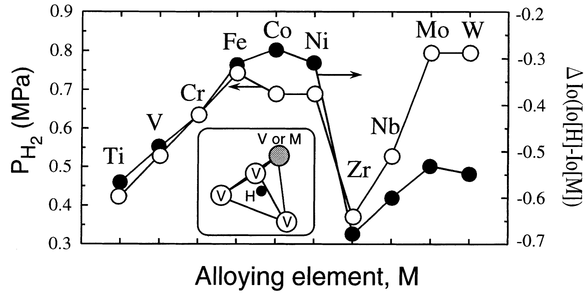

Fig. 5. Comparison between the calculated ionicity difference and the experimental plateau pressures for VH_2 system.

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