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Electronic structure and hydriding property of titanium compounds with CsCl-type structure

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Abstract

The electronic structures of titanium compounds, TiFe, TiCo and TiNi with CsCl-type structure are investigated by the DV-Xα molecular orbital method. From the results of the calculation, it is found that hydrogen interacts more strongly with constituent elements, X (=Fe, Co, Ni), rather than Ti atoms. The bond strength between Ti and X atoms changes in the sequence, Fe>Co>Ni. This is the same order as the capacity of the hydrogen absorption in these TiX compounds. The characteristics of the hydrogen absorption in these compounds are discussed in view of the nature of the chemical bond between atoms. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Electronic structure; TiFe; TiCo; TiNi; CsCl-type crystal structure

1. Introduction

The titanium compounds, TiX (X=Fe, Co, Ni), with CsCl-type structure are promising hydrogen storage materials for the development of a future clean energy system [1,2]. The capacity of the hydrogen absorption in these compounds is known to be smaller than the value which would be expected from the crystal geometry. For example, in the case of TiFe, the atomic ratio of hydrogen to metals, H/M, is almost 1.0 [1,2], whereas the expected ratio is as high as 1.5. Besides, the value of H/M changes, depending on the constituent elements, X, of the compounds. The H/M in the TiNi hydride has been reported to be 0.7 [2], smaller than 1.0 found in the TiFe hydride, despite the fact that both compounds have the same CsCl-type crystal structure. As yet no clear explanation has been given for such a difference between the TiFe and the TiNi hydrides. The experimental results for H/M apparently suggest that some factor other than the geometrical factor [3] determines the capacity of the hydrogen absorption in these compounds. It is important to identify any such factor for the further development of new hydrogen storage compounds with a large capacity.

In this study, the electronic structures of titanium compounds with the CsCl-type structure are calculated by the DV-Xα molecular orbital method [4]. The hydrogen

absorption characteristic of these compounds is elucidated in the light of chemical bond theory.

2. DV-Xα cluster method and cluster model

The DV-Xα cluster method is employed in the calculation of electronic structures. This is a molecular orbital method which assumes a Slater Xα exchange-correlation potential. The detailed explanation of this calculation method is given elsewhere [4].

The cluster model employed in the present calculation is shown in Fig. 1. This cluster, $Ti_{20}Fe_{20}H_{43}$, is made based on the atomic arrangement in $TiFeH_{1.94}$ with the orthorhombic structure (*Cmmm* space group) [5]. The lattice parameters, $a=0.7029$ nm, $b=0.6233$ nm and $c=0.2835$ nm are used in the calculation. Two types of octahedra constructed by four Ti and two Fe atoms ((a) and (b) in Fig. 1) and one octahedron constructed by two Ti and four Fe atoms ((c) in Fig. 1) are picked out and their electronic structures are also calculated separately. There is a difference in the atomic spacing between the octahedra, (a) and (b).

For comparison, the electronic structures of TiFe, TiCo and TiNi, all of which have the CsCl-type crystal structure, are also calculated using octahedral clusters, Ti_4X_2H (X= Fe, Co and Ni), as is shown in Fig. 2. The distances between Ti atoms, which are equal to the lattice parameters
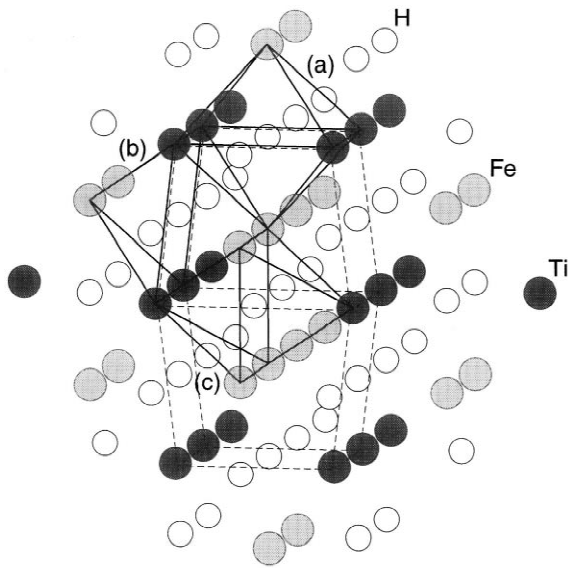
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Fig. 1. Cluster model of $Ti_{20}Fe_{20}H_{43}$ employed in the calculation. A unit cell is surrounded by dotted lines.

of TiFe, TiCo and TiNi compounds, are 0.2976 [6], 0.2995 [7] and 0.3015 nm [6], respectively. In the present study, any lattice expansion due to hydrogenation is not taken into account, since our attention is mainly focused on the change in the chemical interaction between atoms with constituent elements, X, in the TiX compounds.

3. Results

3.1. Spatial electron density distribution in $Ti_{20}Fe_{20}H_{43}$

Fig. 3 shows the contour map of the electron densities on the (102) atomic plane of the $Ti_{20}Fe_{20}H_{43}$ cluster. In the TiFe compound with the CsCl-type structure, it has been considered that the hydrogen atom occupies a central site of the octahedron which is constructed with four Ti and two Fe atoms (hereafter referred to as the Ti_4Fe_2H
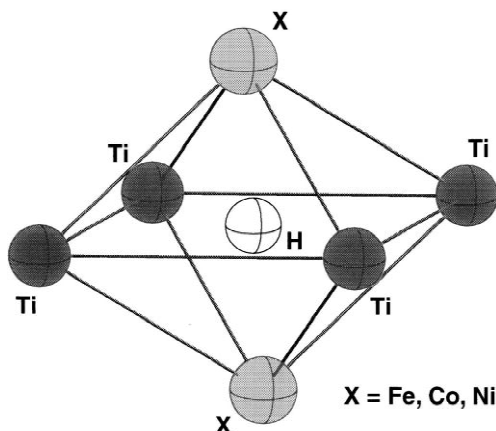

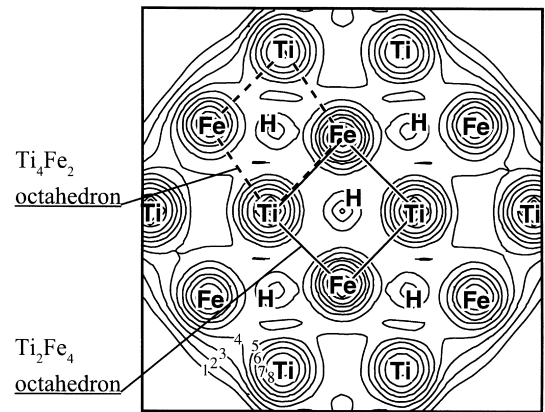Fig. 2. Cluster model of Ti_4X_2H employed in the calculation.

Fig. 3. Contour map of the electron density on the (102) atomic plane. The dotted numbers, 1, 2, 3, 4, 5, 6, 7 and 8 correspond to the electron density values, 0.005, 0.01, 0.02, 0.04, 0.08. 0.16, 0.32 and 0.64 in electrons per cube of the atomic unit, respectively.

octahedron). As shown in Fig. 3, however, the hydrogen atom can occupy a central site of another octahedron which is constructed with two Ti and four Fe atoms (the Ti_2Fe_4H octahedron) in the $TiFeH_{1.94}$ hydride. It can be seen from the figure that there is no significant difference in the electron densities between H atoms occupying both sites.

3.2. Bond order between atoms in $Ti_{20}Fe_{20}H_{43}$

The overlap population, $Q_{\nu\nu'}$, of electrons between two atoms ν and ν' is called the bond order. It is defined as,

$$Q_{\nu\nu'} = \sum_l \sum_{ij} C_{il}^{\nu} C_{jl}^{\nu'} \int \Psi_i^{\nu} \Psi_j^{\nu'} {}^* \mathrm{d}V. \tag{1}$$

Here, Ψ_i^{ν} and $\Psi_j^{\nu'}$ are the wavefunctions of the i and j orbitals of ν and ν' atoms, respectively. C_{il}^{ν} and $C_{jl}^{\nu'}$ are coefficients which show the magnitude of the linear combination of atomic orbitals in the lth molecular orbital. The sum over l runs only over the occupied orbitals. This bond order is a measure of the strength of the covalent bond between ν and ν' atoms.

The bond order between atoms in each octahedral cluster in $Ti_{20}Fe_{20}H_{43}$ is shown in Fig. 4. It can be found that the bond order between Fe and H atoms (hereafter denoted as Bo(Fe–H)) is larger than Bo(Ti–H) in every cluster. This indicates that the hydrogen atom interacts more strongly with Fe atoms than Ti atoms in the TiFe hydride. Concerning the metal–metal bonding there are large differences in both the Bo(Ti–Ti) and the Bo(Fe–Fe) values between the Ti_4Fe_2H and the Ti_2Fe_4H octahedra. This will be mainly due to the differences in their atomic separation. It is important to note here that Bo(Ti–Fe) is the largest of the metal–metal bondings, and the value does not change depending on the type of the octahedron.
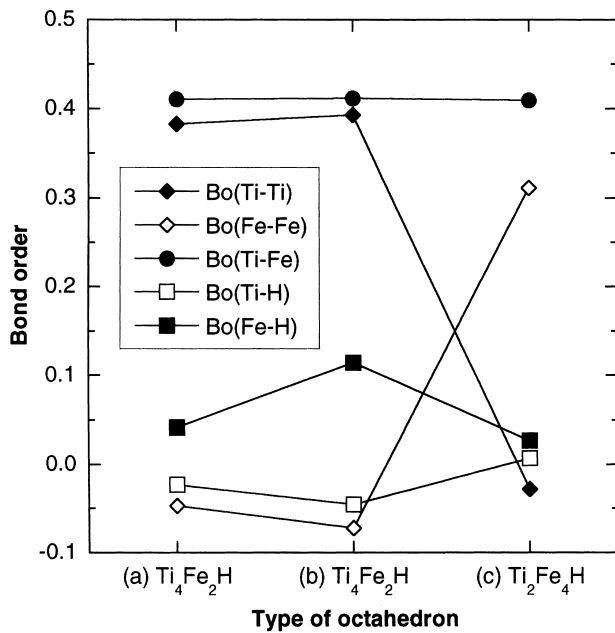
Fig. 4. Changes in the bond order with the type of the octahedron.

3.3. Effect of constituent elements, X, on the bond order

Fig. 5(a) and (b) shows the change in the bond orders between metal and hydrogen and between metals with the
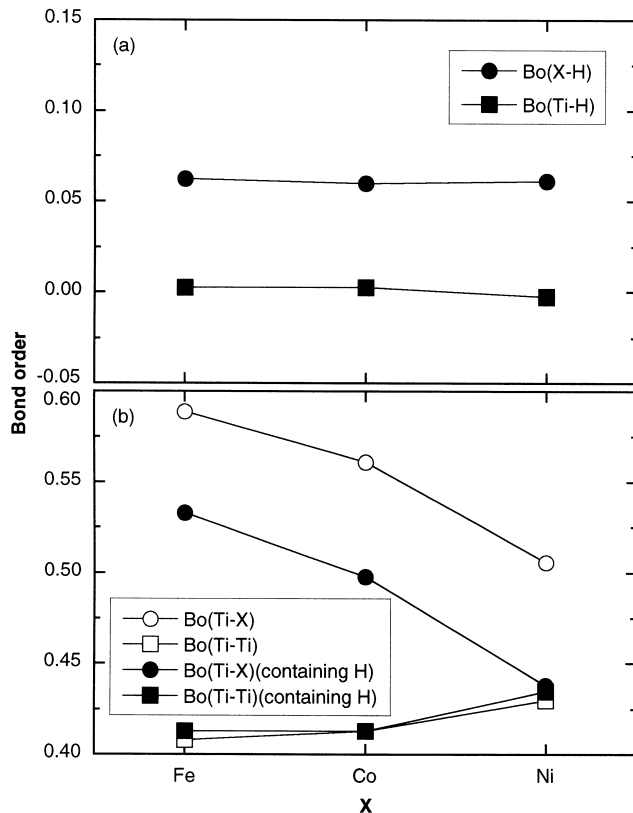

Fig. 5. Changes in the bond order with constituent elements, X (=Fe, Co, Ni); (a) metal–H bond order and (b) metal–metal bond order.

constituent element, X (=Fe, Co, Ni), in TiX compounds, respectively. These results are obtained using a cluster model of Ti_4M_2H shown in Fig. 2. It is evident from Fig. 5(a) that the Bo(Ti–H) is smaller than the Bo(M–H) as is similar to the results presented in Fig. 4. Namely, hydrogen interacts more strongly with constituent elements, X, rather than Ti atoms in these titanium compounds with the CsCl-type structure, despite the fact that Ti is a hydride forming element, whereas X's are hydride non-forming elements in binary metal–hydrogen systems. Such a result is also reported for $LaNi_5$ and Mg_2Ni hydrogen storage alloys [8–10]. Here, La and Mg are hydride forming elements similar to Ti in TiX compounds.

As shown in Fig. 5(b), the bond orders are larger between metal atoms than between metal and H as shown in Fig. 5(a). As is similar to the calculated result for the Ti_4Fe_2H octahedron shown in Fig. 4, the Bo(Ti–X) is the largest among the bond orders between metals, and it decreases with increasing atomic number of X. By comparing the data indicated by open and solid circles with each other, it is apparent that the Bo(Ti–X) value decreases considerably with hydrogenation. In contrast, the Bo(Ti–Ti) value is scarcely modified by hydrogenation. Only a slight increase in the Bo(Ti–Ti) can be seen in Ti_4Ni_2H. However, it is interesting to note that in the case of this hydrogenated cluster, the Bo(Ti–Ti) has almost the same value as the Bo(Ti–Ni).

4. Discussion

4.1. Characteristic of the crystal structure of $TiFeH_{1.94}$

Needless to say, lattice expansion will occur during hydrogenation of these titanium compounds. The maximum expansion and contraction of the interatomic distances between Ti and Ti by hydrogenation, which are estimated from the crystal structure of the hydride [5], are 0.092 and 0.014 nm, respectively. In contrast to this, the expansion of the interatomic distances between Ti and Fe does not occur, and the maximum contraction is 0.023 nm. This fact can be understood by noting the strong bond strength between Ti and Fe atoms as shown in Fig. 4 and Fig. 5(b). Because of such a limitation in the contraction of the interatomic distances between Ti and Fe atoms, large lattice expansion and distortion by hydrogenation will mostly occur between Ti atoms because of the small Bo(Ti–Ti) value. As a result, a Ti_2Fe_4 octahedral site will become one possible site to accept hydrogen [5].

4.2. Effect of constituent elements, X, on the hydrogen capacity

As mentioned before, the capacity for the hydrogen absorption in TiFe, TiCo and TiNi is different in each case, although all of them have the same CsCl-type structure.

The reason is explained in the light of the chemical bonding between atoms.

The hydrides which may be possibly formed in the titanium compounds with CsCl-type structure are schematically illustrated in Fig. 6. As shown in Fig. 6(a), there are six Ti_4X_2 octahedral sites in a unit cell of the CsCl-type structure. If H atoms occupy all of these sites, H/M will become 1.5. In the TiFe compound, however, some hydrogen atoms can occupy the Ti_2Fe_4 octahedral sites as described earlier. Once the Ti_2Fe_4 sites are occupied by H atoms as shown in Fig. 6(b), the nearest Ti_4Fe_2 octahedral sites can not be occupied any more by H atoms because of the limitation in the very short distance between H atoms. So, in the case of the structure shown in Fig. 6(b), the capacity of hydrogen absorption, H/M, is reduced to 1.0, a value close to the measured H/M for TiFe.

In the case of TiNi, the Ti–Ni bond strength is much smaller as compared to the Ti–Fe bond strength. There-fore, the occurrence of expansion and distortion in the TiNi lattice can be expected to be quite different from that in the TiFe lattice, because the distance between Ti and Ni atoms will not be restricted, but possibly extended during hydro-genation [11]. As shown in Fig. 6(c), if a Ti_4Ni_2 octahedral site is occupied by an H atom, the neighbouring Ni atom will easily move away from the position of the occupied H atom. As a result, the opposite Ti_4Ni_2 octahedral site can not have enough space to be occupied by another H atom. Therefore, only three of Ti_4Ni_2 octahedral sites in a unit cell are available for the hydrogen absorption. This causes a small H/M value, 0.75, of TiNi.
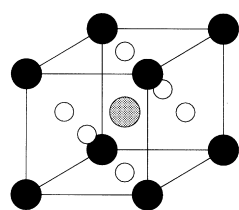
5. Conclusion

The hydriding properties of titanium compounds with the CsCl-type structure are well understood in terms of the nature of the chemical bond between atoms. The bond strength between atoms is one of the important factors to determine the capacity of hydrogen absorption in them.
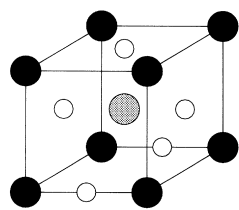
(a) H / M = 1.5

(b) H / M = 1.0

(c) H / M = 0.75

Fig. 6. Schematic illustration of the hydride of the compounds with CsC1-type structure; (a) simple hydride, (b) TiFe and (c) TiNi hydride.
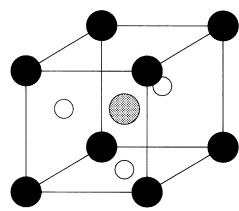
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