Ab Initio Electronic Structure Study of α -Zirconium and Hydrogen

Misako Iwasawa, Toshiharu Ohnuma and Naoki Soneda

Materials Science Research Laboratory, Central Research Institute of Electric Power Industry, Tokyo 201-8511, Japan

The electronic structures of α -zirconium (Zr) and hydrogen (H) were calculated using density functional theory with the ultrasoft pseudopotential and generalized gradient approximation. The binding energy between a Zr vacancy and H, the migration energies of H in Zr with and without a Zr vacancy and the migration energy of a Zr vacancy with H were calculated, and the strong binding between a Zr vacancy and H was quantitatively demonstrated. [doi:10.2320/matertrans.MRA2008184]

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1. Introduction

Recently, the behavior of hydrogen in metal has attracted attention in various fields. In the nuclear industry, it is important to examine the effect of irradiation on structural materials in high burn-up. In zirconium alloy, which is used as a cladding material of light-water-reactor fuel rods, it is known that the absorption of hydrogen increases at high burn-up and that this causes hydrogen embrittlement. Some studies have been reported on the hydrogen embrittlement of Zr from the viewpoint of the electronic structure. Yamanaka *et al.*¹⁾ have performed calculations on a Zr hydride model cluster by the DV-X α method and have shown that the hydrogen contributes to the strength of Zr bonds. Domain *et al.*²⁻⁴⁾ have calculated the electronic structure of hydrogen in bulk Zr using density functional theory^{5,6)} (DFT). They showed that the interaction between the vacancy and hydrogen was important in the mechanism of hydrogen embrittlement in Zr, but their studies focused on more macroscopic features such as dislocations. There are few studies on hydrogen and vacancies at the atomic scale, although vacancies may be a strong trapping center of hydrogen in irradiated zirconium alloy.

In this study, we calculate the binding energy between hydrogen and a Zr vacancy, and then we estimate the migration energy of hydrogen in the vacancy by first-principles electronic structure calculations to clarify the behavior of hydrogen.

2. Method

All calculations in the present work were performed by the Vienna *ab initio* Simulation Package (VASP),⁷⁾ which is an electronic structure calculation package based on DFT using the ultrasoft pseudopotential^{8,9)} and plane waves. The generalized gradient approximation of PW91¹⁰⁾ was used for the exchange correlation term. An energy cut-off of 436.8 eV was adopted, a Monkhorst-Pack¹¹⁾ (2,2,2) set was used for k-space sampling during relaxation calculations and a (3,3,3) set was used in the final electronic structure calculations. All structural parameters, not only lattice constants but also cell shapes and atom positions, were relaxed using the RMM-DIIS algorithm.¹²⁾ The convergence of the total energy was

within 10^{-4} eV in the electronic structure and 10^{-3} eV in the atomic relaxation calculation.

A supercell of 128 atoms ($4 \times 4 \times 4$ α -Zr primitive cell) was used in this study. One Zr atom was removed from the cell to form a Zr vacancy. H was not located at the substituted site but at the interstitial, tetragonal (T) or octahedral (O) site. The binding energy of H with the Zr vacancy was expressed as follows:

$$E_{\text{trap}}(n) = \{E(\text{Zr127} + (n-1)\text{H}) + E(\text{Zr128} + \text{H})\} \\ - \{E(\text{Zr127} + n\text{H}) + E(\text{Zr128})\},$$

where n is the number of H around the vacancy, $E_{\text{trap}}(n)$ is the H-vacancy binding energy, $E(\text{Zr128})$ is the total energy of an ideal cell, $E(\text{Zr127})$ is the total energy of one Zr vacancy, $E(128 + \text{H})$ is the total energy of the ideal cell with H in the interstitial and $E(\text{Zr127} + n\text{H})$ is the total energy of the system with one Zr vacancy and n H.

The migration energies of H and Zr were evaluated by the nudged elastic band method,¹³⁾ which determines the intermediate states and the reaction path from the initial state to the final state. We assumed three intermediate states between the initial and final states. It is well-known that the quantum effect is important for H migration because of its low mass, but in this study, we assume migration at the reactor operating temperature, about 600 K, in which thermal diffusion is expected to be the main mechanism; thus, we neglect the quantum effect in our calculations.

3. Results and Discussion

3.1 H-vacancy binding

We considered many types of H sites in the region surrounded by the first-neighboring Zr atoms of the Zr vacancy. Figure 1 shows the configurations of one types of H site. In this case, three different sites were assumed, the basal plane (Fig. 1(a)), the T site (Fig. 1(b)), and the O site (Fig. 1(c)). The O site is the most stable but the differences between the sites are very small. The calculated H-vacancy binding energies are shown in Fig. 2. In these H sites, the H-vacancy binding energies are 0.18–0.20 eV, which means that it is more stable for H atoms to be near the Zr vacancy than to be at the interstitial site and the Zr vacancy independently. Two H atoms around the vacancy at five

Fig. 1 H configurations around the Zr vacancy. Blue circles are Zr, light blue circles are H and yellow circle is the Zr vacancy. These figures only show the region around the Zr vacancy.

Fig. 2 Calculated H-vacancy binding energies. 1H means one hydrogen in the Zr vacancy system.

Fig. 3 Total density of states of Zr-H systems. Dotted lines indicate the Fermi levels. The upper figure shows H in the ideal Zr system, and the bottom figure shows H in the Zr vacancy system.

different pairs of sites were assumed (two O sites, or an O site and a T site, etc.). Also, the H-vacancy binding energies are 0.19–0.20 eV. We consider four arrangements of three H atoms, three arrangements of four H atoms and one arrangement for five to nine H atoms. For example, nine H atoms are located at six O sites and three basal sites. The H-vacancy binding energies are about 0.2 eV for up to six H atoms, but almost zero for seven H atoms and above. Therefore, H atoms can be easily arranged around the vacancy. Figure 3 shows

Fig. 4 Labelling of interstitial H sites in ideal Zr and migration paths. Blue circles are Zr and light blue circles are H. The green circles are the intermediate points of migration.

Table 1 Migration energies (eV) of H in ideal Zr.

path ¹⁾	this work	Domain ⁴⁾
T1 $\leftrightarrow$ T2	0.66	0.66
T2 $\leftrightarrow$ T3	0.12	0.12
T1 $\leftrightarrow$ T4 ²⁾	—	—
O1 $\leftrightarrow$ O2	0.46	0.41
O1 $\leftrightarrow$ O3	0.62	0.70
T1 $\leftrightarrow$ O1 ³⁾	0.41, 0.37	0.41, 0.35

¹⁾The sites labelling are shown in Fig. 4.
²⁾T1 $\leftrightarrow$ T4 is modified to T1 $\leftrightarrow$ O1 $\leftrightarrow$ T4 path.
³⁾from T1 to O1 is 0.41 eV and from O1 to T1 is 0.37 eV.
⁴⁾Ref. 2)

the density of states of one H in the ideal Zr system and in the Zr vacancy system. The peak of less than -3 eV represents the H 1s and Zr s and d components. This peak of the Zr vacancy system is stronger than that of the ideal system. In the Zr vacancy system, the combination of H and the neighboring Zr is strengthened; H seems to be relatively strongly trapped by the vacancy.

3.2 H migration in Zr

We calculated the migration energy of H without a Zr vacancy in ideal Zr128. It is well-known that the H atom is located at the T site or O site. The energy difference between these sites is very small; the T site is only 0.04 eV more stable than the O site. Thus, we consider the following cases; (1) T1 $\leftrightarrow$ T2, (2) T2 $\leftrightarrow$ T3, (3) T1 $\leftrightarrow$ T4, (4) O1 $\leftrightarrow$ O2, (5) O1 $\leftrightarrow$ O3 and (6) T1 $\leftrightarrow$ O1. (Fig. 4) The calculated migration energies are shown in Table 1 with results calculated in a

previous study.²⁾ The calculated migration paths are also illustrated in Fig. 4. The migration paths in the form of $O \rightleftharpoons O$ or $T \rightleftharpoons T$, except for $T1 \rightleftharpoons T4$, are almost straight, but the path of $T1 \rightleftharpoons O1$ is asymmetric, in which case, the migration energy from $T1$ to $O1$ is 0.41 eV, and that from $O1$ to $T1$ is 0.37 eV. These values are less than the migration energy of $O1 \rightleftharpoons O3$, which is the other case of migration in the basal plane. The $T1 \rightleftharpoons T4$ path is modified to the $T1 \rightleftharpoons O1 \rightleftharpoons T4$ path. Thus, the migration of H in α -Zr may be carried out faster in the basal plane than along the c axis. Our calculations show the same tendency as that in the previous study²⁾ in most cases, but in some cases, the results show different trends. It is thought that these differences are caused by the method of evaluating migration energy. We used the nudged elastic band method; thus, intermediate-point structures are also fully relaxed, but the structures in Ref. 2) were only partially relaxed.

3.3 H migration in Zr with vacancy

We then evaluated the migration energy of H in the presence of a Zr vacancy. H is located at some sites near the Zr vacancy as illustrated in Fig. 5. Table 2 shows the relative energies and the distances between H and the vacancy. In the presence of the Zr vacancy, the energy difference between the O site and the T site is almost zero and the relative energies increase with the distance from the vacancy. The migration energies are shown in Table 3; values in the right column correspond to energies without the vacancy. The migration paths are also illustrated in Fig. 5.

The paths $T1 \rightleftharpoons T2$, $O1 \rightleftharpoons O2$ and $O2 \rightleftharpoons O3$ represent migrations between equivalent positions on the vacancy. In the cases of $T1 \rightleftharpoons T2$ and $O1 \rightleftharpoons O2$, the migration energies are much less than those without the vacancy. The paths are not straight but approach the vacancy side. (see Fig. 5) However, in the case of $O2 \rightleftharpoons O3$, the migration energy is greater than that without the vacancy. The intermediate position of the $O2 \rightleftharpoons O3$ path is closer to the vacancy than the other cases, and the interaction between H and its neighboring Zr is weak. Therefore, the H at the O site near the

Table 2 Relative energies (eV) and distances (nm) between H and the Zr vacancy.

sites ¹⁾	relative energy ²⁾ , E/eV	H-Zr vacancy distance, d/nm
T1	0.00	0.172
T2	0.00	0.172
T3	0.12	0.162
T4	0.18	0.376
T5	0.09	0.304
T6	0.20	0.373
O1	0.01	0.236
O2	0.00	0.236
O3	0.00	0.236
O4	0.21	0.425
O5	0.25	0.505

¹⁾The sites labelling are shown in Fig. 5.

²⁾T1 site is a standard.

Zr vacancy does not migrate directly to the other basal-plane O site.

The paths $T2 \rightleftharpoons T3$, $T1 \rightleftharpoons O1$ and $T3 \rightleftharpoons O3$ represent migrations within the region surrounded by the first-neighboring Zr atoms of the vacancy. These migration energies are also lower than those without the vacancy. H can thus easily move near the vacancy in the same basal plane.

The $T6 \rightarrow T1$ migration energy is greater than that without the vacancy, although this path can be used by H to migrate toward the vacancy. The O1 site, which has the same energy as the T1 site, is located near the T6 site. The $T6 \rightarrow O1$ and $O1 \rightarrow T1$ migration energies are less than that of $T6 \rightarrow T1$; thus, the H at the T6 site migrate via the O1 site.

The other paths also allow H to migrate toward the vacancy (or away from the vacancy). The migration energies toward the vacancy are lower than those without the vacancy, and in contrast, those in the direction away from the vacancy are higher. This tendency is natural considering the relative energies of each site. For example, in the case of $O1 \rightleftharpoons O4$, which is a path from the region surrounded by the first-

Table 3 Migration energies (eV) of H and distances (nm) between intermediate points and the Zr vacancy.

path ¹⁾	migration energy, E/eV					intermediate points- Zr vacancy distance, d/nm
	with vacancy			without vacancy ²⁾		
T1 $\rightleftharpoons$ T2	T1 $\rightarrow$ T2	0.01	T2 $\rightarrow$ T1	0.01	0.12	0.163
T2 $\rightleftharpoons$ T3	T2 $\rightarrow$ T3	0.30	T3 $\rightarrow$ T2	0.18	0.66	0.136
T3 $\rightleftharpoons$ T5	T3 $\rightarrow$ T5	0.11	T5 $\rightarrow$ T3	0.14	0.12	0.233
T1 $\rightleftharpoons$ T6	T1 $\rightarrow$ T6	0.92	T6 $\rightarrow$ T1	0.72	0.66	0.256
O1 $\rightleftharpoons$ O2	O1 $\rightarrow$ O2	0.29	O2 $\rightarrow$ O1	0.30	0.62	0.134
O2 $\rightleftharpoons$ O3	O2 $\rightarrow$ O3	0.63	O3 $\rightarrow$ O2	0.63	0.46	0.129
O1 $\rightleftharpoons$ O4	O1 $\rightarrow$ O4	0.63	O4 $\rightarrow$ O1	0.43	0.46	0.318
O1 $\rightleftharpoons$ O5	O1 $\rightarrow$ O5	0.87	O5 $\rightarrow$ O1	0.62	0.62	0.362
T1 $\rightleftharpoons$ O1	T1 $\rightarrow$ O1	0.28	O1 $\rightarrow$ T1	0.28	0.41, 0.37	0.144
T3 $\rightleftharpoons$ O3	T3 $\rightarrow$ O3	0.28	O3 $\rightarrow$ T3	0.40	0.41, 0.37	0.137
T6 $\rightleftharpoons$ O1	T6 $\rightarrow$ O1	0.27	O1 $\rightarrow$ T6	0.47	0.41, 0.37	0.292
T4 $\rightleftharpoons$ O1	T4 $\rightarrow$ O1	0.32	O1 $\rightarrow$ T4	0.50	0.41, 0.37	0.300
T4 $\rightleftharpoons$ O5	T4 $\rightarrow$ O5	0.44	O5 $\rightarrow$ T4	0.37	0.41, 0.37	0.430

¹⁾The sites are labelled according to Fig. 5.

²⁾our results in Table 1.

Fig. 5 Labelling of interstitial H sites in Zr vacancy system and migration paths. Blue circles are Zr, light blue circles are H and the yellow circle is the Zr vacancy. The green circles are the intermediate points of the $O \rightleftharpoons O$ path, red circles are the intermediate points of the $T \rightleftharpoons O$ path and purple circles are the intermediate points of the $T \rightleftharpoons T$ path.

Fig. 6 Energy diagram of $O1 \rightleftharpoons O4$ path labelled in Fig. 5.

neighboring Zr of the vacancy, the O4 site is more unstable than the O1 site by 0.21 eV, which is equal to the difference between the migration energies $O1 \rightleftharpoons O4$ path (see Fig. 6). The migration energy of $O4 \rightarrow O1$ is 0.42 eV, which is smaller than no vacancy case, 0.46 eV, so the vacancy influence also works in this region. It may be said that the vacancy becomes the trap site of H from these facts.

3.4 Zr vacancy migration

We calculated the migration energy of the Zr vacancy, or, to be precise, the exchange energy of the Zr atom and the neighboring Zr vacancy. Table 4 shows the results of calculations. It is preferable for Zr to move in the same basal plane than to move between the neighboring basal planes. We then calculated the migration energy of the Zr vacancy when an H atom exists. We only calculated the case when H is located at the O site. Table 5 shows the results of the calculations. The sites and intermediate points of migration are illustrated in Fig. 7.

Table 4 Zr migration energy (eV) with Zr vacancy.

direction	migration energy, E/eV
basal plane	0.33
c axis	0.43

Table 5 Zr migration energy (eV) with Zr vacancy and H (O1 site).

path ¹⁾		migration energy, E/eV			
$Zr0 \rightleftharpoons Zr1$	$Zr1 \rightarrow Zr0$	0.41	$Zr0 \rightarrow Zr1$	0.41	
$Zr0 \rightleftharpoons Zr2$	$Zr2 \rightarrow Zr0$	0.48	$Zr0 \rightarrow Zr2$	0.48	
$Zr0 \rightleftharpoons Zr3$	$Zr3 \rightarrow Zr0$	0.38	$Zr0 \rightarrow Zr3$	0.18	
$Zr0 \rightleftharpoons Zr4$	$Zr4 \rightarrow Zr0$	0.38	$Zr0 \rightarrow Zr4$	0.13	
$Zr0 \rightleftharpoons Zr5$	$Zr5 \rightarrow Zr0$	0.49	$Zr0 \rightarrow Zr5$	0.29	
$Zr0 \rightleftharpoons Zr6$	$Zr6 \rightarrow Zr0$	0.48	$Zr0 \rightarrow Zr6$	0.27	
$Zr0 \rightleftharpoons Zr7$	$Zr7 \rightarrow Zr0$	0.43	$Zr0 \rightarrow Zr7$	0.20	

¹⁾The sites are labelled according to Fig. 7.

Fig. 7 Labelling of Zr and migration paths of Zr. Blue circles are Zr, the yellow circle is the Zr vacancy and the light blue circle is H. Green circles are the intermediate points of Zr migration.

The paths to (or from) Zr1 and Zr2 pass through the region that is nearest to H. These paths are not straight and one path slightly approaches the H in the basal plane migration (Zr1), and the other moves away from the H (Zr2). In these cases, the migration energies are greater than those without H. It may be difficult for Zr to migrate near H. The paths of Zr3 and Zr4 are the other paths in the basal plane. In these cases, the migration energies of Zr to the vacancy site (Zr0) are greater than those without H. However, the migration energies from the Zr0 site to Zr3 or Zr4 sites are lower than those without hydrogen. It is because the Zr vacancy is more stable at the Zr3 and the Zr4 sites than at the Zr0 site. The relative energies are equal to the decrease in values; thus, the effect of H is estimated about 0.05 eV (0.38–0.33 eV). Zr5 and Zr6 are the paths for migration to the other basal plane, and in these cases the effects of H are also about 0.05 eV. The path of Zr7 is the furthest from H; the migration energy is equal to the case without H. In the case of Zr migration (equivalent to the Zr vacancy migration), the migration energy become large in the presence of H, although in the

case of H migration, the migration energy becomes small in the presence of the Zr vacancy. Therefore, after an H atom migrates and meets a Zr vacancy, the Zr vacancy cannot easily move, and the Zr vacancy and hydrogens preferentially form a cluster.

4. Conclusion

We examined the behavior of hydrogen around a Zr vacancy by first-principles electronic structure calculations. In the presence of a Zr vacancy, hydrogen can easily be located around the Zr vacancy and move toward the Zr vacancy, but cannot easily move far from the Zr vacancy. In addition, we examined Zr vacancy migration around a hydrogen atom. It was proven that the Zr vacancy also cannot easily move far from the hydrogen. The Zr vacancy and hydrogens prefer entirely form a cluster. This appears to be a cause of the atomic-scale hydrogen embrittlement of Zr.

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