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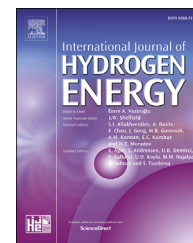
Effects of alloying substitutions on the anti-disproportionation behavior of ZrCo alloy

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ABSTRACT

We perform first-principles calculations to investigate the effects of alloying substitutions (i.e. Ti, Hf, Sc, Fe, Ni and Cu) on hydrogen-induced disproportionation of ZrCo alloy. H at the 8e site of $ZrCoH_3$ (H(8e)) plays the key role in the disproportionation process. It is found that H(8e) prefers to form strong covalent-like binding with the neighboring Co and its substitute elements, which is distinctly different from H at the $4c_2$ and $8f_1$ sites. Alloying substitutions can restrain or accelerate the disproportionation by influencing the Zr–H(8e) bond length and the size of the 8e site. Judged from this, the anti-disproportionation ability of these alloying substitutions is identified. Our results of Ti, Hf, Sc, Fe and Ni are in good agreement with the previous experimental results. It is also predicated that Cu can accelerate hydrogen-induced disproportionation of ZrCo alloy.

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Introduction

ZrCo intermetallic compound is considered as a thrilling AB-type alloy which is believed to be the suitable alternate of uranium for handling of hydrogen (H) and its isotopes tritium [1–5], and it has received considerable attentions in the applications to fusion reactor fuel system in the past decade [6,7]. In the ZrCo–H system the biggest H content is close to three H atoms per Zr atom [8].

In ideal condition, ZrCo alloy will completely transform into $ZrCoH_3$, and vice versa. H atoms only occupy the $4c_2$ and $8f_1$ sites in the crystal structure of $ZrCoH_3$. The chemical change can be expressed by the following equation:

$$2ZrCo + 3H_2 \leftrightarrow 2ZrCoH_3 \qquad (1)$$
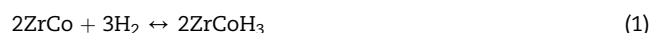
Nevertheless, the major drawback of ZrCo alloy is that after repeated H absorption and desorption cycles the capacity of H storage decreases due to the hydrogen-induced

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disproportionation (HID) phenomenon [9–13]. It is found that during HID $ZrCoH_3$ can convert into ZrH_2 which is highly stable. $ZrCo_2$, a hydrogen non-absorbing phase, is also produced. The HID process can be described by the following reaction:

$$2ZrCoH_3 \rightarrow ZrH_2 + ZrCo_2 + 2H_2 \qquad (2)$$
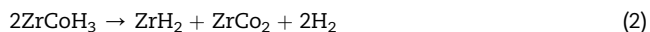
Based on thermal analytical methods and crystallographic considerations, Bekris et al. [8] theoretically predicted that ZrH_2 was induced by about 4% of H atoms which enter the $8f_2$ and 8e sites during the HID process, which was assumed as the driving force of disproportionation of ZrCo alloy.

Furthermore, in order to improve the anti-disproportionation ability of ZrCo, partial substitution of Zr or Co with a third metal has been studied extensively. The most commonly used metals are Ti [14,15,22,23], Hf [16,17,23], Sc [16,22], Ni [18,19,22], Fe [20,22] and Cu. Ti, Hf and Sc elements are used to partly replace Zr, and Ni, Fe and Cu are utilized to partly substitute Co.

According to the H pressure change during HID in Hf-doped ZrCo alloys, Peng et al. [17] found that substitution of Zr with Hf in ZrCo is a promising strategy to improve the ability to resist HID.

By use of the same experimental techniques as Peng [17], Zhang et al. [22] compared the HID phenomena of ZrCo alloys with Ti, Sc, Ni, Fe substitution, and found that Ti substitution can effectively enhance the ability of anti-disproportionation while Fe, Sc, Ni substitution accelerate the disproportionation of ZrCo alloy. The anti-disproportionation ability is in this order: Ti > Fe > Sc > Ni. Zhang also inferred that the changes of hole sizes of the $8f_2$ and 8e sites are the main reason of the effect of alloying substitution on disproportionation of ZrCo alloy.

Among these substitution alloying elements that have been investigated, Ti and Hf can most significantly improve the durability against HID of ZrCo. As a result, Kou et al. [23] fabricated the full-scale thin double-layered annulus beds loaded with ZrCo, Hf-doped ZrCo and Ti-doped ZrCo, respectively, and compared the recovery and delivery of H in this beds, and finally found that Ti-doped ZrCo can improve the disproportionation of ZrCo alloy more significantly than Hf-doped ZrCo.

In all the above experiments, the effects of alloying substitutions on anti-disproportionation of ZrCo alloy were investigated by examining the change of the capacity of H storage after repeated H absorption and desorption cycles. However, all these above experiments did not investigate the effects of alloying substitutions from the microscopic point of view.

Microscopic experimental studies were performed only by Jat et al. [19–21]. Jat and his partners used neutron diffraction to investigate the effect of Ni [19], Fe [20] and Ti [21] substitution for Co, and found that about 3.8% of deuterium (D, H isotope) occupies the 8e site which is in agreement with the prediction of Bekris [8], and the other D atoms occupy the $4c_2$ and $8f_1$ sites. However, they did not find any D atoms occupy the $8f_2$ site. They found that occupancy of 8e site decreases and its Zr-D distance increases with increase of the Ni content, indicating the higher durability against HID in Ni rich compound. In addition, they found that Fe, Ti substitution can reduce the amount of D in 8e site and thus improves the durability against HID. Unfortunately, HID phenomenon or significant decrease in H storage capacity was still observed in the ZrCo alloy with Ni, Fe substitution. Further, they [21] found that $Zr_{0.8}Ti_{0.2}Co$ has better durability against HID and the extent of HID is primarily governed by the occupancy of the 8e site and the corresponding Zr-D distance.

In conclusion, according to the microscopic experimental studies [19,20], the H atoms which go into 8e sites result in the disproportionation of ZrCo alloy. The electronic and atomic structures around the H atom at the 8e site are the key to in-depth understanding of HID and the modification of ZrCo alloys against HID. However, the microscopic physical mechanism of the 8e site is not clear so far.

While it is difficult to directly investigate H behaviors by means of routine experimental techniques, first-principles calculations can explore H behaviors in alloys easily and are very powerful tools to uncover the underlying mechanisms from the view of atomic and electronic structures [24–26]. There have been some first-principles studies on ZrCo–H system [11,27–29]. However, up to now, there are still no first-principles studies on HID especially associated with the effect of the 8e site.

In this work, we used first-principles calculations to investigate the mechanism of HID in ZrCo and the effect of Ti, Hf, Sc, Fe, Ni, Cu substitution on the anti-disproportionation of ZrCo alloys. In particular, the 8e site was paid special attention to achieve a deeper understanding on HID.

Computational methods

First-principles calculations were performed with the spin-polarized density functional theory (DFT) as implemented in the Vienna ab-initio simulation package (VASP) [30–32]. The electron–ion interaction was modeled using the projector-augmented plane-wave (PAW) method [33,34] and the wave functions were expanded in a plane-wave basis set with a cutoff energy of 500 eV. A generalized gradient approximation (GGA) of PBE [35] scheme was employed to describe the exchange correlation energy. The Brillouin zone was sampled using a Monkhorst–Pack $7 \times 5 \times 7$ k-points mesh. The forces on each ion was minimized up to 0.01 eV/Å [36]. The convergence criteria for energy were 10^{-6} eV. A $2 \times 1 \times 2$ supercell is used in order to get the reasonable stoichiometry for the calculations on the effects of alloying substitutions.

The structure of $ZrCoH_3$ used in calculations is shown in Fig. 1. In ideal condition, H atoms only occupy the $4c_2$ and $8f_1$ sites which are represented by black and pink balls in Fig. 1, respectively. For simplicity, H atoms at the 8e, $4c_2$ and $8f_1$ sites are denoted as H(8e), H($4c_2$) and H($8f_1$), respectively. During the disproportionation process, H atoms will go into the 8e sites which are indicated by the red balls in Fig. 1. In Fig. 1, the '8e site' pointed by the arrow is located at the center of the tetrahedron with the four vertexes Zr1, Zr2, Co1 and Co2.

The 8e sites are contained only in $ZrCoH_3$. H atoms in $ZrCoH_3$ enter the 8e sites during the process of disproportionation. When we investigated the role of H(8e) during HID