



Structure and thermodynamic properties of zirconium hydrides by structure search method and first principles calculations

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ABSTRACT

The formation of precipitated zirconium (Zr) hydrides is closely related to the hydrogen embrittlement of the claddings in pressured water reactors. In this work, we systematically investigated the structures of Zr hydrides ZrH_x ($x = 0.5, 1, 1.5, 2$) and their thermodynamic properties by combining the basin hopping algorithm with first principles calculations. All the experimentally identified structures of ZrH_x were reproduced, and new structures that are more stable were found. For $ZrH_{0.5}$, the most stable structure is of $Pn\bar{3}m$ symmetry. The experimentally discovered $P3m1$ ζ - $ZrH_{0.5}$ was found in this work, which is both dynamically and mechanically stable. The corrected lattice constants and atomic coordinates of the $P3m1$ ζ - $ZrH_{0.5}$ are also clarified. For ZrH , the most stable structure found in this work is of $P4_2/mnc$ symmetry, which is in agreement with experiments. For $ZrH_{1.5}$, it was found that the $P4_2/nmm$ structure is most stable at low temperature, while the experimentally observed $Pn\bar{3}m$ structure is most stable at high temperature. For ZrH_2 , the bistable structures of $I4/mmm$ ($c/a = 1.25$) symmetry is most stable, which is consistent with experiments. Furthermore, through analysis of the structural changes of Zr matrixes accompanying the phase transitions of Zr hydrides, we suggest that $\gamma \rightarrow \delta \rightarrow \epsilon$ phase transitions can be explained reasonably using the $P4_2/nmm$ $ZrH_{1.5}$ structure as the reaction intermediate. Additionally, through comparing the formation free energy, we found that δ - $ZrH_{1.5}$ is the most stable Zr hydride at high temperature, while ϵ - ZrH_2 is most stable at low temperature. Our results indicate that fast cooling process will promote the formation of δ - $ZrH_{1.5}$, and slow cooling process will promote the formation of γ - ZrH .

1. Introduction

Zirconium (Zr) alloys have been used as cladding material in pressurized water reactors due to their low thermal neutron absorption cross section, good mechanical properties, excellent waterside corrosion resistance, etc. [1]. However, during the long term service, complex zirconium hydrides (ZrH_x) will form in the cladding due to waterside corrosion and the hydrogen absorption. For decades, several zirconium hydride phases have been identified by experiments, including ζ - $ZrH_{0.5}$ [2], γ - ZrH , δ - $ZrH_{1.5}$ and ϵ - ZrH_2 [3].

Based on first principles calculations, thermal dynamical and mechanical properties of zirconium hydrides have been investigated, and new structures of zirconium hydrides have also been predicted [4–13]. Ackland found that for ϵ - ZrH_2 , two structures with different c/a exist and were almost degenerate in energy [14]. These bistable structures were later studied by Zhang et al. [15]. They suggested that the structure with $c/a > 1$ was dynamically unstable. Domain et al. [10] discovered two $P4_2/nmm$ $ZrH_{1.5}$ structures with different c/a , which are

more stable than the $Pn\bar{3}m$ δ - $ZrH_{1.5}$. Christensen et al. [13] found several new structures of zirconium hydrides, including a $Pn\bar{3}m$ $ZrH_{0.5}$ structure. Besson et al. [8] performed *ab initio* thermal dynamical calculation of *fcc* H-Zr system by cluster expansion method. Although much progress has been made, the systematical study of the structures and phase transitions of Zr hydrides is still necessary, and the stability of zirconium hydrides at different temperatures still remains unclear.

In recent years, crystal structure prediction methods based on first principles calculations have been developed rapidly, such as USPEX [16,17] and CALYPSO [18,19]. These methods have been successfully adopted to accelerate the material discoveries [18,20]. The applications to the structure search of Zr hydrides have also been reported recently. Li et al. investigated the structures of Zr hydrides at 50, 100 and 150 GPa through structure search [21]. Han et al. performed structure search for ZrH_x ($x = 1 \sim 3$) [22] by using the CALYPSO method. They found a novel ZrH_3 structure that is thermodynamically stable at ambient pressure.

In this work, employing structure search method, we focused on a

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systematic investigation of the structures of ZrH_x ($x = 0.5, 1, 1.5, 2$), the mechanisms of their phase transitions, and the influence of temperature on the structure stability and phase transitions. All of the structures of Zr hydrides observed by experiments have been reproduced, and several new zirconium hydride phases which are more stable than the known zirconium hydride phases were found. By analyzing the structures of Zr matrix of the corresponding zirconium hydrides, pathway of the $\gamma \rightarrow \delta \rightarrow \epsilon$ phase transitions has been proposed. Furthermore, the stability and phase transitions between different zirconium hydride phases at different temperatures were studied.

2. Method and computational details

Geometry optimizations and energy evaluations were carried out using the projector-augmented wave (PAW) method [23] within density functional theory framework by using Vienna *ab initio* simulation package (VASP) [24,25] and Correlated Electron System Simulation Package (CESSP) [26–29]. Exchange and correlation were treated in the generalized gradient approximation (GGA) as parameterized in the Perdew-Burke-Ernzerhof (PBE) [30,31] functional. The plane-wave cutoff energy was set to be 500 eV to guarantee a total energy convergence of less than 1 meV per atom. The Brillouin zone k-point sampling was performed by Monkhorst–Pack scheme [32] with the smallest allowed k-points spacing of $2\pi * 0.02 \text{ \AA}^{-1}$. The geometry optimization was performed using the conjugate-gradient (CG) algorithm until all the forces acting on the atoms are smaller than 10^{-4} eV/\AA . The Methfessel–Paxton function [33] with a smearing width of 0.1 eV was used to perform the integration over eigenvalues. The tetrahedron method with Blöchl corrections [34] was used to obtain the accurate total energies. Structure searches were performed with STEPMAX module of the CESSP package, which is based on the basin hopping (BH) algorithm [35–38] for structure evolutions. The formation enthalpy of $Zr_{1-x}H_x$ was calculated as

$$E^f(Zr_{1-x}H_x) = E_{Zr_{1-x}H_x} - (1-x)E_{Zr} - \frac{x}{2}E_{H_2} \quad (1)$$

where $E_{Zr_{1-x}H_x}$, E_{Zr} and E_{H_2} are the total energies of $Zr_{1-x}H_x$, Zr and H_2 respectively.

After the structure search, the dynamical stability of new structures was investigated by the phonon density of states (DOS). The phonon DOS was calculated through Phonopy [39] package. Furthermore, the elastic constants of these Zr hydrides were calculated. Based on these elastic constants, the mechanical stability of the predicted hybrids was examined through Born stability criteria [40–42], and their polycrystalline elastic moduli were further derived according to Voigt-Reuss-Hill approximations [43–45].

To take the temperature effect into account, the quasi-harmonic approximation (QHA) theory was applied to calculate the Helmholtz free energy, and both contributions of the electron excitation free energy and the phonon were included [5]. The calculations of phonon and the thermal properties were also performed by Phonopy [39] package. The free energy of H_2 gas at finite temperature was calculated according to [46].

3. Results and discussion

3.1. Stable and meta-stable structures of zirconium hydrides

3.1.1. $ZrH_{0.5}$

For $ZrH_{0.5}$, ζ - $ZrH_{0.5}$ with $P3m1$ (space group #156) symmetry has been experimentally identified and characterized by Zhao et al. [2]. However, we found several new structures which are more stable than the ζ - $ZrH_{0.5}$ phase. The formation enthalpy and lattice constants of the new structures were listed in Table 1. Some key structures were also listed in Fig. 1. Detailed lattice vectors and atomic coordinates were provided in the supplementary materials.

Firstly, we would like to discuss the stability of the $P3m1$ ζ - $ZrH_{0.5}$ structure using the lattice constants and atomic coordinates reported in previous work [2]. The optimized lattice constants of the $P3m1$ ζ - $ZrH_{0.5}$ ($a = b = 3.26 \text{ \AA}$, $c = 10.85 \text{ \AA}$) are in good agreement with previous work [2]. We further checked the stability of the $P3m1$ ζ - $ZrH_{0.5}$ structure through calculations of phonons and elastic constants. As shown in Fig. 2(a), there are several imaginary frequencies in the simulated phonon DOS, indicating that the $P3m1$ ζ - $ZrH_{0.5}$ structure is dynamically unstable. Besides, the calculated elastic constants (Table 2) showed that it is also mechanically unstable. We further optimized the $P3m1$ ζ - $ZrH_{0.5}$ structure with higher accuracy and without symmetry constraints. The $P3m1$ ζ - $ZrH_{0.5}$ structure transforms to a Cm structure ($a = 5.44 \text{ \AA}$, $b = 3.44 \text{ \AA}$, $c = 12.06 \text{ \AA}$, $\beta = 118.5^\circ$). The energy of the Cm structure is 30 meV per atom lower than the $P3m1$ ζ - $ZrH_{0.5}$ structure.

According to the work by Zhao et al., ζ - $ZrH_{0.5}$ belongs to the trigonal crystal system. Through our structure searches, two new trigonal crystal structures were found. The symmetry of one structure is $R\bar{3}m$ (space group # 166, $a = b = 3.28 \text{ \AA}$, $c = 32.09 \text{ \AA}$). The length of c is about three times of that of the $P3m1$ ζ - $ZrH_{0.5}$ structure. The energy of this structure is 43 meV per atom lower than the $P3m1$ ζ - $ZrH_{0.5}$ structure.

Another trigonal structure is also of $P3m1$ symmetry ($a = b = 3.26 \text{ \AA}$, $c = 10.78 \text{ \AA}$), but the position of hydrogen atoms differ from the $P3m1$ ζ - $ZrH_{0.5}$ structure of [2]. The total energy of the new $P3m1$ structure is 37 meV per atom lower than that of Zhao's. In addition, it is both dynamically and mechanically stable as shown in Fig. 2(a) and Table 2, respectively.

We notice that in Table 4 of Ref. [2], the atomic coordinates are incorrect. The distance between the Zr atom at position (1/3, 2/3, 1/8) and H atom at position (1/3, 2/3, 1/16) is $c/16$, 0.677 \AA , which is unreasonably short. In addition, the atomic coordinates in Table 4 of Ref. [2] is inconsistent with $ZrH_{0.5}$ -S2 structure in Fig. 6 of Ref. [2]. It was noticed that the more stable $P3m1$ structure found in this work is actually identical to the $ZrH_{0.5}$ -S2 in Fig. 6 of Ref. [2], which should be the correct experimentally discovered structure. And this structure is both dynamically and mechanically stable.

The most stable structure of $ZrH_{0.5}$ predicted in our structure search is a cubic crystal with $Pn\bar{3}m$ symmetry (space group #224, $a = 4.648 \text{ \AA}$), which is in agreement with the results by Christensen et al. [13]. The Zr matrix of the $Pn\bar{3}m$ structure is of $Fm\bar{3}m$ symmetry with $a = 4.648 \text{ \AA}$. Based on our calculations, the total energy of the $Pn\bar{3}m$ structure is 78 meV/atom lower than the $P3m1$ ζ - $ZrH_{0.5}$ structure.

However, the $Pn\bar{3}m$ $ZrH_{0.5}$ structure has not been observed by experiment. Thus, we further investigated the stability of $Pn\bar{3}m$ $ZrH_{0.5}$ at finite temperature by calculations of Helmholtz free energy using the quasi-harmonic approximation. As shown in Fig. 3(a), with the increase of temperature, the relative stability of the $Pn\bar{3}m$ structure decreases, while the $Cmmm$ and $C2/m$ (S1 and S2) structures of $ZrH_{0.5}$ become more stable. The $Cmmm$ and the $C2/m$ (S2) structures turn to be more stable than the $Pn\bar{3}m$ structure when the temperature is higher than 900 K, while $C2/m$ (S1) becomes as stable as the $Pn\bar{3}m$ structure at 1100 K. The $P3m1$ structure is also getting more stable as the temperature increases, but it is still less stable than the $Pn\bar{3}m$ structure even at 2000 K. The existence of $P3m1$ ζ - $ZrH_{0.5}$ is possibly due to the lattice matching between α -Zr and $P3m1$ $ZrH_{0.5}$ which stabilizes the Zr/ $ZrH_{0.5}$ interface, the high transformation barrier to other more stable structures, or the existence of alloying elements in the commercial zirconium alloys used in experimental observations. The factors that stabilized the formation of $P3m1$ ζ - $ZrH_{0.5}$ remain to be clarified in the future work.

Through the above analyses, we corrected the long existing mistake in Ref. [2] and clarified the corrected $P3m1$ ζ - $ZrH_{0.5}$ structure. The most stable $ZrH_{0.5}$ structure is a $Pn\bar{3}m$ structure, but it becomes less stable at high temperature.

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