First-principles study of the relative stability of various zirconium hydrides using the special quasirandom structures approach

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ABSTRACT

We present a detailed study on the bulk properties and relative stability of the ordered and disordered phases of zirconium hydrides by using first-principles calculations combined with the special quasirandom structures (SQS) method. The formation energy, density of states (DOS) and elastic constants are calculated to judge the relative stability of these phases. For the ordered phases, the relative stability of different configurations of the γ and δ phase is especially concerned. It is found that the ζ-Zr_2H, "diamond-like" γ-ZrH, [111] configurations of the δ-$ZrH_{1.5}$ and fcc-ZrH_2 phase are not stable. For the disordered phases, the SQS method, which is a well-proven method to mimic the random alloys, is used to construct supercells of zirconium hydrides with four structures. It is found that the random alloy gradually transforms from an hcp (solid solution phase) into an fcc (δ phase) and then an fct ($c/a < 1$, ε phase) phase with the increasing H concentration. The equilibrium states are also determined. The γ phase is energetically not favorable at all H concentrations.

Introduction

Zr and its alloys are widely used in nuclear fission energy systems [1,2] due to their low thermal neutron absorption cross-section, good mechanical and aqueous corrosion properties. The uptake of H and its precipitation as hydrides in Zr alloys can result in significant embrittlement and severely reduce their useful life in storage and service condition [3,4]. Therefore, numerous studies have been focused on the

characteristics of zirconium hydrides both experimentally [5—9] and theoretically [10—16].

The solubility of H in α-Zr is dependent on the temperature, from only 10^{-4} at% at room temperature to 130 wppm at reactor operating temperature (about 623 K) [17]. When the terminal solid solubility of H is reached, further H absorption leads to the formation of zirconium hydrides. Due to the differences of the H content, zirconium hydrides have four different phases [8,18], known as ζ-Zr_2H (space group: P3m1) [8], γ-ZrH (space group: P42/n) [18], δ-ZrH_x (nonstoichiometric,

x = 1.31–1.73 at eutectoid temperature, space group: Fm$\bar{3}$ m) [18,19], ε-ZrH$_2$ (space group: I4/mmm) [18]. Among these four hydrides, δ-ZrH$_x$ is the most commonly observed phase, and is believed to be the most brittle one. It is assumed to be the main cause of the significant embrittlement of zirconium alloys [11]. γ-ZrH is less commonly observed and there are still some controversies about its stability [7,10,11,14,20]. ε-ZrH$_2$ is a face-centered tetragonal phase with its eight available tetragonal interstitial sites all being occupied. ζ-Zr$_2$H is a metastable ordered phase fully coherent with α-Zr, recently found by Zhao et al. [8].

Although these different zirconium hydride phases have been extensively studied, their relative stability as a function of H concentration is still not very clear. Specially, the relative stability of different configurations of the γ and δ phase has not been studied systematically. Domain et al. [10] studied the relative stability of different zirconium hydrides with the same H concentrations. They suggested that for ZrH$_{1.5}$, the most stable phase should be of fct type (c/a < 1) while the phase diagram predicts the δ-fcc phase to be the most stable one [18]. Zhu et al. [11] claimed that the δ hydride is the most stable hydride and is the most easy to form in zirconium alloys. However, more recently, Lumley et al. [14] published their density functional theory (DFT) results combined with SQS techniques and a statistical analysis of many randomly generated cells. They concluded that the γ phase is the most stable and assumed that other mechanisms such as precipitate interface lattice strain may be responsible for the observed presence of δ hydrides.

The present work aims at investigating the bulk properties of the various hydrides and their relative stability (at 0 K) using first-principles calculation methods based on DFT combined with the SQS methods. Their formation energy, DOSs and mechanical properties have been studied.

Methodology

Special quasirandom structure generation

In this study, both ordered and disordered models of Zr–H solid solutions and different types of hydrides (ζ, γ, δ and ε hydrides) have been examined. For perfectly ordered systems, like α-Zr, ζ-Zr$_2$H, γ-ZrH, δ-ZrH$_{1.5}$, ε-ZrH$_2$ et al., we simply optimize the supercells with periodic boundary conditions. However, for systems which display atomic disorder, like the above mentioned hydrides with various H concentrations, the situation can be more complicated. One way is to construct large supercells and randomly exchange the host sites with desired atoms. However, this is computationally unaffordable for DFT calculations. The concept of SQS was proposed by Zunger et al. [21,22] to adequately mimic the statistics of a random alloy using only a relatively small supercell.

The main idea of the SQS approach is to use a specially designed small-unit-cell periodic structure to closely mimic the most relevant nearest-neighbor pair and the multisite correlation functions of random alloys [13,21,22]. The atomistic nature of the SQS approach ensures that a distribution of distinct local environments is maintained, which is essential in random alloys. Details of the SQS approach can be found in

Refs. [22,23]. This approach has been widely employed to study the structural, electronic, and thermodynamic properties of solid solution phases [13,14,22,24,25] in conjunction with first-principles calculations.

We have generated 96-atom (including vacancies) SQS cells for hcp (solid solution phase), fct (c/a > 1, denoted as γ phase), fcc (denoted as δ phase) and fct (c/a < 1, denoted as ε phase) hydrides with H composition x = 3.03–61.9 at% using the mcsqs code in the Alloy-Theoretic Automated Toolkit (ATAT) [26,27]. It should be mentioned that, the cubic β-Zr, which presents in Zr–Nb alloys is not studied here. The interaction between the β-Zr and H can be found in several recent studies [28–30]. The ζ phase is also not taken into consideration since it is not a stable phase according to our calculation and others' experimental [8] and theoretical work [11,14]. The best SQSs we get always have lower symmetry. To facilitate the calculation of the bulk parameters as well as to get a better comparison with other's results, we impose a constraint in the final structures of the SQSs to maintain their symmetry. Consequently, the SQSs we get match fewer correlations to the disordered state values. However, according to the pair correlation functions of the generated SQS structures listed in Table 3, they are still very good.

DFT calculations

First-principles calculations are performed by using the VASP code [31] with the generalized-gradient approximation for the exchange correlation functional (Perdew-Burke-Ernzerhof parameterization [32]).

The k-point meshes for Brillouin zone sampling are constructed using the Monkhorst-Pack scheme [33]. As a result of a series of k-point convergence test calculations, for pure Zr, ζ-Zr$_2$H, γ-ZrH, δ-ZrH$_{1.5}$, fcc-ZrH$_2$ and ε-ZrH$_2$, the k-meshes of 13 × 13 × 13, 3 × 13 × 5, 8 × 8 × 7, 8 × 8 × 8, 8 × 8 × 8, 8 × 8 × 9 are employed for relaxation calculations, respectively, while 19 × 19 × 19, 15 × 15 × 5, 13 × 13 × 12, 12 × 12 × 12, 12 × 12 × 12, 12 × 12 × 13 for the calculations of the DOS. For the 96-atom SQSs of the hcp Zr–H solid solution, the k-meshes of 3 × 6 × 4, 5 × 10 × 6 are adopted for relaxation and DOS calculations respectively. For the 96-atom SQSs of γ, δ and ε hydrides, the k-meshes of 4 × 4 × 4, 6 × 6 × 6 are adopted instead. The total energy is converged numerically to less than 0.01 meV/atom. After structural optimization, calculated forces are converged to less than 1 meV/Å.

Results and discussion

Ordered phases

Among the four zirconium hydrides, the ζ, γ and ε phases exhibit more order than the δ phase, which is a non-stoichiometric phase. Usually, a simplified formula of ZrH$_{1.5}$ is used to simulate the structure of the δ phase [10,11,14], as is employed in this work. Furthermore, as mentioned by Lumley et al. [14], the random occupation of the eight tetragonal interstitial sites by six H atoms in the unit cell of fcc Zr will result in three different configurations. We use their designations of [100], [110] and [111] to represent the three