The thermodynamics of hydride precipitation: The importance of entropy, enthalpy and disorder

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Abstract

The precipitation of zirconium hydrides from Zr solid solution was investigated using first-principles lattice dynamics simulations. These included the temperature-dependent vibrational enthalpy and vibrational entropy combined with the configurational entropy terms. In contrast with previous approaches, it was found that the latent enthalpy alone is not sufficient to fully describe precipitation of hydrides; a full thermodynamic assessment is required. In particular, the vibrational enthalpy of precipitation assists in stabilizing hexagonal close-packed hydrides and is especially important in forming the metastable ζ phase. The configurational entropy change during precipitation favours face-centred cubic hydrides. Given this, at concentrations below 300 ppm H, no hydride precipitation is predicted, suggesting that when hydrides are seen in those materials it is because the local concentration of H is greater than that measured globally. While γ hydride is the most stable phase, it is very close in energy to the δ phase.
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1. Introduction

Zr alloys are used for fuel cladding and other in-core structures in water-cooled nuclear reactors due to their good mechanical and corrosion properties and low capture cross-section for thermal neutrons. The uptake of H and its precipitation as hydrides in Zr alloys is important in the ongoing development of fuel cladding for water-cooled reactors [1]. At reactor operating temperatures, H is soluble up to around 100 ppm and extremely mobile in α-Zr [2,3,5]. However, if sufficient H is present or if the solubility limit of H in α-Zr is lowered (commonly due to a reduction in temperature during reactor transients [6]), then H will precipitate out, forming zirconium hydrides. The hydrides are brittle and cause component degradation and may lead to failure of the fuel cladding; this is especially likely if they align along the radial direction of the fuel pin due to stress reorientation [1,4]. Recently proposed changes in the regulations for nuclear fuel cladding to limit H uptake [7] and proposals for ever-longer dry storage times [8] make understanding H solubility and hydride precipitation increasingly important for operators and manufacturers alike.

Current understanding suggests that there are five main ways that H can be sequestrated in Zr metal, namely via the formation of four hydrides (ζ, γ, δ and ε), and via solid solution in Zr [9–12]. The structures of these different

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hydrides are shown in Fig. 1. There is a general relationship of decreasing c/a ratio with increasing H content. Of particular interest is that the most commonly observed δ phase is often reported to have a formula of $ZrH_{1.66}$ and a disordered fluorite structure, while simulators often use a simplified ersatz of periodic $ZrH_{1.5}$ [12,13]. The γ hydride has been assumed to be metastable, as it is less readily observed than the δ hydride [14]. However, other investigations have observed the γ hydride at room temperature [15], under both slow cooling [10] and fast cooling regimes [16]. Overall, it appears that the stability and occurrence of these phases is a complex phenomenon, where the H concentration, thermal treatments, alloying additions and stress states all have a part to play in determining which phases are observed [17].

The focus of this study is on modelling hydrides using ab initio atomistic simulation techniques based on density functional theory (DFT). In α-Zr metal, H preferentially occupies tetrahedral sites in the Zr lattice, rather than other sites [12,18,19]. Some works have focused on the octahedral site as the main location for H atom solution; however, such works appear to be in the minority [20,21]. It has been theoretically predicted that the face-centred tetragonal structure of ZrH_2 can have another stable phase for c/a greater than 1 [22,23]. Zhu et al. [13] studied the ordered hydride phases using DFT; they concluded that δ $ZrH_{1.5}$ is thermodynamically less stable than the other phases at high temperature. Zhong and MacDonald, who published previous DFT results combined with new calculations of the γ phase, suggest the γ phase is stable at temperatures below about 523 K [24].

The simulation of hydrides is complicated due to the random distribution of the H atoms in some phases. Although hydrides have been simulated in the past, few studies have attempted to examine hydrides whilst taking into account the disorder. One of the most successfully used techniques for simulating disordered atomic structures is the special quasi-random structures (SQS) method developed by Zunger et al. [25], which has been used to simulate a range of non-stoichiometric materials and structures. It has also recently been applied to this system [26]. In this study SQS techniques are combined with a statistical analysis of a large number of randomly generated cells, in order to examine the impact of disorder on hydride precipitation. Phonon calculations are also used to calculate thermodynamic properties such as the vibrational entropy and the sensible enthalpy changes during precipitation. Previous studies on other systems by DFT have shown the importance of vibrational entropy on the solubility limit in precipitation reactions from solid solution, and its importance in creating a temperature-dependent understanding of hydride precipitation [27,28]. Thus, a comprehensive view of the enthalpy and entropic contributions towards hydride precipitation in Zr is developed.

2. Methodology

2.1. Simulation parameters

For this investigation, CASTEP 5.5 was used to simulate the different structures [29]. As a plane-wave pseudopotential code, it is particularly appropriate for modelling crystals. Ultrasoft pseudopotentials were generated "on-the-fly", under the formalisation of Vanderbilt et al. [30]. Valence electrons for Zr were modelled as $4s^2 4p^6 5s^2 4d^2$. Convergence with respect to basis-set cut-off energy and k-point grid density was tested in a series of electronic self-consistency calculations. It was found that the simulations were accurate to 2 d.p. for a cut-off energy of 400 eV and a k-point grid spaced of 0.3 nm^{-1}. k-Points were arranged in a gamma-centred Monkhorst–Pack grid [31]. As the system displays metallic characteristics, the integration of the Brillouin zone is achieved via a Methfessel–Paxton scheme, with a band smearing width of 1 eV [32].

All cells used in this work are geometry relaxed in order to approach their minimum energy configuration. Cells were considered relaxed when the difference between two successively modified iterations met all of the following criteria:

- Energy change <0.001 eV.
- Force on ions <0.5 eV nm^{-1}.
- Displacement of ions change <0.01 nm^{-1}.
- Total stress <0.1 GPa.

Relaxation of atomic positions was carried out under the quasi-Newtonian BFGS scheme [33]. Both atomic positions within the cell, the lattice constants and cell aspect ratios were unconstrained during relaxation. This means that volume and cell distortions due to H accommodation are fully accounted for. Previous works [1,34,4] showed that constrained expansion of the hydrides may delay
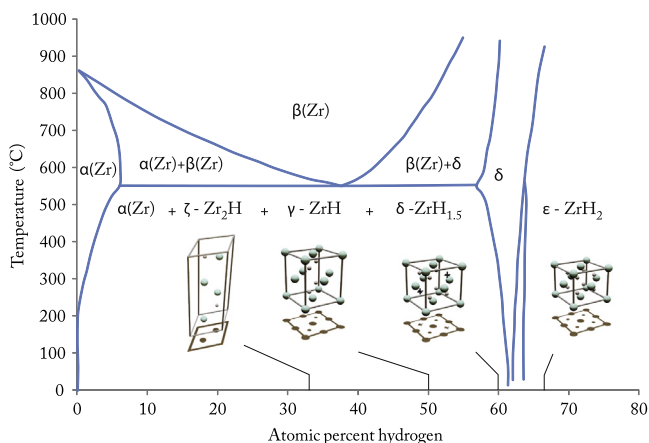

Fig. 1. Structures and formulae of different hydrides found in the Zr–H system. The Zr and H atoms are represented by the larger and smaller spheres, respectively. The δ hydride shown here is as commonly simulated, while real δ phase hydrides have a formula of $ZrH_{1.6}$ and have H atoms arranged randomly across all tetrahedral sites, including the black crosses shown in the diagram. The phase diagram has been reproduced from Ref. [9].