



Hydrogen and vacancy clustering in zirconium



Céline Varvenne¹, Olivier Mackain, Laurent Proville, Emmanuel Clouet*

CEA, DEN, Service de Recherches de Métallurgie Physique, F-91191 Gif-sur-Yvette, France

ARTICLE INFO

Article history:

Received 20 March 2015

Received in revised form

9 September 2015

Accepted 10 September 2015

Available online 28 September 2015

Keywords:

Ab initio calculations

Vacancies

Stacking faults

Dislocation loops

Zirconium

Hydrogen

Segregation

ABSTRACT

The effect of solute hydrogen on the stability of vacancy clusters in hexagonal closed packed zirconium is investigated with an *ab initio* approach, including contributions of H vibrations. Atomistic simulations within the density functional theory evidence a strong binding of H to small vacancy clusters. The hydrogen effect on large vacancy loops is modeled through its interaction with the stacking faults. A thermodynamic modeling of H segregation on the various faults, relying on *ab initio* binding energies, shows that these faults are enriched in H, leading to a decrease of the stacking fault energies. This is consistent with the trapping of H by vacancy loops observed experimentally. The stronger trapping, and thus the stronger stabilization, is obtained for vacancy loops lying in the basal planes, *i.e.* the loops responsible for the breakaway growth observed under high irradiation dose.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Macroscopic properties of metals and their alloys are known to be strongly affected by hydrogen, which is a common impurity found in structural materials. Among hydrogen effects, one can mention phase transformations leading to hydrides [1], interactions with structural defects modifying the plastic activity of materials [2], the interplay with point defects provoking swelling [3], or the so-called H embrittlement, via different possible mechanisms [4–6].

Hexagonal closed packed (hcp) zirconium alloys, that are used as a cladding material in nuclear industry, suffer an in-service hydrogen pickup due to the oxidation of the rods by water. Under irradiation, the apparent solubility limit of hydrogen in zirconium increases [7–10]. This has been associated with a trapping of hydrogen by the defects created by irradiation, in particular the vacancy clusters [7]. This hydrogen in solid solution influences not only the mechanical properties of hcp Zr alloys [11,12], but also their macroscopic structure: it impacts the stress free dimensional change experienced by these alloys under irradiation [13]. Indeed, under irradiation, a Zr single crystal undergoes an elongation along

the $\langle a \rangle$ axis and a shortening along the $\langle c \rangle$ axis, without significant volume change [14]. The growth strain remains small at low irradiation dose, whereas a breakaway growth is observed at higher fluence [14,15]. This breakaway growth at high doses has been correlated to the appearance of faulted vacancy dislocation loops lying in the basal planes. These vacancy clusters are called $\langle c \rangle$ loops because of the $\langle c \rangle$ component of their Burgers vectors. At low irradiation dose, where the growth strain remains moderate, only perfect dislocation loops, either of interstitial or vacancy types, with $\langle a \rangle = 1/3\langle 11\bar{2}0 \rangle$ Burgers vector and with an habit plane close to the prismatic planes of the hcp structure, are observed.

Experiments have shown that an increase of the H content leads to an increase of irradiation growth in Zr alloys under neutron irradiation [13]. This is consistent with the TEM observations of Tournadre et al. [16,17] who demonstrated that the amount of $\langle c \rangle$ loops formed under proton irradiation is notably higher when pre-hydrogenating the zirconium alloys. This suggests that hydrogen promotes the stability of these $\langle c \rangle$ loops compared to other vacancy clusters, an hypothesis also supported by the calorimetry and X-ray diffraction experiments of Vizcaíno et al. [9,10]. These experiments showed that a higher annealing temperature is needed in zirconium alloys exposed to a high irradiation dose, hence when $\langle c \rangle$ vacancy loops are present, for the H solubility limit to reach its unirradiated value.

Understanding the potential trapping of hydrogen by irradiation defects as well as the hydrogen influence on the stability of the

* Corresponding author.

E-mail address: emmanuel.clouet@cea.fr (E. Clouet).

¹ Present address: Institute of Mechanical Engineering, École Polytechnique Fédérale de Lausanne, Lausanne CH-1015, Switzerland.

different vacancy clusters is therefore of prime importance for modeling then the kinetic evolution of Zr alloys under irradiation and the associated macroscopic behavior in presence of hydrogen. In this paper, we study the elementary interactions between H and vacancy clusters, going from small clusters containing only a few vacancies to large dislocation loops. Atomistic simulations are a well-suited tool to address this question, since they give information at defect sizes not accessible by other techniques. In particular, *ab initio* methods, having a high level of accuracy and transferability, will be used all along this work, as they appear unavoidable to study structural defects in hcp Zr. A proper account of angular contributions is indeed necessary to correctly describe the stacking fault energies and the interactions between vacancies [18–20]. Previous *ab initio* studies of hydrogen interaction with defects in zirconium mainly focused on plasticity and embrittlement [11,12] or on single point-defect properties [21,22]. The work presented in this paper extends thus these studies by modeling H interaction with vacancy clusters of various sizes.

The paper is organized as follows. We first investigate the interactions of hydrogen with small vacancy clusters and with the different stacking faults of interest. We then model the evolution of the stacking fault energies with the H bulk concentration. Finally, including this variation into analytical laws describing the formation energies of extended vacancy clusters, we discuss the influence of H on the relative stability of vacancy dislocation loops in hcp Zr.

2. Modeling method

2.1. *Ab initio* simulations

In this work, all the *ab initio* calculations are based on the Density Functional Theory (DFT), as implemented in the PWSCF code of the QUANTUM ESPRESSO package [23]. Calculations are performed in the Generalized Gradient Approximation with the exchange–correlation functional of Perdew, Burke and Ernzerhof [24]. Valence electrons are described with plane waves, using a cutoff of 28 Ry. The pseudo-potential approach is used to describe the electron–ion interaction. For Zr and H, ultrasoft pseudo-potentials of Vanderbilt type have been chosen, including 4s and 4p electrons as semicore in the case of Zr. The electronic density of state is broadened with the Methfessel–Paxton function, with a broadening of 0.3 eV. The integration is performed on a regular grid of $14 \times 14 \times 8$ k-points for the primitive cell and an equivalent density of k-points for larger supercells.

Atomic relaxations are performed at constant volume, using a conjugate gradient algorithm. For calculations involving point defects, we use supercells of $5 \times 5 \times 4$ repeated unit cells (200 atoms) with fully periodic boundary conditions. The elastic correction of Ref. [25] is applied, so as to remove the spurious interaction energy between the defect and its periodic images. Appendix A demonstrates that the obtained corrected energies are well converged with respect to the supercell size.

2.2. Vibrations

To consider the contribution of vibrations in the computed energies, we use the harmonic approximation [26], which validity is assessed in Appendix B for both a single H atom and an H interacting with a vacancy in an hcp Zr matrix. Within this approximation, the vibrational free energy is

$$F^{\text{vib}}(T) = kT \sum_i \ln \left[2 \sinh \left(\frac{\hbar \omega_i}{kT} \right) \right], \quad (1)$$

with the sum running over all vibration modes of pulsation ω_i . We further make the assumption that the vibration modes of the Zr atoms are not affected by the presence of hydrogen and consider only the three vibration modes of the H atom. This is justified by the small mass and the small radius of hydrogen compared to zirconium.

To obtain the H vibration frequencies for a given atomic configuration, we rigidly displace the H atom from its equilibrium position in six different directions, using four intermediate positions for each direction with a maximal displacement of 0.04 Å. We then make a least-square fitting of the calculated energy variations to obtain the 3×3 Hessian matrix, from which the eigenfrequencies are obtained by diagonalization.

2.3. Validation of the modeling approach

Our choice of cutoffs, k-mesh, GGA functional for the exchange correlation and pseudo-potential for zirconium have already been validated both on the hcp bulk and on vacancy cluster properties in previous studies [19,20,25]. For H, the validation of the chosen pseudo-potential consists first in comparing with experimental data the intrinsic properties of the H₂ molecule, such as the equilibrium distance d_{H_2} , the vibrational frequency ν_{H_2} and the dissociation energy $E_{\text{H}_2}^{\text{diss}}$ (see Table 1). The dissociation energy includes both the binding and vibrational $\frac{1}{2} h \nu_{\text{H}_2}$ contributions. The vibrational frequency ν_{H_2} is calculated according to the harmonic oscillator approximation:

$$\nu_{\text{H}_2} = \frac{1}{2\pi} \sqrt{\frac{2k}{\mu}} \quad (2)$$

where k is the bond stiffness obtained by *ab initio* calculations and $\mu = m_{\text{H}}/2$ is the reduced mass of the H₂ molecule. The obtained quantities are all in good agreement with the experimental ones, within less than 5%. This validates our choice of pseudo-potential for the calculations involving hydrogen.

As we are interested in the interplay between hydrogen solute and vacancies in an hcp zirconium matrix, we also check the insertion of the H atom in substitutional position and in different interstitial sites: the tetrahedral (T) and the octahedral (O) sites. Our DFT calculations show that the substitutional position for the H

Table 1

Properties of the H₂ molecule (equilibrium distance d_{H_2} , vibration frequency ν_{H_2} and dissociation energy $E_{\text{H}_2}^{\text{diss}}$) and solution energies $E_{\text{H}}^{\text{sol}}$ of H in the hcp Zr matrix. Values in parenthesis include zero point vibration energy of H in the Zr matrix.

	<i>Ab initio</i>				Exp [27]
	This work	Udagawa [12]	Domain [28]	Lumley [29]	
d_{H_2} (Å)	0.75	0.75	0.76	0.75	0.74
ν_{H_2} (THz)	130.1	–	134.4	129.8	130.8
$E_{\text{H}_2}^{\text{diss}}$ (eV)	4.25	4.50	4.27	4.53	4.48
$E_{\text{H}}^{\text{sol}}$ (eV) T site	–0.609 (–0.387)	–0.52	–0.604	–0.60	–0.66
$E_{\text{H}}^{\text{sol}}$ (eV) O site	–0.549 (–0.414)	–0.44	–0.532	–0.56	–

Download English Version:

<https://daneshyari.com/en/article/1445182>

Download Persian Version:

<https://daneshyari.com/article/1445182>

[Daneshyari.com](https://daneshyari.com)