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Effect of hydrogen on degradation mechanism of zirconium: A molecular dynamics study

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ABSTRACT

Using large scale molecular dynamics simulation, we investigate the deleterious effect of hydrogen in Zr. We consider both dilute and concentrated limit of H. In the dilute and concentrated H limits, we study the effect of 1–5 atomic percentage of hydrogen, and that of ε-ZrH_2 precipitate having 5–10 nm diameters, respectively. From the stress–strain curves and micro-structure analysis at different strain values, we characterize the deformation behavior and correlate our result with previously reported mechanisms. We show hydrogen atoms in dilute limit help in dislocation multiplication, following the hydrogen-enhanced localized plasticity mechanism. In the concentrated limit, on the other hand, dislocations and cracks nucleate from precipitate–matrix interface, indicating the decohesion mechanism as primary method for Zr degradation. These findings are corroborated with a nucleation and growth model as expressed in Kolmogorov–Johnson–Mehl–Avrami equation.

1. Introduction

Zirconium (Zr) and its alloys have attracted much attention in the structural research community in past few decades due to its usage as cladding material for light water reactors. Zr is suitable as cladding material due to its very low capture cross-section of thermal neutrons and good corrosion resistance at high temperatures [1]. While the reactor is in operation, the Zr-based cladding is oxidized by waterside corrosion and it absorbs the generated hydrogen. At lower concentration, the absorbed hydrogen (H) occupies interstitial site in the Zr matrix to form Zr–H solid solution, as detailed in our earlier reports for other materials [49,50]. On the other hand, at higher H concentration, zirconium–hydrides are formed. In both the dilute and concentrated regimes, inclusion of H deteriorates the mechanical properties of Zr, via defect nucleation and defect evolution [51,52] within the system and thus causing embrittlement. Hydrogen embrittlement in Zr alloys is one of the main causes of mechanical degradation of light water reactor fuel cladding and is regarded as one of the most important issues in safety regulation for light water reactor type nuclear power plants [2]. The Zr–H equilibrium phase diagram [3] is shown schematically in Fig. 1. In the present study we focus on two regions of the phase diagram, shown as encircled in Fig. 1: 1) The dilute limit of H, where Zr–H solid solution forms and 2) The concentrated limit of H where a few varieties of hydride phases are formed. Among different concentrated phases of hydride we focus on the ε-ZrH_2 phase, which has the maximum amount of H incorporated.

In the dilute limit of H, several different microscopic mechanisms underlying the H induced degradation have been proposed in literature. For example, several studies have reported H-induced lowering of the critical cleavage stress that affects opening up or propagation of cracks [4–6]. Adsorption of H on surfaces has been reported to reduce the surface excess free energy [7]. The hydrogen enhanced localized plasticity (HELP) mechanism has been proposed in literature [8–10] as a predominant cause for degradation in metals. A few *ab-initio* studies have evaluated the planar defect properties for a Zr–H solid solution, based on density functional theory (DFT) calculations [7,9,11]. These studies indicate that hydrogen in a Zr–H solid solution can enhance dislocation mobility while it lowers surface energy. However, these speculations are yet to be confirmed either through advanced experimental techniques or large scale atomistic simulation, where one can identify specifically the effect of H in Zr deformation behavior. As hydrogen solubility limit is fairly low even at the operating temperature of light

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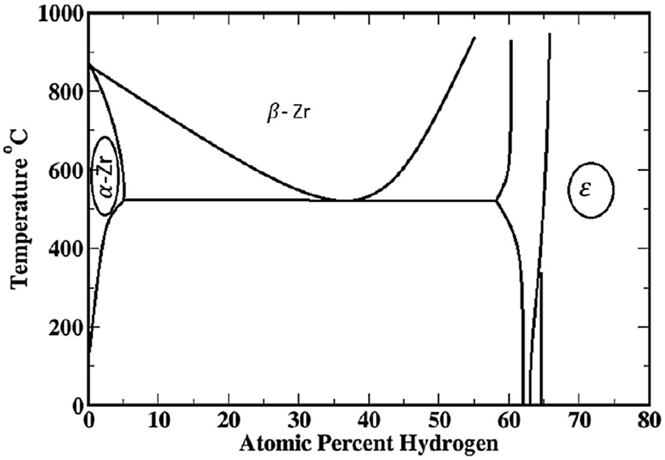

Fig. 1. A schematic phase diagram of the Zr–H system. The encircled regions are the two phases considered in the present study.

water reactor plants, large scale atomistic modeling of Zr–H systems with different atomic percentage of H may determine the details of the influence of hydrogen on macroscopic mechanical behavior.

In the concentrated limit of H, the hydrides are brittle and produce cracks on application of stress, that reduces the performance and life expectancy of nuclear reactor, thereby increasing the cost of nuclear power plants. Various studies focusing on the deformation [12–15] or fracture [16–18] behavior of zirconium hydrides suggest that hydride precipitates play an important role in the hydrogen embrittlement of various zirconium alloys. Farrow et al. have claimed that voids or micro-cracks, generated as a result of interaction between hydride precipitates and twinning structures around the precipitates contribute to embrittlement [19]. It has further been suggested that voids nucleate at interfaces between the hydride and zirconium matrix to develop micro-cracks [20]. However, in comparison to experimental studies, there are very few computational studies to shed light on such deformation behavior. The large scale atomistic simulation which can provide a unique capability to capture details of deformation and fracture processes at the atomic level with various precipitate sizes, is ideally suited to examine the aforementioned proposed mechanisms.

2. Computational details

All the molecular dynamics simulation in this study are performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), developed at the Sandia National Laboratory [21]. This fully parallelized program uses spatial decomposition technique to partition the simulation domain that significantly decreases the simulation time. All simulations are carried out using Zr–H modified embedded atom method (MEAM) semi-empirical potential. Over the last two decades the MEAM methodology has been successfully applied to metals and alloys for studying deformation mechanisms [22,23,53]. The original methodology, where only up to the first nearest neighbor interactions are considered, is improved recently by Lee et al. to extend the interactions up to second nearest neighbors [24]. A few of these second nearest neighbor (2NN) MEAM potentials are recently used in large scale atomistic simulations to study the microscopic mechanism for void growth [25], nature of dislocation core structure in Ti [26], ductile to brittle transition [27], etc. The 2NN MEAM potential used in present work was originally used for comparative study on hydrogen diffusion in amorphous and crystalline metals [28].

We first consider the case of pure Zr in bulk. The atomic positions are first generated in accordance with the crystal symmetry, followed by a structural optimization. The energy per atom as a function of atomic volume is then fitted in order to obtain the relaxed lattice parameters and cohesive energy of pure Zr. Our obtained lattice parameters ($a = 3.23$ Å, $c/a = 1.59$) and cohesive energy (6.36 eV/atom) agree well with other theoretical [11] and experimental [29] observations, reflecting the reliability of the chosen 2NN MEAM potential, which has been already tested in literature [29]. Similarly, we found that the calculated lattice parameter, $a = 4.2$ Å for ε-ZrH_2 phase matches closely with experimental results [28,30]. Various structural and elastic properties, other than lattice constant and cohesive energy, such as dilute heat of solution of hydrogen, vacancy formation energy, planar defect properties including surface energies and stacking fault energies in α-Zr, heat of formation of ε-ZrH_2 and elastic constants including C_{11}, C_{12}, C_{44}, etc of α-Zr have been further tested by Kim et al. [29] and Lee et al. [28]. These results are found in good agreement with either ab-initio calculation or experimental observation, showing the capability of this potential in describing mechanical properties correctly. In Ref. [29] the authors have also tested the reliability of this potential for thermal properties, such as thermal expansion coefficients, specific heat, melting point, enthalpy of melting etc.

The large scale simulations are performed on rectangular simulation cells having x, y, and z axes oriented along the $[10\bar{1}0]$, $[1\bar{2}10]$, and [0001] directions, respectively with dimensions $20.67 \times 20.70 \times 41.22$ nm^3. The total number of atoms considered are ~750,000 for both the dilute and concentrated cases. To study the dilute limit, simulations are carried out with different percentages of H, where hydrogens are placed randomly in interstitial sites. In general, there are two interstitial locations in HCP Zr; octahedral, and tetrahedral. In the α-Zr phase the H atoms are placed in the octahedral site, which is the most stable site for our system. However, as shown in Ref. [28], based on a comparative study on hydrogen diffusion in amorphous and crystalline Zr, the site preference between octahedral and tetrahedral location does not play a significant role for studying the dynamic behavior of hydrogen, since the migration energy between the two sites is not very high. The structures upon introduction of H are completely relaxed including the volume. Five different systems are studied, with H concentration chosen between 1 and 5 atomic percentage of H. For our study in the concentrated limit, we placed a spherical ε-ZrH_2 precipitate of three different sizes (5, 7, and 10 nm diameter) in the Zr matrix as starting configuration. Note bulk Zr and ZrH_2 have different lattice parameters and have different crystal structures [31]. Keeping this aspect in mind, to prepare the starting configuration, we have cut out a spherical volume in bulk Zr and inserted an equal volume of sphere in its place. We have tried to match the volume of the precipitate with that of the hollow sphere cut in bulk Zr, instead of matching the number of removed Zr atoms and number of inserted ZrH_2 atoms. The lattice mismatch caused at the interface by the insertion of the spherical precipitate is taken care by complete relaxation of the whole structure. During this relaxation process, the interface region thickens up in order to relieve the interfacial strain. No dislocation is pre-constructed at the starting configuration. Initially all the atoms in the simulation cell are relaxed at $T = 0$ K through energy minimization using the conjugate gradient (CG) method [32]. In the next step, the simulation cells are equilibrated at a temperature of 500 K by using a Nose-Hoover thermostat [33,34] for 20,000 time steps (20 ps) and further equilibrated under constant pressure and temperature (NPT) condition using Parrinello and Rahman barostat [35] for