Homogeneous hydride formation path in α -Zr: molecular dynamics simulations with the charge-optimized many-body potential

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Abstract

A path for homogeneous γ hydride formation in hcp α -Zr, from solid solution to the ζ and then the γ hydride, was demonstrated using molecular static calculations and molecular dynamic simulations with the charge-optimized many-body (COMB) potential. Hydrogen has limited solubility in α -Zr. Once the solubility limit is exceeded, the stability of solid solution gives way to that of coherent hydride phases such as the ζ hydride by planar precipitation of hydrogen. At finite temperatures, the ζ hydride goes through a partial hcp-fcc transformation via $\frac{1}{3} < 1\bar{1}00 >$ slip on the basal plane, and transforms into a mixture of γ hydride and α -Zr. In the ζ hydride, slip on the basal plane is favored thermodynamically with negligible barrier, and is therefore feasible at finite temperatures without mechanical loading. The transformation process involves slips of three equivalent shear partials, in contrast to that proposed in the literature where only a single shear partial was involved. The adoption of multiple slip partials minimizes the macroscopic shape change of embedded hydride clusters and the shear strain accumulation in the matrix, and thus reduces the overall barrier needed for homogeneous γ hydride formation. This formation path requires finite temperatures for hydrogen diffusion without mechanical loading. Therefore, it should be effective at the cladding operating conditions.

1. Introduction

The safe operation and long-term storage of nuclear fuels require the integrity of fuel pins. In light water reactors, cylindrical UO₂ fuel pellets are enclosed by Zr-based alloy claddings. During operation, claddings directly contact coolant (primarily water) at temperatures of about 350°C (623 K) at the interface. Consequently, Zr reacts with water, forming zirconium oxides and producing hydrogen (H) [1], which diffuses into the Zr matrix at room temperature or higher. Hydrogen has very limited solubility in α -Zr at cladding operating temperatures [2]. Once the solution limit is exceeded, hydrides form with various H/Zr ratios, ZrH_X with $X \geq 1$ in general [3]. With increasing H/Zr ratio, three different hydrides have been widely characterized experimentally: the γ (ZrH), δ (ZrH_{1.5–1.7}) and ϵ (ZrH₂) hydrides. The γ hydride has a face-center-tetragonal (fct) structure with $c > a$. The δ hydride has a face-centered-cubic (fcc) structure, with a stoichiometry close to ZrH_{1.6}. For the ϵ hydride, the structure is also fct but with $c < a$. we note that here the structures of hydrides are defined based on the Zr lattice.

Hydrides are brittle and they severely degrade the integrity of fuel pins by reducing the overall fracture toughness [3, 4]. Experimentally, it has been shown that the fracture stress of a zircaloy-4 tube decreases substantially with increasing thickness of the hydride layer [5]. Under tensile stress, hydrides precipitate into

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a geometry with the hydride/matrix interface normal to the principle stress direction. The interface can serve as an easy fracture path [6]. Even under stress levels much lower than the fracture stress, hydrides may still cause cladding failure via so-called delayed-hydride-cracking (DHC) [7], which is one of the primary concerns for the safety of fuel pins during used fuel disposition and transportation [1]. Fundamental understanding of the formation process of hydrides is highly desired to mitigate these detrimental effects.

The formation of hydrides in α -Zr or Zr-based alloys has been widely observed [1, 3, 4, 8]. However, the formation mechanisms are not fully clear [9–12]. The γ , δ and ϵ hydrides have similar crystal structures (fcc or fct) with decreasing c/a ratio upon increasing H/Zr ratio. They may coexist and can transform to each other under varying H content or under heat treatment via a martensitic transformation - contraction or dilatation in c and/or a [3]. It was suggested by recent experiments that the formation of δ hydrides may start with γ hydrides [13], in agreement with previous experiments that upon increasing H loading, γ hydrides precipitated first and then evolved into a mixture of γ and δ hydrides [14]. The δ hydride can further grow into the ϵ hydride at even higher H/Zr ratio. Therefore, understanding the formation of the γ hydride is critical to understanding how these cubic and tetragonal hydrides form.

Since the crystal structure of the γ hydride is distinct from the hcp structure of α -Zr, a transformation from hcp to fcc/fct (referred to as an hcp-fcc transformation) is necessary for homogeneous formation in an α -Zr matrix. Although heterogeneous nucleation may occur at grain boundaries [15] or radiation induced defects [16], such a transformation is still required for subsequent growth. Without pre-existing defects, it has been proposed that the γ hydride may nucleate by shearing of some coherent clusters [9]. However, the nature and the existence of such coherent clusters have remained unclear for decades. Based on computational and experimental observations, two prominent candidates have recently been identified for such coherent clusters. The first is the ζ hydride which has a stoichiometry of about $\text{ZrH}_{0.5}$. It has recently been characterized in experiments [17] and predicted to be stable or metastable by DFT calculations [10, 12, 18–20]. In addition to the ζ hydride, the γ -hcp hydride has also been identified as a candidate for the coherent clusters, by investigating the thermodynamic stabilities of various possible ZrH_X phases using atomistic scale calculations [10, 11]. The γ -hcp hydride has the same stoichiometry as the γ hydride (ZrH), but has a hcp crystal structure coherent with α -Zr. Using DFT based thermodynamic analysis, it was further found that the formation of γ hydride could start with either the γ -hcp or the ζ hydride, depending on the H content [11]. However, the detailed mechanisms and the associated barriers towards the γ hydride are unknown.

Here, using molecular static (MS) calculations and molecular dynamics (MD) simulations, the possible formation paths of the γ hydride involving the ζ and the γ -hcp hydride were investigated. The feasibilities of the formation paths were demonstrated by evaluating the driving forces and the associated barriers that need to be overcome. A most probable formation path was suggested based on the results. In the following, we first introduce our simulation method in Section II, followed by the results and discussion. Finally we conclude in section IV.

Table 1: Compositions and crystal structures of hydrides mentioned in the present work.

Hydrides	ζ	$\zeta - fct$	γ	$\gamma - hcp$	δ	ϵ
Composition	Zr_2H	Zr_2H	ZrH	ZrH	$\text{ZrH}_{1.5-1.7}$	ZrH_2
Crystal structure	trigonal (hcp)	fct	tetragonal, $c > a$	hcp	fcc	tetragonal, $c < a$

2. Methods

In this work, MS calculations were used to obtain the solution energy of H at various compositions, the formation energies of different hydride phases, and the stacking fault energy (SFE) curves for the α -Zr phase and the ζ and γ -hcp hydrides. For reference, the names, compositions and structures of various hydrides used in this work are given in Table 1. In these calculations, the system was quenched into energetic minima by setting the velocity v_i of atom i to zero if $f_i \cdot v_i \leq 0$; f_i is the force acting on atom i . In addition to MS calculations, MD simulations were also performed to explore the stabilities of embedded ζ and γ -hcp

hydride clusters in an α -Zr matrix at 600 K, which is relevant to the cladding operating temperatures in reactors. For the variety of simulations, the details of simulation set-ups will be described along with the results. In all calculations and simulations, we used the recently developed charge-optimized many-body (COMB) potential [21] to describe the interatomic interaction. The COMB potential has been fitted with properties of the bulk, stacking faults and surfaces in α -Zr, and the energetics of all experimentally observed hydride phases. It can handle both H solid solutions and various hydride phases, and is therefore suitable for the current work. The COMB potential optimizes the atomic charges based on the local environment [22]. The detailed formalism and parametrization of the COMB Zr-H potential can be found in Liang et al. [23] and Noordhoek et al. [21], respectively. We note that among the several potentials proposed in the literature for the Zr-H systems [24, 25], the COMB potential is currently the only one that can describe hydride phases.

We used the LAMMPS package [26] for all MS calculations and MD simulations. In post-processing the results, we used the common-neighbor-analysis [27] to classify the atoms into those with fcc or hcp structures, and others, which are denoted as disordered atoms. This analysis was done for the Zr sub-lattice only. With the c/a ratio in hcp close to the ideal value (1.633), atoms with local fct structure can be identified as fcc with careful choice of cutoff. Visualization and presentation of the atomic configurations were done using AtomEye [28].

3. Results and discussion

3.1. Hydride formation energy

Figure 1: (Color online) Hydride formation energy per ZrH_x molecule as a function of the H/Zr ratio (left) and the crystal structure of hydrides used in the calculations (right). For the γ hydride, only the tetrahedron sites on alternative $\{110\}$ planes (connected by lines) are occupied.

As a test of the COMB potential, the formation energies of various hydrides with the H/Zr ratio varying from 1.0 to 2.0 were calculated. Here, the hydrides were constructed as the fluorite phase, with Zr atoms on an fcc lattice and H atoms at the tetrahedron sites, as shown in Fig. 1. If all tetrahedron sites were occupied, the ϵ hydride was created. By randomly removing H atoms, the δ and the γ hydride could be obtained at H/Zr ratios of 1.6 and 1.0 [3], respectively. The ϵ and the γ hydride manifest the fct structure with different c/a ratios. However, with the COMB potential, for both hydrides the fcc structure was predicted as the most stable structure. Therefore, the hydrides considered here can be regarded as δ hydrides with various H/Zr ratios. In addition, previous studies have shown that for the γ -hydride, H atoms occupy the tetrahedron sites on alternative $\{110\}$ planes (Fig. 1), instead of being randomly distributed. This configuration has also been considered for the γ hydride. With this new configuration, the fcc structure was still predicted for the γ hydride by the COMB potential.

The hydride formation energy is defined by taking α -Zr and H_2 molecule as references, and normalized to per ZrH_X , by $\Delta E_f = (E(Zr_yH_x) - E(Zr_y) - \frac{x}{2}E(H_2))/y$. Here, the lower case x and y are the numbers of H and Zr atoms contained in the simulation cells, with the H/Zr ratio $X = x/y$. $E(Zr_yH_x)$ is the total energy of a simulation cell with x H and y Zr atoms; $E(Zr_y)$ is the energy of α -Zr with y atoms; and $E(H_2)$ is the energy of an H_2 molecular, about -4.5 eV as given by the COMB potential. we note that in MD simulations the energy of an isolated H atom is zero, so that $E(H_2)$ is actually the dissociation energy of H_2 molecule, which was predicted to be -4.5 eV by previous DFT calculations [29]. In the calculations, we used a cubic 8 by 8 by 8 simulation cell with 2048 Zr atoms. The number of H atoms was determined by the H/Zr ratio X . The simulation cell was quenched to obtain the total energy at 0 K.

In Fig. 1, the hydride formation energies are plotted as a function of the H/Zr ratio. For comparison, data from previous DFT calculations [21, 29, 30] and experiments [31, 32] are included. In the previous DFT calculations, the formation energies were normalized to eV per atom. Here they were normalized to eV per ZrH_X (containing one Zr and X H atoms). Therefore the values in ref.[29] and [30] need be multiplied by $1+X$, and they were so converted in this work for comparison. For the δ hydride, the formation energy was found to decrease linearly with H/Zr ratio, with a slope of about 1.08 eV per H atom. The same trend has been reported previously by DFT calculations with a slope of about 1.0 eV per H atom [30], and by experiments with a slope of 1.1 ± 0.15 [33]. At the H/Zr ratio of 1.0, the γ hydride with ordered H occupancy was found to have a lower formation energy than that of the δ hydride. This means that at this composition, the γ hydride is the most stable phase, in agreement with previous DFT calculations [20, 30]. Overall, the formation energies of hydride predicted by the COMB potential are lower than those obtained from DFT calculations and experiments, indicating some overestimation in the stabilities of hydrides. However, the good agreement in the trend and the small discrepancies in absolute values suggest that the COMB potential is suitable for modeling hydrides.

3.2. Hydrogen solution energy

Hydrides precipitate from H solid solution when the solubility limit is exceeded and the stabilities of hydrides out-compete that of H solid solution. Here, the solution energy of H at various compositions was calculated and compared with the formation energies of several hydrides to elucidate their precipitation tendencies. To calculate the H solution energy, H atoms were randomly introduced into the tetrahedron sites in α -Zr, as shown in Fig. 2(b). In α -Zr, H atoms prefer to occupy the tetrahedron sites as predicted by previous DFT calculations [29, 30, 34] with rare exceptions [35]. The simulation cell contained 2048 Zr atoms, with the number of H atoms varying from 1 to 2048 to represent various compositions. For hydride formation energies, four hydrides were used in the calculations, including the experimentally observed ζ and γ hydrides. Two other hydrides predicted by previous DFT calculations, ζ -fct [20] and γ -hcp [10, 11], were also included for the purpose of exploring possible formation paths of γ hydrides. The ζ and γ -hcp hydrides are coherent with α -Zr with misfit strains. They have been considered as candidates for the coherent clusters, shearing of which leads to the formation of γ hydride nuclei. The crystal structures used for the ζ , the ζ -fct, and the γ -hcp hydrides are shown in Fig. 2 (c)-(e). The structure of the γ hydride can be found in Fig. 1. Again, we quenched the simulation cells at 0 K for the total energies.

The results on H solution energy (normalized to eV per H atom by $\Delta E = (E(Zr_yH_x) - E(Zr_y) - \frac{x}{2}E(H_2))/x$) are plotted in Fig. 2. For each H/Zr ratio considered, the calculation was repeated three times with random H atom distributions. The fluctuation in the solution energy was found to be small, particularly when the H/Zr ratio is high. As the H/Zr ratio increases, the H solution energy calculated with the COMB potential increased, indicating reducing stability of H solid solution. The same trend has been suggested by previous DFT calculations [29]. The COMB potential was found to strongly overestimate the stability of H solid solution. In the dilute concentration regime, the H solution energy was predicted to be -1.28 eV per H atom, much lower than that from experiments (-0.66 eV) [31], and DFT calculations, about -0.60 to -0.38 eV per H atom [3, 20, 29, 30, 34]. Even with such a low solution energy, driving forces for hydride precipitation were still suggested by the COMB potential at high H concentration. As shown in Fig. 2, at the H/Zr ratio of 0.5, both the ζ and the ζ -fct hydride were predicted to have lower formation energies than the H solution energy, so were the γ and the γ -hcp hydride when H/Zr=1.0. We note that here only the formation energies were considered at 0 K. At finite temperatures, the precipitation tendencies of hydrides should be

Figure 2: (Color online) (a) Normalized H solution energy and hydride formation energies per H atom; and the atomic structures for (b) H solid solution, (c) ζ , (d) $\zeta\text{-fct}$ and (e) $\gamma\text{-hcp}$ phases. Large atoms represent Zr and small atoms represent H.

assessed using their free energies [18, 19], by taking the contributions of entropies including the vibrational and configuration entropies into consideration [12]. Furthermore, to form a stable hydride nucleus in an $\alpha\text{-Zr}$ matrix, the effects of interface energies and misfit strains need be included [11].

The homogeneous formation of γ hydrides requires a high local H concentration and an hcp-fcc transformation. As proposed in the literature [9–11], this may happen by the formation of either ζ or $\gamma\text{-hcp}$ hydride clusters, followed by shear slips on the basal plane to transform the hcp crystal structure into fct. Correspondingly, two formation paths can be drawn from Fig. 2: (1) $\alpha\text{-Zr} \rightarrow \zeta \rightarrow \zeta\text{-fct} \rightarrow \gamma$, and (2) $\alpha\text{-Zr} \rightarrow \zeta \rightarrow \gamma\text{-hcp} \rightarrow \gamma$. The two paths differ from each other as to where the hcp-fcc transformation takes place, in the ζ hydride for the former and in the $\gamma\text{-hcp}$ hydride for the latter. At H/Zr ratios of 0.5 and 1.0, hydrides with a fct structure were found to be more stable than those with a hcp structure. Therefore, thermodynamic driving forces exist for the hcp-fcc transformation for either path. However, as will be shown in the next subsections, the two paths involve substantially different barriers and thus different probabilities to occur at finite temperatures.

3.3. hcp-fcc transformation of the ζ -hydride

To explore the probabilities of the above two formation paths at finite temperatures, MD simulations were performed on the stabilities of ζ and $\gamma\text{-hcp}$ hydride clusters embedded in an $\alpha\text{-Zr}$ matrix. A temperature of 600 K was used in these simulations, which is close to the cladding operating temperatures in light water

Figure 3: (Color online) Atomic configurations (a) before and (b) after annealing at 600 K showing the hcp-fcc transformation of a ζ hydride cluster embedded in an α -Zr matrix. In (c) the ϵ_{yz} component of the atomic strain involved in the phase transformation is shown, by taking the configuration in (a) as the reference and (b) as the final state. The atomistic strain was calculated for Zr atoms only. The enclosed region in (a) will be further analyzed in Fig. 5.

reactors. The simulation cells were 19.5 by 8.9 by 20.7 nm³ in size, with an ellipsoidal cluster of either ζ or γ -hcp phase at the center. The shape of the cluster was given by $x^2 + \frac{y^2}{4} + z^2 = r_0^2$, with r_0 being 5.2 nm. The simulation cell was first relaxed at 0 K, and then brought to a temperature of 600 K in 200 ps, followed by an annealing at 600 K for another 200 ps. After annealing, the atomic configurations were quenched to characterize any possible structural transformation. Before annealing, all Zr atoms were on the hcp lattice. Planes of fcc Zr atoms were expected after annealing if an hcp-fcc transformation took place. Disordered Zr atoms were also expected at the interface between the matrix and the cluster, denoting dislocation cores if any shear slips were involved. The atomic strain as defined in Zimmerman et al. [36] was also calculated to aid the analysis.

After annealing, a structural transformation was observed in the embedded ζ hydride cluster but not in the γ -hcp cluster. As shown in Fig. 3(a)-(b), planes of fcc atoms have been identified by the common-neighbor-analysis, indicating the occurrence of hcp-fcc transformation in the ζ cluster. In addition, planes of disordered Zr were also identified. These atoms were found still in a crystalline structure, but with a stacking in-between hcp and fcc, close to the fcc side. As will be shown later, they were produced by incomplete shear slips on the basal planes. Disordered Zr atoms were also present at the interface, representing the cores of shear partials. These observations agree well with the mechanisms proposed by Carpenter for γ hydride nucleation [9], with the differences in detailed transformation mechanism as described below..

The occurrence of shear slips can be detected by calculating the atomic strain, which was defined in Zimmerman et al. [36]. In Fig. 3(c), the ϵ_{yz} component of the atomic strain involved in the hcp-fcc transformation is plotted. Here, the y axis is along the $[1\bar{1}00]$ direction and the z axis along the $[0001]$ direction. In the calculation we took the initial configuration as the reference, and the annealed configuration as the deformed state. As shown in Fig. 3(c), seven shear events, one every four $\langle c \rangle$ layers, took place during annealing. If complete, each of the seven shear events converted two hcp layers into fcc ones, leading to the formation of an I2 stacking fault. In hcp crystals, stacking faults can form by slip of $\frac{1}{3} \langle 1\bar{1}00 \rangle$ partials. The atomic shear strain produced by each shear slip is given by the ratio of the Burgers vector over c : $|\frac{1}{3} \langle 1\bar{1}00 \rangle|/c = \frac{\sqrt{3}a}{3c} \approx 0.36$. Here a c/a ratio of 1.593 was used for α -Zr. The ϵ_{yz} component calculated from the annealing simulation was 0.32 for one of the seven shear events, and 0.16 for the others, suggesting

that the transformation process may involve incomplete slips and different shear partials (Burgers vectors).

Figure 4: (Color online) (left) Schematic of ABA stacking for hcp crystals and (right) the three equivalent partials (b_1 , b_2 , and b_3) that changes the ABA to ABC stacking during an hcp-fcc (fcc) transformation. The three base vectors in the hcp basal plane are labelled as a_1 , a_2 , and a_3 .

Figure 5: (Color online) (left) Atomic displacement map for the hcp-fcc transformation from Fig. 3(a) to Fig. 3(b), projected into the $\{11\bar{2}0\}$ plane. On the right the corresponding in-plane shear components for layers A, B and C are plotted, projected into the basal plane. The analysis was done for atoms in the enclosed region in Fig. 3(a) only.

At the ideal c/a ratio, the only difference between hcp and fcc phases is the stacking along the $\langle c \rangle$ direction, ABABAB for hcp and ABCABC for fcc. The hcp stacking can be converted into fcc by a $\frac{1}{3} \langle 1\bar{1}00 \rangle$ slip on the basal plane, as shown in Fig. 4. One such slip event is needed for every two $\langle c \rangle$ layers to entirely change an hcp crystal into an fcc one. Due to the crystal symmetry, three equivalent shear partials, $\frac{1}{3}[1\bar{1}00]$ (b_1), $\frac{1}{3}[10\bar{1}0]$ (b_2), and $\frac{1}{3}[01\bar{1}0]$ (b_3), exist and their summation gives zero macroscopic displacement. These three partials produce the same change in stacking along $\langle c \rangle$ and the same amount of shear strain [37, 38]. As the y axis is along the $[1\bar{1}00]$ direction, the slip with the Burgers vector b_1 should produce a ϵ_{yz} of 0.36 if complete, and those with b_2 and b_3 should produce a ϵ_{yz} of 0.18 due to projection. Therefore, the results on ϵ_{yz} in Fig. 3(c) indicate that all three shear partials (or at least two of them) were involved in the transformation process, and the slips were incomplete.

To further characterize the Burgers vectors involved in the hcp-fcc transformation, the displacement (Fig. 5(a)) of each atom during annealing was calculated by $\Delta r_i = r_i(t) - r_i(0)$. Here $r_i(0)$ and $r_i(t)$ being the positions of atom i before and after annealing. The atomic displacement vectors are substantially non-zero only inside the initial ζ cluster. They change in both length and direction every four $\langle c \rangle$ layers, indicating one shear event for every four $\langle c \rangle$ layers. All slips were characterized to occur between a Zr and a Zr(H) $\langle c \rangle$ layer. Here a Zr layer means a $\langle c \rangle$ layer with Zr only, and a Zr(H) layer means that with both Zr and H sub-layers. One possible reason for this could be that the interaction between two Zr

layers is weakened by the presence of a H sub-layer near one of the Zr layers. As the shear took place once every four $\langle c \rangle$ layers, only half of the clusters were transformed into fcc. To be more accurate, out of every four $\langle c \rangle$ layers in the cluster, two of them were observed to transform into fcc while the other two remained hcp, resulting in a mixture of γ hydride and α -Zr.

Based on the atomic displacement, a relative shear vector can be calculated for each atom i with respect to its first nearest neighbors (1NNs) j as: $s_i = \sum_j (\Delta r_i - \Delta r_j) / 3$. Here the summation goes over all j . In hcp crystals, each atom has 12 1NNs: 6 in the same $\{0001\}$ plane, and 3 on each of the two neighboring $\{0001\}$ planes. When a slip as shown in Fig. 4 takes place, only 3 of the 12 1NNs of atom i displace differently from i . A non-zero s_i shared by a plane of atoms indicates the plane where slip occurs with a Burgers vector given by s_i . In Fig. 5(c)-(d), the relative shear vectors, or the Burger vectors, for the atoms on three $\langle c \rangle$ layers (A, B, and C) are plotted. Slip events have been identified on these planes. Interestingly, the Burgers vectors responsible for the slip events on these three planes were different from each other, taking $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ respectively. The actual Burger vectors characterized were slightly smaller than ideal ones due to incomplete slips. Therefore, it is now confirmed that all three possible shear partials have been involved in the hcp-fcc transformation of the ζ cluster. For the 7 slip events, $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ were characterized once, 4 times and twice, respectively, showing the stochastic nature of this process. As will be discussed later, the involvement of multiple shear partials is very important for the formation process.

The above transformation process was observed for the ζ hydride cluster only. For the γ -hcp cluster, no structural change was found. To reduce the artificial effect of short MD simulation time, another 500 ps annealing was performed for the γ -hcp cluster. The potential energy converged during the simulation, without any sign of transformation observed. Therefore, we conclude that the hcp-fcc transformation may not be possible for the γ -hcp cluster, or at least much less likely than that for the ζ cluster at the cladding operating temperatures.

3.4. Generalized stacking fault energy

The different stabilities of the ζ and the γ -hcp clusters can be understood by calculating the so-called generalized SFE curves, which give the energetic barriers associated with the hcp-fcc transformation. For this purpose, simulation cells as shown in Fig. 6 were used. The simulation cells were periodic except for the top and bottom surfaces. The top half of the cell was displaced along the $[01\bar{1}0]$ direction with a step length of 0.05 Å until a total displacement of $\frac{1}{3}[01\bar{1}0]$ was reached. After each displacement step, surface layers of 1 nm were fixed at the top and the bottom, while the rest of the simulation cell was fully relaxed at 0 K. At the end of the displacement, an I2 stacking fault was generated by changing the stacking from ABABAB to ABCACA with the shear occurring at the first C layer. As can be seen by the stacking after shear, this process produces two fcc layers in the hcp matrix. For comparison, the calculation was done for α -Zr, the ζ and the γ -hcp hydride. For α -Zr and the γ -hcp hydride, the shear or the cutting between the top and the bottom halves can be done at any $\langle c \rangle$ plane as they are identical. For the ζ hydride, the cutting was done between a Zr and a Zr(H) $\langle c \rangle$ layer (Fig. 6), to be consistent with the annealing simulations. The SFE curve can be obtained by plotting the excess energies of the systems as functions of the slip displacement, taking the energies at zero displacement as the references.

In Fig. 6, the SFE curves for α -Zr, the ζ and the ζ -hcp hydride are presented. For the γ -hcp hydride the results are divided by a factor of 4 for better visualization. From the SFE curves, the stable SFEs (γ^s) can be defined using the excess energies for the final configurations. The unstable SFEs (γ^{us}) can also be defined using the maximum excess energy in each curve, and they are taken as zero if below zero. For α -Zr, γ^s and γ^{us} were found to be 104 and 134 mJ/m² with the COMB potential. For comparison, the same properties were predicted to be 227 and 285 mJ/m² by previous DFT calculations [29]. Thus, the COMB potential underestimates the barriers for hcp-fcc transformation in α -Zr.

For the ζ -hydride, negative γ^s was predicted by both the COMB potential (-51 mJ/m²) and DFT calculations (-95 mJ/m²), indicating that fcc stacking is thermodynamically preferred over hcp. The entire SFE curve predicted by the COMB potential was below zero. The excess energy was found to decrease almost monotonically upon increasing displacement along $[01\bar{1}0]$, with a very shallow minimum at about 0.8 of the total displacement. Therefore, for the ζ -hydride, the hcp-fcc transformation via slip on the basal plane is favored thermodynamically with a negligible barrier. This is consistent with the observation of

structural transformation in the annealing simulations (Fig. 3). The SFE curve also indicates incomplete slips during the transformation. Without external loading, the product of the hcp-fcc transformation should be the configuration giving the minimum excess energy, which has a stacking close to but not yet fcc stacking for the ζ -hydride. As a result, the shear strain involved in the transformation during annealing (Fig. 3(c)) was found to be smaller than that expected from a complete slip, 0.36. It should be emphasized that for the ζ -hydride, the shape of the SFT curve obtained with the COMB potential was very similar with that from previous DFT calculations, which also suggested a negligible barrier for slip on the basal plane and a most preferred state produced by incomplete slip [29].

In contrast to that for the ζ hydride, a high barrier (902 mJ/m²) was predicted by the COMB potential for the hcp-fcc transformation in the γ -hcp hydride. With such a high barrier, the hcp-fcc transformation may not be possible at the cladding operating temperatures if no mechanical loading is applied. Indeed, no structural transformation was observed in the annealing simulations on the γ -hcp cluster. As a reference, the barrier predicted by previous DFT calculations was about 420 mJ/m² [29]. Although the results obtained with the COMB potential differ from DFT calculations in absolute values, the general trends actually agrees well with each other. For both methods, a negligible barrier was predicted for the slip on the basal plane for the ζ hydride, and a high barrier for the γ -hcp hydride.

Figure 6: (Color online) (left) Schematic simulation cell for general stacking fault energy surface calculation and (right) excess energies as functions of slip displacement along the $\frac{1}{3}\langle 0110 \rangle$ direction. The results for the γ -hcp hydride is divided by a factor of 4.

3.5. Discussion

In this work, we have used MS calculations and MD simulations with the COMB potential to investigate the two possible formation paths for the γ hydride proposed in the literature [11]: (1) α -Zr $\rightarrow$ ζ $\rightarrow$ ζ -fct $\rightarrow$ γ , and (2) α -Zr $\rightarrow$ ζ $\rightarrow$ γ -hcp $\rightarrow$ γ . Both paths involve an hcp-fcc phase transformation. They differ from each other as to where the transformation takes place, in the ζ phase for the former, and in the γ -hcp for the latter. For both paths, the end product is the γ hydride. To be more accurate, the transformation of the ζ hydride leads to the formation of a mixture of γ hydride and α -Zr, due to the fact that in the ζ phase only two of every four $\langle c \rangle$ layers contain H sub-layers. Although driving forces have been identified by thermodynamic analysis for both paths [11], it is found in this work that only the former may be feasible at the cladding operating temperatures. For the latter, a very high barrier was predicted for the slip needed for the hcp-fcc transformation (Fig.6), and it practically forbids the formation of γ hydrides from γ -hcp

hydrides. In contrast, the shear slip in ζ hydride as shown in Fig.5 requires a negligible barrier, as shown in Fig. 6. Therefore, the slip can occur at finite temperatures and the corresponding formation path is relevant at fuel operating temperatures. The trend in the slip barriers predicted by the COMB potential is in good agreement with previous DFT calculations [29], indicating the validity of the present results. Although this work focuses on the formation of γ hydride, the results are also relevant for the δ and ϵ hydride. It has been suggested by previous experiments that the δ hydride may form from the γ hydride [13], and it can further grow into the ϵ hydride [14]. Formation of the fcc δ hydride from the γ hydride will possibly require a martensitic transformation, which converts the fct structure of γ hydride to fcc.

It has been proposed by Carpenter [9] that the formation of γ hydride may take place by shear, *i.e.*, slip on the basal plane, of coherent clusters. The mechanism obtained in the annealing simulation here is in general consistent with that proposed by Carpenter. As shown in Fig. 3(b), the coherent ζ hydride cluster embedded in the α -Zr matrix was found to transform into a mixture of hcp and fcc stacking under annealing at 600 K. The transformation took place via slips on the basal planes, with dislocation cores stored at the interface. However, the mechanism described in this work differs from Carpenter's in some details. First of all, three equivalent shear partials were identified in our MD simulations during the transformation, in contrast to Carpenter's hypothesis where only a single partial was involved. The presence of multiple shear partials has significant effect on the formation process. Since the summation of the three equivalent partials (b_1 , b_2 , and b_3) is zero, a random combination produces negligible change in the macroscopic shape of the cluster and negligible shear strain in the surrounding matrix [37]. If a single slip partial is responsible to complete the hcp-fcc transformation, a high shear strain will be induced in the matrix along with a change in the shape of the cluster [9]. This will substantially increase the barrier for transforming a coherent cluster into a fct hydride. Actually, in our MD simulations no obvious change in the shape of the ζ cluster was observed during the transformation. The shear strain in the matrix was also found to be much lower than that predicted in the literature [39]. Second, the complete hcp-fcc transformation may take two steps as suggested by the annealing simulation. To fully transform an hcp crystal into fcc, slips on the basal plane are needed once for every two $\langle c \rangle$ layers. However, in the ζ hydride cluster, slip events were characterized once every four $\langle c \rangle$ layers, leading to the formation of a mixture of γ hydride and α -Zr. Thus, another series of slips would be needed upon further absorption of H. Moreover, the slips in the ζ hydride were found to be incomplete and the most stable configuration after transformation was found not fcc. At higher H/Zr ratio, the fcc stacking is expected to be stabilized by the increasing barriers for hcp-fcc transformation, as indicated by the SFE curve for the γ -hcp hydride.

The last piece of discussion is on the materials fidelity of the COMB potential. Although good agreement with DFT calculations has been obtained regarding the formation energies of hydrides, the COMB potential substantially overestimates the stability of H solid solution at the tetrahedron site in α -Zr. In reality the driving force for hydride precipitation should be even stronger than that given in Fig. 2. Besides the H solution energy, the stable and unstable SFE energies given by the COMB potential also differ from DFT predictions as to absolute values. However, the general trends obtained with the COMB potential on the SFE curves of various phases agree well with DFT calculations [29]. It has been shown previously by DFT calculations that γ^{us} decreases from 285 mJ/m² to zero when H/Zr ratio increases from 0 to 0.5, where minima in both γ^s and γ^{us} were reached. Further increase in the H/Zr ratio led to increases in both γ^s and γ^{us} . Therefore, the ζ hydride with a H/Zr of 0.5 is the most possible state for the hcp-fcc transformation. At the H/Zr of 1.0, a high γ^{us} was predicted by DFT calculations as well [29], suggesting that the hcp-fcc transformation is not feasible at this state. These conclusions are consistent with those predicted by the COMB potentials.

In spite of the discrepancies in absolute numbers produced by the COMB potential and DFT calculations, the conclusion of this work can still be well justified. The above proposed formation path of γ hydride is drawn upon three critical factors: (1) a driving force exists for the precipitation of the ζ hydride from H solid solution, (2) a driving force exists for the hcp-fcc transformation in the ζ hydride, and (3) the shear barrier for the hcp-fcc transformation in the ζ phase is much lower than that in α -Zr and in the γ -hcp hydride. For all the three factors, the COMB potential predicts the right trends in reference to DFT calculations, regardless of the discrepancies in absolute values. Therefore, the conclusion made in this work is valid, and should not be affected by further improvement of the current potential. Currently, an effort is being made

to improve the COMB potential for better description of the kinetic behavior of H solid solutions.

4. Conclusions

A homogeneous formation path for the γ hydride in α -Zr has been demonstrated using molecular static calculations and molecular dynamics simulations with the COMB potential. When the H concentration is high, the solid solution state becomes less stable, and H precipitates into ζ hydride clusters which are coherent with the α -Zr matrix. Favored thermodynamically, an hcp-fcc transformation takes place in these clusters, bringing the hcp stacking into fcc for γ hydride formation. At the H/Zr ratio of 0.5, a negligible barrier is required for the transformation. Three alternative, equivalent $\frac{1}{3} < 1\bar{1}00 >$ partials are involved in the transformation, with their combination giving minimal shear strain accumulation in the matrix. The formation path demonstrated in this work is relevant at cladding operating conditions in reactors.

Acknowledgement

The INL authors gratefully acknowledge the support of INL Laboratory Directed Research and Development Program under project #14-026, "Multiscale modeling on delayed hydride cracking in zirconium: hydrogen transport and hydride nucleation". This manuscript has been authored by Battelle Energy Alliance, LLC under Contract No. DE-AC07-05ID14517 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a nonexclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

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H solution/hydride formation energies

hcp-fcc transformation barrier for α -Zr, ζ and γ -hcp hydride phases

Dynamic transformation of an embedded ζ cluster into γ -hydride