DISLOCATION ACCELERATED VOID FORMATION UNDER IRRADIATION IN ZIRCONIUM

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We conduct molecular dynamics simulations to model defect creation in alpha zirconium with tensile strains comparable to the elastic strains near the interfaces between zirconium and hydrides. Irradiation induced vacancy cluster under the strain field could be an initiation site for dislocation nucleation, and the gliding of these dislocations provides channels for transporting atoms from the cascade core, significantly accelerating the growth of the vacancy clusters to a void. The critical number of vacancies in a cluster that is enhanced to grow by the external stress is estimated. The present results provide an atomic-level mechanism to explain the stress enhanced void growth under irradiation in Zr, as observed in experiments. The acceleration of delayed hydride cracking under irradiation might be partially attributed to the formation of these voids.

keywords: Displacement cascade; Void growth; Dislocations; Zirconium; Molecular dynamics simulations.

Introduction

In both fission and fusion environments, the basic effects of irradiation damage in solids are the displacement of atoms from their equilibrium positions and the formation of point defects (vacancies and interstitial atoms), as well as defect clustering. These defects can be annihilated with the defects in opposite nature or accumulate with the same type defects to form defect clusters. Due to the surface energy, vacancy clusters tend to agglomerate to vacancy loops unless insoluble gases or large enough net vacancy flux are present to stabilize the formation of voids from vacancy clusters. Voids and bubbles (voids containing gas) have been observed in numerous neutron, heavy ion and high-voltage TEM irradiation experiments in metals and alloys[1-13]. The significant contributions of insoluble gases (from pre-implantation or nuclear (n, α) transmutation reactions) to the cavity (voids and bubbles) nucleation and growth have been extensively discussed [1-7]. The formation of voids has also been observed with an increase of the dose by in-situ heavy ion irradiation [8]. Without insoluble gases, void growth

has been also demonstrated by high-voltage TEM [9] because of the much higher displacement damage rate seen in heavy ion irradiation than observed in neutron irradiations. Furthermore, previous experimental work also demonstrates that the tensile stress can enhance the cavity growth during irradiation [1, 10-12].

Deuterium ingress due to the corrosion of zirconium alloys can lead to the presence of hydride precipitates, and when those hydrides are large enough cracks can also be initiated and propagate in the alloy by so called Delayed Hydride Cracking (DHC) process [14-19]; neutron irradiation also can increase the velocity of DHC in cold-worked Zr-2.5Nb[20]. A recent nano-beam electron diffraction experiment suggests that the elastic strain in the zirconium close to a hydride could be very high at local scale, up to 5% in one crystallography direction because the hydride is coherent with zirconium matrix. This high strain only extends 10 or 20 nm away from the hydride [21]. It has been noticed that strain effects have been studied by MD in bcc alpha iron [22], fcc copper [23] and hcp zirconium[24]. In hcp zirconium, the external strain (up to 1%) mainly affects defect clustering. In this report, we show that the strain field induced by precipitates (hydrides) could be a physical origin giving rise to the stress enhanced void growth during irradiation.

Methods

We have used molecular dynamics (MD) simulations in alpha-zirconium to study the effect of strain field on irradiation induced defect generation. The zirconium potential selected is Embedded Atom Method (EAM) potential developed by Mendelev and Ackland [25]. This potential provides a better description of stacking fault energy than previous potential [26]. In this zirconium potential, the most stable interstitial defect configuration is the O (octahedral) configuration. However, recent ab initio studies of self-interstitial atoms in HCP zirconium indicated higher stability of BO (basal octahedral) configuration than the O position [27-29]. With respect to the small difference of interstitial defect formation energies at different configurations, the 2007 potential is still one of the latest and best available EAM potentials for cascade simulation. The size of the simulation block is either $56 \times 32 \times 35$ unit cells with a total of 250,880 atoms or $72 \times 41 \times 45$ unit cells with a total of 531,360 atoms, depending on the energy of a PKA. In displacement cascade simulation, the PKA energy is given as 5 keV or 10

keV, and the simulation temperature is set to 100 K. To study the strain effects, a tensile strain is applied along $\langle c \rangle$ axis ([0001]) to represent the volume expansion (based on Fig.2b in reference [21], and the selected tensile strains are 3% and 5%. The simulation system is first equilibrated at 100 K for 10 ps to achieve thermal equilibrium, then one PKA is introduced into the system and the production runs of duration to 50 ps is followed. For each strain condition, 20 simulations with different PKA positions and recoil directions are carried out. Periodic boundary conditions and various time-step approaches are applied in the MD simulations. Ovito is used to visualize the final results [30].

Results

Figure 1 illustrates several snapshots of the zirconium atomic positions at different time within a cascade with 10 keV Primary knock-on Atom (PKA) energy and 5% $\langle c \rangle$ -axial tensile strain. Red spheres and gray spheres in Figure 1 represent the atoms in an hcp structure and a deformed structure respectively, where Common Neighbor Analysis (CNA) is applied to structure identification. Right after the collision stage, the temperature at the cascade core is very high exceeding the melting temperature which lasts for hundreds of femtosecond. As shown in the snapshot at 1 ps in Figure 1, the atoms near the cascade core become disordered and a large number of atoms are ejected from the core, several small voids being formed at the center of the cascade; this atomic configuration is commonly observed at the initiation stage of irradiation cascade simulations. Normally, soon after cascade, the heated zone will cool down to a relative stable status from 1 ps to 10 ps, and vacancies and interstitials can annihilate with each other or agglomerate to form defect clusters. Thus, these large empty spaces can also be recovered by the displaced atoms, and the remaining defects in the lattice are the material response to the irradiation damage. However, in our results (Figure 1, Supplementary Movie 1-2 [31]), it is of great interest to note that the voids keep growing, which leads to the formation of a stable void at the cascade core. In the current simulations, the external strains have been applied, as compared to the aforementioned normal simulations [32, 33], and thus, could play a key role in enhancing the void growth. Common neighbor analysis in Figure 1 indicates that starting from 2.0 ps, the $\langle c+a \rangle$ type dislocations initiate near the edges of the voids in the system. After then (from 5.0 ps to 20.0 ps), the $\langle c+a \rangle$ dislocations start to slip on the pyramidal plane along the $\langle 11\bar{2}3 \rangle$

directions, transporting atoms out from the cascade core, and thus, the voids grow into a large void with the increase of the deformation. Due to the size limitation and periodical boundary conditions, some dislocations cross boundaries and dislocation slips are pinned by other dislocations (as shown at 30.0 and 50.0 ps in Figure 1).

Figure 2 demonstrates the detail analysis of the final atomic configuration (at 50.0 ps in Figure 1). Figure 2 (a) shows the cross-section of the upper-left area to the central void, where the gray and black spheres indicate atomic positions along the $\langle 01-10 \rangle$ direction at two adjacent prism planes. The broken line in Figure 2 (a) illustrates the position of the stacking fault plane [34] and the slip direction $\langle 2-1-13 \rangle$, and, three-dimensional analysis indicates that the slip system is active on the $\{10-11\}$ plane. The stacking fault and atomic configurations suggest that the $\langle c+a \rangle$ dislocation on the pyramidal planes dissociates into two partial dislocations, as demonstrated in the following equation and Figure 3 [35, 36]:

$$\frac{1}{3}[2\bar{1}\bar{1}3] \rightarrow \frac{1}{6}[20\bar{2}3] + \frac{1}{6}[2\bar{2}03] \quad (1)$$

Figure 2 (b) represents the cross-section of the lower-left area to the central void, where the dislocation symbol indicates a perfect $\langle a \rangle$ dislocation with a Burgers vector of $1/3\langle 11-20 \rangle$. The dislocation starts from a nearby stacking fault surface and ends to another stacking fault plane. It is also noticed from the snapshots of 30 ps to 50 ps in Figure 1, that the $\langle a \rangle$ dislocation glides on the basal plane. Although the basal $\langle a \rangle$ slip system is not the most favoured slip system in zirconium, local activation of the basal slip in zirconium has been observed in experiments near the crack[37, 38], free surface[39] and near hydride precipitate in thin foils[40]. It is also illustrated in Elasto-plastic self-consistent (EPSC) model fitting with neutron diffraction data that the basal $\langle a \rangle$ slip is likely to occur and is very active[41]. The further studies on the dislocations reveal that the small void serves as an initiation and nucleation sites for initiating the dislocations upon straining [42-45]. To accommodate the 5% external strain along the $\langle c \rangle$ axis, several $\langle c+a \rangle$ pyramidal dislocations are nucleated in the system, and then dissociated to partial dislocation to reduce the dislocation energy. Also, a stable $\langle a \rangle$ dislocation is formed

during the deformation process and glides on the basal plane. The central void extends and grows along with the slip of the surrounding partial dislocations and the increase of the deformation [46-49].

In our simulation results, a void is always observed in each of the simulations with a PKA energy of 10 keV and a 5% $\langle c \rangle$ -axial tensile strain. However, when the tensile strain decreases to 3% and the PKA energy remains the same (10 keV), voids are not observed to form in all the twenty simulations (Table 1). The final products are interstitial clusters, vacancy clusters and single defects, and these vacancy clusters do not form voids, as observed with 5% strain condition. This strongly suggests the effects of strain magnitude on the void formation and growth.

PKA energy is another important factor controlling microstructural evolution in displacement cascade, because higher PKA energy produces larger and more complex defect clusters than low PKA. Figure 4 shows the vacancy cluster size distribution at PKA energies of 5 keV and 10 keV (the values on the figure for each PKA energy are averaged from 20 simulations, but without strain). As illustrated in Figure 4, the largest vacancy cluster contains 16 vacancies with 5 keV PKA energy, whereas the largest vacancy cluster reaches 24 vacancies at 10 keV. To understand if the PKA energy has any effect on the void formation and growth, we then perform the simulations with a PKA energy of 5 keV and remain the same tensile strain of 5%. In the $\langle c \rangle$ -axis tensile simulations, voids are formed at 15 out of 20 simulations. The probability of void formation decreases compared with the results with the PKA energy of 10 keV (Table 1). Hence, the PKA energy also affects the void formation and growth. In short, the void formation and growth during the displacement cascade simulations with larger tensile strain depends on two factors: the strain magnitude and the PKA energy.

Table 1 The probability of void formation out of twenty simulations at different strain and PKA energy conditions.

Strain	3%	5%	5%
PKA energy	10keV	10keV	5keV
$\langle c \rangle$ -axis	0 (20)	20 (20)	15 (20)

Theoretically, if pre-implanted or transmuted gases are available, the gas pressure will mainly outweigh the collapse of vacancy clusters to vacancy loops; without the assistance of gases, but the high displacement damage rate (like HVEM irradiation) can produce large enough vacancy supersaturation to outweigh the surface energy. Since no gas presents in our simulation and only one single cascade is introduced into the system, the stress (σ) is the most significant part of the void growth in our simulation. To elucidate the preceding factors affecting our simulation results, the stress enhanced void growth mechanism [50, 51] is applied. The void growth rate is proportional to the parenthetical term in Eq. (2)

$$\frac{dR}{dt} \sim \left(\sigma + p - \frac{2\gamma}{R} \right) \quad (2)$$

Where R is the void radius, t is time, σ is the external stress, and p is the gas pressure and γ is the surface energy. In a gas-free case, when the external stress (σ) overrides the stress due to surface tension ($2\gamma/R$) as shown in Eq.3, the void growth rate (Eq.2) can become positive and the external stress will enhance the growth of the voids.

$$\sigma > \frac{2\gamma}{R} \quad (3)$$

A critical number of vacancies in a void embryo that is enhanced to grow by external stress can be calculated as shown in Eq.4

$$N_c = \frac{\left(\frac{2\gamma}{\sigma} \right)^3}{r_a^3} \quad (4)$$

, where N_c is the critical number of vacancies in a void, r_a is the atomic radius. Eqs. 3 and 4 show that at a certain strain condition, a small void embryo (which contains fewer vacancies rather than N_c) cannot be evolved to a large void by the external stress because of the high surface tension of a small void. Therefore, a void embryo,

which is produced in a cascade process and can be enhanced to grow by the external stress, should contain at least the number of vacancies equal to or larger than N_c .

From Eq. 4, a relationship between the stress (σ) and the critical number of vacancies in a void embryo (N_c) is illustrated in Figure 5. The surface energy (γ) value is taken as 1 J/m², the atomic radius of zirconium is 160 pm[52], and the stress is calculated from the stiffness constants [25] and the applied strain. The gray area in the lower part of Figure 5 presents the size range of typical irradiation produced vacancy clusters with a PKA energy of 10 keV (up to 24 vacancies in a vacancy cluster according to Figure 4), and the hatched area presents the size range for 5 keV (the size is up to 16 vacancies). Figure 5 demonstrates the strain magnitude that is required to form a void embryo. In the 3% tensile strain simulation, the N_c (~60) is much higher than that of the 5% strain and is also much larger than the number of vacancies in clusters produced in a 5 or 10 keV cascades. Therefore, the external applied stress corresponding to the 3% tensile strain is not sufficient to overcome the stress due to the surface energy to form a void embryo from the vacancy clusters produced in the cascades. The effects of the different PKA energies on the void formation and growth are mainly attributed to the size difference of the vacancy clusters produced at different PKA energies. As shown in Figure 4, the size of the largest vacancy cluster drops from 24 vacancies in 10 keV simulations to 16 vacancies in 5 keV simulations. With smaller vacancy clusters in 5 keV simulations, it is expected that the probability of void formation and growth is smaller as compared with 10 keV simulations under stress.

Discussion

Experimentally, electron irradiation in Zr suggested that the solubility of gases and the presence of stresses are likely to be important whether voids or vacancy loops are formed during irradiation [53]. It seems that the vacancies diffuse to the metal-oxide interface to relieve the stress, leading to the nucleation and growth of vacancy loops. The nucleation, growth and character of c-component vacancy loops are governed to a large extent by a stress in the matrix, and the results would be accelerated or ‘breakaway’ growth in neutron irradiated Zr [54]. Brager et al. [12] have also shown that applied tensile stresses enhance swelling in neutron-irradiated 316 stainless

steel and the number density of both voids and Frankel loops are sensitive to the stress level. The results presented provide an atomic-level mechanism for the nucleation of a void embryo and its growth under applied stress (c-component) in Zr, which explains the stress-enhanced void formation and swelling observed in neutron irradiated materials.

In summary, irradiation produced vacancy clusters take the role as an initiation site for dislocation nucleation under applied stress, and the glide of dislocation and related deformation due to the external strain provide channels to transport atoms from the cascade core, enhancing the evolution of the vacancy cluster to a void. Also, the critical number of vacancies in a cluster to form a void embryo is calculated for initiating the growth process of a void. We found that the void growth in the simulation depends on two factors: strain magnitude and PKA energy. Those factors can be explained using stress enhanced void growth. The strain condition in this work represents the condition observed at the interface of hydride and zirconium matrix, those formed voids potentially could influence crack propagation by the DHC process, by acting as crack initiation sites. Previously it has been assumed that the primary influence of irradiation on DHC is via the loss of ductility of the matrix due to irradiation hardening, but these results suggest that the hydrides, or at least the hydride-matrix interface, will appear weaker.

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Figure captions:

Figure 1 A series of snapshots of Zirconium atoms in a 10 keV cascade evolution within a cross section thickness of a_0 , viewed along the [01-10] direction. Red spheres represent atoms in an hcp structure and gray spheres atoms in a deformed structure, where the atoms are identified based on common neighbor analysis.

Figure 2 Projections of atom configuration at selected areas of the final state. The gray and black spheres in (a) and (b) indicate the atoms in two adjacent prism-planes. The broken line in (a) reveals the pyramidal stacking fault. The Burgers vector of the dislocation in (b) is $\langle 2-1-10 \rangle$.

Figure 3 $\langle a+c \rangle$ dislocation dissociation on the (10-11) plane. The gray scales of the spheres indicates atoms at two adjacent planes (Interplanar spacing is around 0.4 Å)

Figure 4 Vacancy cluster distribution in displacement cascades at PKA energies of 10 keV and 5 keV without strain

Figure 5 The relation between N_c and external applied strain, where the gray area is a typical range of vacancy cluster size at displacement cascade simulation with a PKA of 10 keV, and the hatched area shows the range for a PKA of 5 keV.

Figure(1)

Figure(2)

Figure(3)

Figure(4)

Figure(5)