Comparative molecular dynamics study of fcc-Al hydrogen embrittlement

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Abstract

Hydrogen embrittlement studies using reactive molecular dynamics have been conducted for Al metal nanoslabs with oxidized surfaces. These have provided evidence for possible grain boundary decohesion and void formation related range of hydrogen embrittlement mechanisms at different loading conditions with different initial defect configurations. Particularly, the effect of initial vacancy concentration on hydrogen diffusivity and localization, as well as on the amount of plasticity and grain formation is estimated. The results indicate significant reduction in diffusivity due to vacancy concentration, as well as hydrogen embrittlement effect through increase in dislocation emission and increase in dislocation slip propagation rate.

Keywords: aluminum, hydrogen embrittlement, ReaxFF

1 Introduction

Among the environmentally assisted cracking (EAC) structural material failures a few main types can be distinguished [1]. These include stress corrosion cracking (SCC), which occurs through a material's interaction in stressed state with chemically active fluid environment species and hydrogen embrittlement (HE) due to bulk dissolved atomic hydrogen, which tends to migrate to high stress regions. Both phenomena have been explored extensively both experimentally and computationally for a wide range of materials. A comprehensive review of known and suggested SCC and HE mechanisms, as well as

outstanding issues, can be found in [2]. A review of H diffusion and dislocation channeling related intergranular SCC and irradiation assisted SCC studies is published in [3]. In particular, detailed atomistic failure mechanisms involving increased dislocation emission barriers by H atoms on crack surface [4, 5], reduced dislocation emission barriers by H atoms on the slip plane [5], H migration to crack tip [5, 6], as well as combined atomistic/kinetic models [6, 7] have been presented. In the latter, atomistic/kinetic model, studies a kinetic analysis is used to calculate the size of a H-rich region formed at the crack tip. By combining the kinetic analysis with the deformation/fracture analysis a ductile-to-brittle transition mechanism map is proposed, which is validated by experimental results. Related HE mechanisms include hydrogen-enhanced decohesion (HEDE) [8], as well as adsorption-induced dislocation emission/void coalescence (AIDE) [9] and hydrogen-enhanced localized plasticity (HELP) [10]. Likewise, related thermodynamic Al hydride properties [11-15], including Al-vacancy binding and other H trapping states, have been studied. Accordingly, for H facilitated fracture, void coalescence mechanisms, as discussed, e.g., for an Al alloy [16], may be applicable [9, 12, 17].

For the current HE study fcc (face-centered cubic) Al was used as a model material due to its low H solubility [11] and, hence, a high expectation for chemical activity in proximity of crack surfaces [5]. For an analysis of slip systems of dislocations emitted from crack tips in pure Al, which serves as the reference structure in the present study, we would like to refer to a density functional theory (DFT) study of [18].

2 Material and methods

The metal slab structures have periodic dimensions of 15.23×0.977 nm in directions $[1\bar{1}0]/[11\bar{2}]$, respectively, and metal layer thickness of 12.34 nm. The (111) outer slab surfaces were interfaced with unit-cell thick (1.271 nm) Al_2O_3 layers having an orientation identical to the structures above. The (0001) oxide interface was defined as Al-terminated, which energetically matches -273°C (0K) scaled experimental results according to [19]. An atomistically blunt notch was defined for one of the oxide layers, the Al part was initially intact. On the notch side the fcc stacking with respect to O positions of alumina, which has been found to be the most stable configuration among Al-terminated oxide surfaces and the closest to experimental values [19], was used, whereas for the defect free side the on-top stacking was applied for comparison.

For the hydrogen interactions two systems were implemented. In the first system 162 H atoms were located in place of 162 Al vacancies, distributed in pairs periodically throughout the Al slab part. In the second system 162 H atoms were distributed randomly in the Al slab part. For the latter system no initial

vacancies were introduced in the structure. It should be stressed that the chosen concentrations are intended to represent local oversaturated densities, since the experimental hydrogen solubility is of an order of 10^{-8} H/Al atomic fractions [11].

For this study the LAMMPS [20, 21] implementation of the reactive force field ReaxFF, as described in [22], was used. The ReaxFF force field versions used in the simulations have been based on earlier published versions of Al/O [23, 24], Al/H [25], O/H [26] and Al/O/H [27] force fields (Table 1). To enable the Al/H bulk simulations presented here, we extended the ReaxFF Al/H training set used previously to study hydrogen storages and alane chemistry [25] with DFT-data describing the hydrogen binding strength and diffusion barriers in the Al-bulk interstitial sites and the hydrogen binding energies to aluminum metal subsurface vacancy sites and neighboring sites.

Table 1. fcc-Al elastic constants (C_{11} , C_{12} , C_{44}), fracture toughness values (K_{Ic}), intrinsic (ISF) and unstable (USF) stacking fault energies.

	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	K_{Ic} (MPa·m ^{1/2}) $\langle 1\bar{1}0 \rangle \{111\}$	ISF(mJ/m ²)	USF(mJ/m ²)
DFT/experiment	104 [28]; 116 [29]	55.9 [28]; 64.8 [29]	29.5 [28]; 30.9 [29]	0.45 [5]; 0.52 [18]	140; 93 [18]	188; 143 [18]
ReaxFF (AlOH_Oct2013)	133	64.3	58.1	0.91	98	140

DFT calculations [30] for force-field training were performed with VASP software [31] using the projector-augmented-wave (PAW) potentials [32] in the spin-polarized form [33] and the generalized gradient approximation (GGA-PBE) [34]. The 32-atom $2 \times 2 \times 2$ conventional supercell of fcc aluminum was used for bulk calculations. The wavefunctions were expanded in a plane-wave basis set with 33.8 MJ/mol (350 eV) energy cutoff. A $9 \times 9 \times 9$ Monkhorst-Pack k -mesh was used, in conjunction with first-order Methfessel – Paxton smearing [35] with smearing parameter $\sigma = 0.2$, to sample the Brillouin zone. The choice of energy cutoff and k -point mesh were determined by energy convergence testing for the Al bulk supercell. Optimizations were done with the conjugate gradient algorithm implemented in VASP using the default total energy convergence criteria, 9.65 J/mol (10^{-4} eV) for the electronic loop and 96.5 J/mol (10^{-3} eV) for the ionic optimization (comparison of convergence settings available in the Supplementary material).

With these computational choices, the energy versus volume curve for fcc Al was fitted to the Murnaghan equation of state, obtaining the value 0.4054 nm for the lattice constant, in excellent agreement with experiment [36] (0.405 nm).

The energetics of interstitial H binding and diffusion in bulk aluminum has been studied computationally in the past [15, 37]. The present results for the binding energy of the H atom at the tetrahedral (T_d) and

octahedral (O_h) interstitial sites are in excellent agreement with the results in [15], and indicate a positive (endothermic) dilute heat of solution of H_2 in bulk Al, in perfect agreement with experiment (~ 67 kJ/mol with respect to half the energy of the H_2 molecule) [15]. The calculations also predict a slight preference for adsorption at the T_d site that binds H stronger than the O_h site by 7.3 kJ/mol. Furthermore, we computed the reaction coordinate for the migration of the H atom between the T_d and the O_h sites, via constrained optimizations, as shown in Figure 1. The transition state for this pathway was further verified by sampling the energy profile between the transition state and all high-symmetry points in the potential energy surface. The value of the computed diffusion barrier (15.5 kJ/mol) is in excellent agreement with an experimental activation energy for H diffusion in high-purity aluminum (16.3 kJ/mol) [38]. These DFT data were used for force-field training. According to our DFT data, a hydrogen atom has a binding energy to a subsurface tetrahedral site of -147.7 kJ/mol and a binding energy to a subsurface octahedral site of -140.4 kJ/mol, and the barrier for migration between these sites is 15.5 kJ/mol (with respect to the tetrahedral site). The ReaxFF parameters used in this study provide binding energies of -152.7 kJ/mol and -144.8 kJ/mol to the tetrahedral and octahedral sites respectively, and give a barrier of 15.5 kJ/mol for migration from the tetrahedral to the octahedral site.

Figure 1. Top: Interstitial H at the tetrahedral (T_d) and octahedral (O_h) bulk fcc Al sites and the transition state for migration between the two high-symmetry sites. Bottom: DFT-calculated energy versus reaction coordinate for the migration pathway. The reaction coordinate is approximately represented as the fraction along the T_d - O_h connecting line.

Considering the expected effect of Al vacancies in hydrogen embrittlement mechanisms, additional DFT optimizations were performed to calculate the binding energy of hydrogen atoms in the vicinity of Al

vacancies for the purpose of training of the force-field. A volume-optimized 31-atom supercell was used to simulate the Al vacancy and, based on the computational setup described above, the calculated vacancy formation energy was 59.4 kJ/mol, in good agreement with experimental values (64.4 ± 3.0 kJ/mol) [39]. In the vicinity of the vacancy, H prefers a slightly off-center tetrahedral position, as shown in Figure 2. The binding strength at this site (180 kJ/mol) is favored by 32.5 kJ/mol compared to the tetrahedral site of the perfect crystal. Figure 2 shows select structures and compares the DFT and ReaxFF binding of hydrogen to a subsurface Al-vacancy substitutional site and to nearest neighbor and next-nearest neighbor tetrahedral and octahedral sites. These results indicate that subsurface hydrogens have a substantially higher binding energy to sites neighboring a vacancy compared to non-vacancy sites (by about 25 kJ/mol) indicating that hydrogens will preferentially migrate to these subsurface vacancy sites. Furthermore, the ReaxFF – DFT comparisons indicate that the force field has the capacity to predict the energetics of H solution and diffusion in perfect and defective bulk aluminum.

Figure 2. Top: DFT-Optimized structures of H atom binding at interstitial sites near an Al-atom vacancy: H at the vacancy-site and at the nearest-neighboring tetrahedral and octahedral sites. Bottoms: DFT and ReaxFF binding energies for hydrogen to a subsurface aluminum vacancy sites and to neighboring (Nearest) and Next-nearest (N-nearest) tetrahedral (T) and Octahedral (O) sites.

The ReaxFF simulations were performed with the constant size, pressure and temperature ensemble (NPT) with the strained dimension kept fixed, using simulation step size of 0.2 fs, at 300°C (573K) with temperature damping of 100 fs and 0 Pa lateral pressure with damping of 10000 fs. In particular, the implementations of Nose-Hoover thermo- and barostats, coupled with equations of motion in velocity Verlet formulation [40], were applied. 3 Nose-Hoover chain thermostats were used for the thermostating

of the volume variables in pressure equilibration [41]. A deformation rate of $5\text{e-}6\text{ fs}^{-1}$ with 0.25%/0.5 ps stretching in $[\bar{1}\bar{1}0]$ direction alternating with 2.5 ps relaxation periods was used. The boundary conditions correspond to plane stress conditions, which favor a ductile material failure. Hence any enhancement of material embrittlement is expected to be readily distinguishable. For the structure without H impurities an additional stiffness enhancing constrain was imposed by fixing $[\bar{1}\bar{1}0]$ direction displacements for a 6 Å layer of atoms perpendicular to the loading direction at a maximum distance from the notch. For evaluation of strain rate and constant strain effects additional simulations of the hydrogen containing systems at fixed strain levels were performed, starting from selected configurations of the deformation simulations.

For the validation of $\{111\}$ slip prediction two Al $\{111\}$ slab structures, containing a rectangular notch initial defect, with periodic dimensions of $2.97\times 0.857\text{ nm}$ in directions $[11\bar{2}]/[\bar{1}\bar{1}0]$ and $3.43\times 3.96\text{ nm}$ in directions $[\bar{1}\bar{1}0]/[11\bar{2}]$, respectively, and thickness of 3.50 nm were used. Static simulations of 0.25% $[11\bar{2}]$ and 1.0% $[\bar{1}\bar{1}0]$ direction strain increments, defined with respect to the previous step configurations, were performed under plane strain (fixed $[\bar{1}\bar{1}0]$ dimension) and plane stress (0 Pa in $[11\bar{2}]$) conditions, respectively. At each strain increment energy minimization was performed, using a conjugate gradient method with a 69.5 aN ($1\text{e-}6\text{ kcal/mol/\AA}$) global force vector length tolerance [20] as a convergence criterion.

A cutoff radius of 1 nm and simulation time increments of 20 ps were used for the atomic strain calculation [42]. For the characterization of plastic deformation the octahedral strain was defined as proportional to the shear strain on octahedral planes in principal strain space. Thereby a representation of the effective plastic strain for vanishing elastic strain components was obtained for the case when principal strains are parallel to the principal stress directions [43]. In particular, the Almansi strain tensor, defined as finite strain tensor referenced to the deformed configuration [44], was used for the strain analysis.

For the calculation of H diffusivities (D) the Einstein relation [45], expressed as proportional to the mean squared displacement (MSD) vs time, was used. The adequacy of simulation length was based on the linearity of MSD vs time curves and/or apparent convergence of D vs time curves. With regard to the diffusivity calculations for bulk and surface 10-atom samples from the structure without initial vacancies (Figure 10), we attribute the observed comparatively slow convergence mainly to the small sets of H atoms considered, since for all other diffusivity calculations, which included all H atoms of the respective systems, the convergence requirements could be satisfied within shorter sampling times. However, we consider that the lengths of the simulations were sufficient to observe the qualitative differences in the diffusion behavior of both subsets.

3 Results and Discussion

3.1 Material embrittlement mechanisms

The similarity of stress responses (Figure 3b) indicates that overall deformation in all cases involves a similar level of plasticity. However, the potential energy response indicates that the tensile toughness, considered as a measure of the energy capacity of the material and defined as the total deformation work up to fracture [1], the latter being characterized for the current systems by the potential energy level reached after yielding, is most significantly reduced for the structure with H-filled vacancies, that of the bulk distributed H being slightly higher. The observations are confirmed by the structure snapshots (Figure 4 – Figure 6), which indicate void initiated ($\varepsilon=0.25$, ε - engineering strain) ductile slip failure along grain boundaries for the pure metal case (Figure 4), whereas the structure with H-filled vacancies fails after a void coalescence facilitated locally plastic fracture ($\varepsilon=0.2$), without slab cross section size reduction before fracture, propagates through the metal thickness (Figure 6), revealing H populated surfaces. The mechanism is identified as AIDE type. Similarly, the bulk distributed hydrogen structure failure initiates with a brittle fracture along a newly formed grain boundary ($\varepsilon=0.18$), revealing H populated surfaces (Figure 5). The mechanism is identified as HEDE type. Yet, due to the presence of a few voids at grain boundaries, the AIDE mechanism is also assumed to be active. Upon approaching the opposite slab surface the crack propagates further in a sliding manner along grain boundaries, which explains the closer similarity with the pure metal case and is in qualitative agreement with the finding that H may facilitate brittle fracture and localized dislocation emission simultaneously [10, 46]. We also observed that for the same system only a single grain is formed, which merges with the initial lattice after the formation of a second crack. We suggest, however, that less extensive grain formation events would occur for fixed $[11\bar{2}]$ dimension due to increased level of constraint and stress triaxiality. The oxide/metal interface effect, which is known to decrease strength and increase ductility significantly at certain strain rates in Al nanowires [23, 47], could be estimated by the transition from increase in potential energy to an approximately constant level at $\varepsilon\approx 0.2$, coinciding with the rupture of the second oxide layer, for the H-containing systems (Figure 3a). The difference from the pristine structure, for which a more gradual transition is observed at $\varepsilon\approx 0.25$, is attributed to the reduced dislocation barriers due to H atoms on slip planes.

Figure 3. fcc-Al potential energy (ΔE_{pot} – changes with respect to the stress-free state) (a) and tensile stress (σ) (b) vs. strain (ϵ) comparison for $[1\bar{1}0]$ strained $\alpha\text{-Al}_2\text{O}_3$ -terminated fcc-Al slab (H1 - structure with initial H-filled vacancies, H2 - structure with bulk distributed H, without initial vacancies).

Figure 4. Configuration snapshots for a $[1\bar{1}0]$ strained $\alpha\text{-Al}_2\text{O}_3$ -terminated fcc-Al slab (Al – grey, O – red).

Figure 5. Configuration snapshots for a $[1\bar{1}0]$ strained α - Al_2O_3 -terminated fcc-Al slab with bulk distributed H, without initial vacancies (Al – grey, O – red, H – black).

Figure 6. Configuration snapshots for a $[1\bar{1}0]$ strained α - Al_2O_3 -terminated fcc-Al slab with initial H-filled vacancies (Al – grey, O – red, H – black).

3.2 Dislocation mechanisms

The observed dislocations are emitted predominantly along $\{113\}$ planes instead of expected $\{111\}$ slip for cracks in single crystal Al structures [18] or fcc metals generally [47-51]. The difference may be due to the quasi 2-dimensional (2D)/plane strain boundary condition in $[11\bar{2}]$ direction, $\{113\}$ being the 2D projection of a $\{111\}$ plane. The particular ($\{113\}$) plane, however, can be also related to the experimental findings of low angle $\langle 112 \rangle$ tilt axis grain boundary formation in fcc-Al [52], which is suggested as a possible mechanism for the observed partial dislocation facilitated grain formation in the initially single crystalline Al slabs. More generally, scale effects due to change in surface to volume ratio [53] at small strain levels [54] could account for the dislocation behavior in response to the particular boundary conditions.

The ability of the force field to produce slip along $\{111\}$ planes was verified by performing two additional incremental minimization simulations with smaller size $\{111\}$ fcc-Al slabs (section 2). Dislocation propagation along $\{111\}$ planes was observed both for a structure with a loading direction that favors $\{111\}$ slip (Figure 7a) and a structure with initial loading direction, but equivalent sizes in both periodic dimensions (Figure 7b). This is also in agreement with an earlier study using a related force field for Al nanowire simulations, which indicates only $\{111\}\langle 112 \rangle$ slip [47].

Figure 7. Central symmetry parameter [55, 56] distribution for $[11\bar{2}]$ (a) and $[1\bar{1}0]$ (b) strained fcc-Al slabs during the propagation of dislocations.

The overall behavior of void and slip assisted fracture, as present in the pristine Al simulation results, has been observed both experimentally and computationally in an aluminum alloy for positive average stress triaxiality below ~ 0.4 [57], which corresponds to the estimated stress triaxiality of ~ 0.33 for a uniaxially deformed structure with lateral stress relaxation in the current study. Yet the presence of H on crack surfaces indicates its effect on weakening the material prior to failure and the related void formation, which can be attributed to strong H-vacancy bonding [15] and the mechanism of surface-H facilitated transport of other H atoms to a surface [46]. Another possible mechanism is related to the increase in

dislocation nucleation energy barriers [4, 6], which may cause stresses at the crack tip that exceed the yield stress of the metal. This mechanism is in agreement with the current results, since less grain formation, particularly in the structure with initial vacancies, is observed for the H containing structures. Moreover, the extent of dislocation nucleation barriers ($\varepsilon=0.1$ and $\varepsilon=0.18$) clearly indicates H effect in the structure with initial vacancies, as compared against almost barrier-less dislocation emission in pristine Al (Figure 3). However, the H migration to the crack tip, in contrast to the high H concentration model in [6], does not exceed segregation on grain boundaries or in the vicinity of other defects. That can be attributed to the obtained stress distributions (Figure 8), which do not indicate extended stress gradient around the crack tip, instead suggesting localized stress concentration along grain boundaries, dislocations and other defects. Similarly, distinct Almansi strain tensor based octahedral strain localization [43] is observed along traces of slip bands, which form bridges between grain locations (Figure 9), as well as in the oxide layers and at oxide/metal interfaces before the dislocation nucleation.

Figure 8. Maximum normal virial stress [58] distribution for a $[1\bar{1}0]$ strained $\alpha\text{-Al}_2\text{O}_3$ -terminated fcc-Al slab.

configuration	ε	$e_{\text{oct-min}}$	$e_{\text{oct-max}}$
a	0.03	0.22	0.36
b	0.09	0.35	0.45
c	0.10	0.38	0.51
d	0.22	0.39	0.79

Figure 9. Atomic octahedral Almansi strain distribution for a $[1\bar{1}0]$ strained $\alpha\text{-Al}_2\text{O}_3$ -terminated fcc-Al slab.

3.3 Plasticity effects on hydrogen diffusivity

Two known H diffusion related mechanisms were distinguished in the simulations. First, the Gorski effect, which is attributed to long-range order relaxation by migration of solutes to regions of dilatation under stress gradient conditions until balance/equilibrium between chemical potential and solute concentration gradients is obtained. The mechanism is supported by simulation snapshots which indicate H accumulation at grain boundaries, voids and interfaces (Figure 5, Figure 6) [59]. Second, the Zener effect, which is defined as stress caused directional short-range order relaxation of interstitial atom pairs or solute-vacancy pairs due to lower symmetry strain fields [59]. The mechanism is in agreement with the obtained diffusivity estimates for different strain levels (Figure 11), which indicate a nonlinear relation between fcc-Al stress and the H diffusivities. Furthermore, a hysteresis type relation above 1 GPa is obtained with a saturation limit of about $2.5\text{e-}6\text{ cm}^2/\text{s}$, which suggests that plastic deformation may induce higher H migration, most likely occurring in high stress concentration regions, e.g., grain boundaries.

Likewise, the saturation limit is assumed to result from plastic deformation that limits the extent of local elastic strain, which accounts for the diffusion mechanisms discussed above. A further insight can be obtained by comparing diffusivities of sample sets of H atoms distributed in the bulk metal and on the newly formed inner Al surfaces (Figure 10), which indicate that the mean squared displacement of the surface H atoms approaches a constant value, hence a comparatively negligible diffusivity. This result correlates with the low H diffusivity in the H-filled vacancies structure (Table 2), which indicates that the H atoms primarily get trapped close to the vacancies or other defects. The latter observations significantly reduce the crack tip diffusion mechanism possibility [6]. This behavior is found to be in qualitative agreement with DFT calculated H diffusion barriers between tetrahedral and octahedral sites vs. migration away from a vacancy [15], the ab initio molecular dynamics (MD) results based theory for diffusion dependence on concentrations of lattice and trapped site H atoms [14] as well as in quantitative agreement with experimental data (Table 2). Furthermore, the agreement of non-strained bulk distributed H structure H diffusivities with ab initio reference data (Table 2) suggests that only lattice or only vacancies/defects placed H diffusivities are not strictly dependent on the respective H concentrations.

Figure 10. Comparison of bulk (a) and surface (b) 10-atom sample H diffusivities (D) and mean square displacement (MSD) in a $[1\bar{1}0]$ strained α - Al_2O_3 -terminated fcc-Al slab with bulk distributed H, without initial vacancies, at $\varepsilon=0.37$.

Figure 11. H diffusivity (D) vs. fcc-Al tensile stress (σ_{Al}) (a) and strain (ϵ) (b) in a $[1\bar{1}0]$ strained $\alpha\text{-Al}_2\text{O}_3$ -terminated fcc-Al slab with bulk distributed H, without initial vacancies.

Table 2. H diffusivity comparison for fcc-Al.

	$D[\text{cm}^2/\text{s} \times 10^{-6}]$
Experiment [11]	~ 0.15
DFT [14, 15] ^a	~ 1.7
Reax ($\epsilon=0$, no vacancies)	~ 1
Reax ($\epsilon=0$, vacancy trapped)	< 0.3

^a estimated using an Arrhenius relation, without vacancy effects

3.4 Strain rate effects

The strain rate effects for the structure with bulk distributed H were evaluated by comparing the potential energy and stress responses (Figure 12) for the dynamic stretching and fixed deformation relaxation at different tension strain levels. The fixed strain relaxation at maximum potential energy, which coincides with crack initiation, yields void formation ($\epsilon=0.17$, Figure 13), which significantly reduces the potential energy and stress. Likewise, a significant relaxation, by dislocation motion, occurs instantly after yielding ($\epsilon=0.06$). Related strain rate effects in plastic materials have been described by an MD validated empirical temperature dependent phonon damping terms, which result in sharp increase of flow stress, if a threshold strain rate value is exceeded [53]. In contrast, there are no potential energy or stress reductions at strain levels before yielding and comparatively small and slow reductions at strain levels after crack propagation. Subsequently, we concluded that, except for the crack initiation and propagation stages, the applied strain rate approaches a quasi-static state.

Figure 12. Potential energy (E_{pot}) (a) and tensile stress (σ) (b) vs. time: loading rate comparison for a $[1\bar{1}0]$ strained α - Al_2O_3 -terminated fcc-Al slab with bulk distributed H, without initial vacancies.

Figure 13. Relaxation of a $[1\bar{1}0]$ strained α - Al_2O_3 -terminated fcc-Al slab with bulk distributed H, without initial vacancies, at $\epsilon=0.17$: configuration snapshots at 280 ps (a) and 550ps (b) (Al – grey, O – red, H – black).

4 Conclusions

Al metal nanoslabs with oxidized surfaces, different initial defects and hydrogen distribution were studied by reactive molecular dynamics simulations. The purpose of the study was estimation of HE effects and comparison with known HE mechanisms.

It was found that under partial confinement conditions due to surface oxide layers, pristine material fails due to dislocation slip along grain boundaries and void formation. Hydrogen in initially defect free material migrates locally to newly formed grain boundaries and facilitates void assisted intergranular brittle crack initiation. Due to slow H surface migration further crack propagation occurs by dislocation slip. Hydrogen in uniformly volume distributed vacancies has significantly lower diffusivity than in defect free material, resulting in comparatively high dislocation emission barriers, limited grain formation

and void coalescence initiated locally plastic fracture failure without slab cross section size reduction before fracture.

Both hydrogen containing systems yield reduced predicted failure strains and strain energy capacity. Since the material strength is not significantly affected, the changes in material response are attributed to embrittlement effects. Finite temperature and strain rate effects on HE are manifested through diffusivity temperature dependence, the extent of relaxation at crack initiation and propagation, and negligible hydride region formation. Subsequently, the HE effect is expected to increase for quasi static strain rates. Hydrogen diffusivity dependence on microstructure is evident due to the presence of hysteresis in diffusivity as a function of tensile stress, which indicates an increase during plastic deformation, compared to purely elastic deformation.

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6 References

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