

α -Al₂O₃ nanoslab fracture and fatigue behavior



Osvalds Verners^a, George Psogianakis^b, Adri C.T. van Duin^{c,*}

^a Department of Mechanical and Nuclear Engineering, Pennsylvania State University, 235 Research East Building, University Park, PA 16802, USA

^b Department of Mechanical and Nuclear Engineering, Pennsylvania State University, 129 Research East Building, University Park, PA 16802, USA

^c Department of Mechanical and Nuclear Engineering, Pennsylvania State University, 136 Research East Building, University Park, PA 16802, USA

ARTICLE INFO

Article history:

Received 11 November 2014

Received in revised form 23 February 2015

Accepted 24 February 2015

Available online 28 March 2015

Keywords:

Fatigue

Phase transition

Alumina

Fracture

Molecular dynamics

ReaxFF

ABSTRACT

Strain rate effects and cyclic loading behavior, relevant for fatigue initiation processes, of single crystalline α -Al₂O₃ nanoslab structures in vacuum have been characterized and compared under finite temperature dynamic loading and incremental static loading conditions by reactive molecular dynamics and ionic relaxation simulations, respectively. Different failure mechanisms for each loading case are observed and compared in view of known applicable material failure mechanisms. In particular, structure size effects along with unit cell and bulk defect distribution based mechanisms are considered. The effects of lateral pre-strain are assessed. Conclusions are drawn regarding conditions which could lead to low cycle failure of the material.

The results indicate that finite temperature and strain rate result in lower failure strains, as compared to static relaxation calculations, however low strength enhancement of ductility with kinematic strain hardening upon repeated loading may occur. We suggest that the latter facilitates a shakedown mechanism. Positive pre-straining results in increased stress triaxiality (hydrostatic vs. equivalent stress), which significantly reduces crack healing probability, due to single sharp crack propagation. Instead, volume pre-relaxation results in multiple crack branching and/or amorphous band formation, which facilitates crack healing and deformation induced transition to purely elastic response (shakedown) possibility. Amorphization, which manifests as small strain plasticity enhancement, is found to occur ahead of propagating cracks due to multiple dislocation mechanism as a low energy barrier partially reversible low density phase transition, both at static and finite temperature/strain rate conditions. The observed property changes and phase change related defect healing mechanisms have been investigated further by bulk unit cell simulations and validated against DFT calculations.

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1. Introduction

The cyclic and static fatigue behavior of polycrystalline Al₂O₃ or Al₂O₃ based ceramics has been studied experimentally and analytically, considering strength and crack propagation rate dependence on grain boundary content and air vs. water [1–3] or inert vs. moist air [4] environment, as well as grain bridging shielding degradation dependence on grain size and loading level [5–7]. The interface strengthening effects, along with splat cracking and void coalescence development mechanisms, of Al₂O₃ coating application, e.g., for steel substrates [8], have also been studied. However, to the best of our knowledge, no atomistic fatigue studies beyond unit cell α -Al₂O₃ calculations [9] have been done. Yet, according to an experimental study [10], transgranular fracture, which may be dominant for unstable fracture [3,10], constitutes

~30% of fatigue fracture surfaces. Moreover, since experimental fatigue studies may not identify incipient atomistic failure mechanisms of single α -Al₂O₃ crystals in cyclic loading, this simulation study is intended as a contribution to the purpose. In order to form a link with general characteristics of single- and polycrystalline Al₂O₃ cracking, a brief overview of known phenomena will be presented in the remainder of this section.

The experimental data on polycrystalline, in particular nanocrystalline, Al oxide crack propagation indicate that cracks primarily propagate along grain boundaries [7,11]. In contrast, the brittleness of bulk crystalline Al₂O₃ has been explored in context of density distribution and extent of surface relaxation during crack opening in a DFT study [12]. Furthermore, the brittle vs. ductile deformation behavior of the material beside temperature can be influenced by deformation rate, grain size and the structure of the grain boundaries. In particular, the increase of deformation rate corresponds to increase in brittle to ductile transition temperature (BDTT) [13], whereas the presence of other elements, like Mg, may result in

* Corresponding author. Tel.: +1 814 863 6277.

E-mail address: acv13@psu.edu (A.C.T. van Duin).

Table 1
 α -Al₂O₃ elastic constants and fracture toughness values.

	$C_{11} + C_{12}$ (GPa)	C_{13} (GPa)	C_{33} (GPa)	K_{Ic} (MPa m ^{1/2}) 0001{10 $\bar{1}$ 0}	K_{Ic} (MPa m ^{1/2}) 10 $\bar{1}$ 0{0001}
DFT/experiment	660 [42]; 604.35	116 [42]; 109.12	500 [42]; 455.84	2.345 [43]	4.54 [44]
ReaxFF (AlOH_Oct2013)	781.33	344.04	506.16	2.413	4.528

formation of amorphous grain boundary phases that have lower melting temperatures than pure Al oxide. As a result, a transition from ductile to brittle at high temperatures may occur [14]. The grain size is found to be proportional to the slope of stress intensity vs. crack length (*R*-curve behavior), which implies that the fracture toughness of the material decreases with decreasing grain size [13,15]. This particular material behavior is explained by the corresponding reduction in crack path length surrounding the bridging grains (grains in compression due to mismatch between elastic and thermal properties of grains) and the mean value of residual stresses [15]. Lower residual stresses imply reduction of friction forces upon grain pullout from the embedding matrix. The residual stress reduction, in turn, is attributed to stress relaxation due to grain boundary diffusion, which is higher for smaller grains [16]. Likewise, the *R*-curve behavior may be significantly reduced by addition of second phase particles, like ZrO₂ or SiC, due to resultant reduction in grain size [15].

For brittle transgranular fractures at room temperature fracture, morphologies of even fracture surfaces, surfaces with step-terraces and surfaces mainly composed by curved fracture have been identified [17]. Likewise, single sapphire crystal plates fatigue mechanism has been studied phenomenologically, indicating loading orientation dependent spatial perturbations along low energy cleavage planes [18]. Beside transgranular fractures that occur along the primary crack line along with intergranular fractures, the crack-interface grain bridging [19], which may appear between overlapping cracks, separated by several grain diameters, has been identified as a mechanism for explaining the *R*-curve behavior of the material under the assumption that no phase transformation takes place. This behavior is found to correlate with the findings of an acoustic emission study which attributes the propagation of the primary crack at room temperature to two crack resistance mechanisms which consist in coalescence of microcracks behind the crack tip and energy dissipation in the flanks of the crack [20].

Crystalline to amorphous (CA) transformation due to overall pressure has been reported for TiO₂ [21] and Y₂O₃ [22], as well as for hypervelocity impact deformations [23,24]. Specifically, amorphization in α -alumina under hypervelocity impact has been observed in large-scale MD simulations [23], where the amorphous regions are found to act as a source of dislocations. Instead, at the interface between amorphous domains and crystalline phases domains cracks are reported to initiate [23]. Likewise, amorphization has been observed in mullite (3Al₂O₃–2SiO₂) samples shocked above the phase-transition pressure [24]. Alternatively, CA transition in elastic loading can be a sudden collapse of the lattice when the crystal is brought to become mechanically unstable, e.g., due to the loss of shear rigidity [25,26]. The latter, according to [26], is valid for homogeneous processes of mechanical melting, which can be observed at extremely high deformation rates, or upper limit of superheating. Another deformation mechanism by amorphization induced plasticity has been introduced in [27]. According to this mechanism, nanoscale amorphization (NA) serves as a special plastic shear deformation mode in initially crystalline Ni and Si nanowires. For alumina such phenomenon could be partially attributed to the observed reduction of yield strength and stiffness in amorphous phases, which is related to lower density of the amorphous phases [28]. Similarly, in [29] non-viscous, plastic deformation behavior at low stress values ($\sim$ 360 MPa) in amorphous ZrO₂–Al₂O₃ under compression has been attributed to the

low density of the amorphous phase [29]. In the latter case plasticity onset is associated with a sharp yield drop and the formation of localized shear bands throughout the sample [30]. In contrast, Al nanowire amorphization has been explained by increased defect concentration, presumably due to a large surface/volume ratio, which results in reduction of plasticity due to necking type fracture [30]. Subsequently, it is suggested that amorphization may serve as a locally plastic, macroscopically brittle failure mechanism in materials with large dislocation barriers, including ceramics [31].

2. Method

(10 $\bar{1}$ 0) slab structures with periodic dimensions of 15.23 $\times$ 0.488 nm in [10 $\bar{1}$ 0]/[$\bar{1}$ 2 $\bar{1}$ 0] directions, respectively, thickness of 15.25 nm and a rectangular (10 $\bar{1}$ 0)/[10 $\bar{1}$ 0] surface notch were considered in the study.

The Nose–Hoover thermo- and barostats, coupled with equations of motion in velocity Verlet formulation [32], were used for the simulations. Single chain thermostat was used for the pressure equilibration.

Both dynamic and static cyclic deformation in [10 $\bar{1}$ 0] direction was simulated in order to evaluate finite temperature effects versus the static/low temperature case. For the dynamic simulation a loading rate of 5e–6 fs^{–1} in 0.25% (0.5 ps) strain increments alternating with 5 ps relaxation periods was applied. The corresponding loading frequency was 1.9 ns^{–1}. The constant size, pressure and temperature ensemble (NPT) with the strained dimension kept fixed, at 300 K with 100 fs damping, 0 Pa with 5000 fs damping

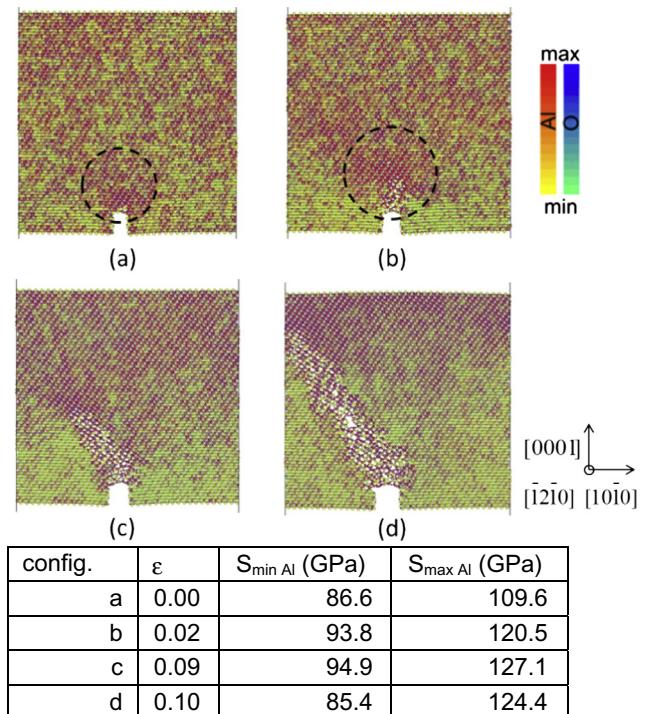


Fig. 1. Maximum normal virial stress [50] distribution for a [10 $\bar{1}$ 0] strained α -Al₂O₃ slab (300 K).

and 1 thermostat chain on barostat, was used in the MD simulations. The simulation step size was 0.2 fs. For the static simulations 0.25% strain increments with subsequent minimization were applied. In addition to the 0 atm volume-minimized structure a 7% $[10\bar{1}0]/[\bar{1}2\bar{1}0]$ pre-strained structure was simulated for

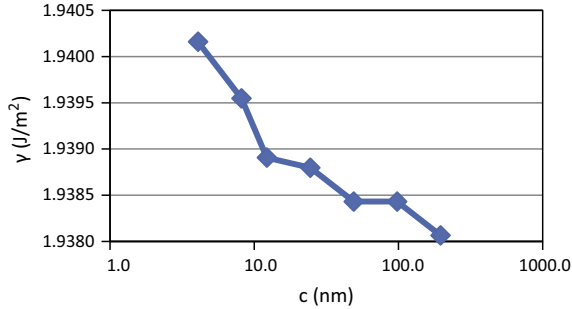


Fig. 2. α - Al_2O_3 Al-terminated (0001) surface energy vs. slab thickness.

Table 2

1st and 2nd loading cycle failure strains, virial stresses and potential energies for $[10\bar{1}0]$ strained α - Al_2O_3 slabs.

T (K)	ε_0	ε_{f1}	ε_{f2}	S_{f1} (GPa)	S_{f2} (GPa)	ΔE_{f1} (GJ/mol)	ΔE_{f2} (GJ/mol)
300	0	0.095	0.13	27.4	17.7	0.086	0.071
0	0.07	0.150	0.120	68.9	35.5	0.251	0.096
0	0	0.145	0.125	81.1	70.9	0.255	0.197

comparison. For static simulations the $[\bar{1}2\bar{1}0]$ dimension was kept fixed at its initial value. Thus plane stress conditions were obtained for the dynamic simulation and mixed plane strain/plane stress conditions in directions $[\bar{1}2\bar{1}0]/[0001]$ for the static systems. For all systems the tensile strain was increased up to a strain level after fracture initiation, subsequently reduced to a compression level within elastic response range and reloaded in tension up to a second fracture initiation. For the volume-minimized static simulation a second loading cycle was performed. For comparison separate compression simulations from the initial state for all systems were performed for comparison.

The incremental α - Al_2O_3 unit cell minimization calculations were done using conjugate gradient (CG) and damped MD based methods [33] (algorithm ‘fire’ [34]) with a root mean square force per atom tolerance of 41.84 TJ/mol/m (0.1 kcal/mol/Å).

For the study the LAMMPS [33,35] implementation of the reactive force field ReaxFF, as described in [36], was used. The ReaxFF force field versions used in the simulations have been based on earlier published versions of Al/O [37,38], Al/H [39], O/H [40] and Al/O/H [41] force fields (Table 1).

To examine the structural and energetic behavior of α - Al_2O_3 upon expansion and compression in the $[10\bar{1}0]$ direction (Fig. 9), DFT calculations [45] were performed with VASP software [46] using the projector-augmented-wave (PAW) potentials [47] and the generalized gradient approximation (GGA-PBE) [48]. The 30-atom (12 Al and 18 O) conventional hexagonal unit cell of the corundum crystal structure was used. The wavefunctions were expanded in a plane-wave basis set with 50.2 MJ/mol (520 eV) energy cutoff, much greater than the minimum recommended 38.6 MJ/mol (400 eV) energy cutoff for the Al, O PAW-PBE

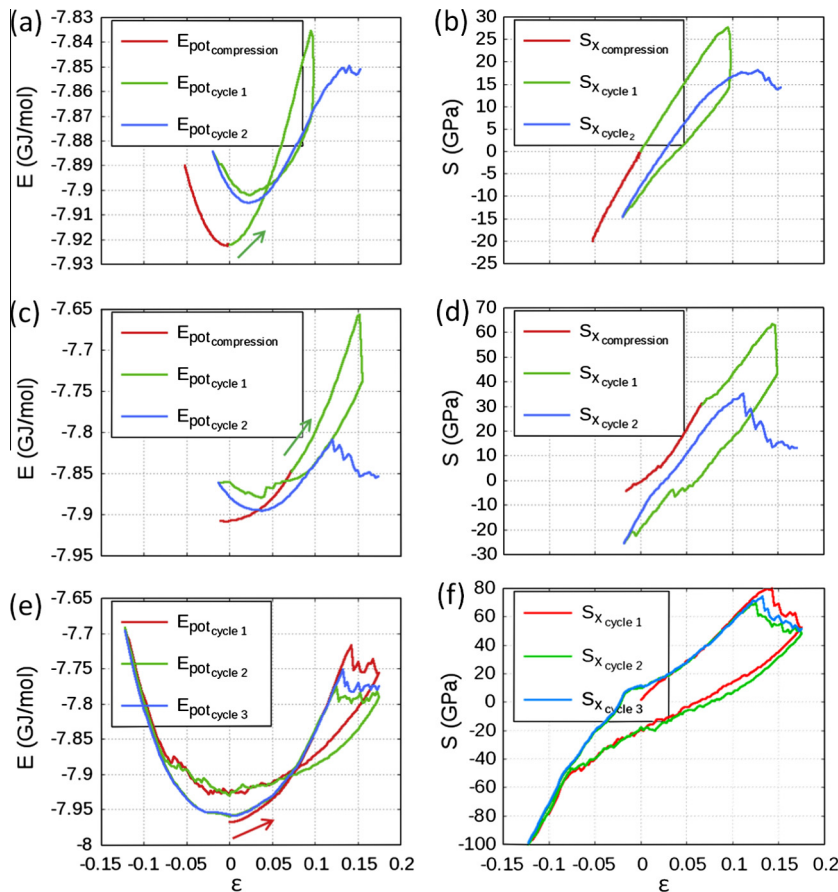


Fig. 3. Potential energy and tensile virial stress vs. strain for $[10\bar{1}0]$ strained α - Al_2O_3 slabs at 300 K (a and b), $\varepsilon_0 = 0.0$, and at 0 K with $\varepsilon_0 = 0.07$ (c and d) and $\varepsilon_0 = 0.0$ (e and f).

potentials. A $6 \times 6 \times 2$ Γ -centered k-point mesh was used (much longer c -axis), in conjunction with Gaussian smearing with smearing width $\sigma = 0.05$, to sample the Brillouin zone. Optimizations were done with the conjugate gradient algorithm implemented in VASP using the default total energy convergence criteria, 9.6 J/mol (10^{-4} eV) for the electronic loop and 96 J/mol (10^{-3} eV) for the ionic optimization. The hexagonal lattice of α -Al₂O₃ was first optimized, and thereafter the cell was expanded in the relevant direction and ionic optimizations were performed with fixed lattice vectors.

3. Results and discussion

Stress distributions for all structures indicate structure-wide stress gradients up to crack surface vicinity (Fig. 1), which correspond to purely elastic/brittle material response. The absence of uniform stress regions is attributed to the estimated size effect limit of about 5 nm from a (0001) surface, according to the change in slope of surface energy vs. slab thickness curve at around 10 nm

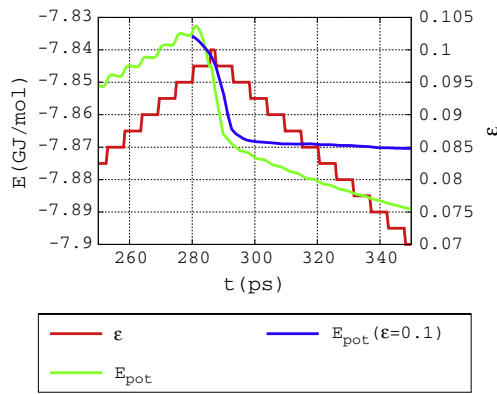


Fig. 4. Potential energy vs. time for a $[10\bar{1}0]$ strained α -Al₂O₃ slab at 300 K: relaxation effect comparison.

(Fig. 2). The main numerical results are summarized in Table 2. These indicate that temperature enhances plasticity upon repeated loading, since the system at 300 K fails at a larger strain during the second tension cycle, as compared to the first cycle (values ε_{f1} , ε_{f2}). Yet the overall brittleness is increased at 300 K due to lower failure strains, stresses (S_{f1} , S_{f2}) and potential energy (differences with respect to the $[10\bar{1}0]$ tensile stress free state ΔE_{f1} , ΔE_{f2}), as compared to the static simulations. Furthermore, the pre-expanded structure ($\varepsilon_0 = 0.07$) indicates lower failure stresses and potential energy, particularly for the second loading cycle, as compared to the volume-minimized static structure, although both failure strains are approximately identical and decreasing for repeated cycles. Thus it may be concluded that pre-expansion weakens the material response, as expected due to increased stress triaxiality, and that under the given loading conditions low cycle fatigue is likely to occur in static systems under positive pre-strain, whereas shakedown [49] (deformation induced transition to purely elastic response) may occur for the 300 K system at constant strain amplitude loading.

More insights can be obtained from the potential energy and stress response plots (Fig. 3). Due to the positive shifts in minimum energy locus along potential energy and strain axes it can be concluded that temperature and pre-expansion reduce crack healing probability and facilitate kinematic strain hardening effect. Instead, the volume-minimized static structure indicates no kinematic hardening and notable crack healing due to negligible increase in potential energy and evident closing of most of the cracks upon compression.

The extent of strain rate effect for the 300 K system could be estimated by performing a constant strain relaxation shortly before reaching the maximum strain of $\varepsilon = 0.1$ during the first cycle (Fig. 4), which indicates that fracture strain level is slightly overestimated compared to quasi-static loading, the deviation being ascribed to differences in dynamics of loading and amorphization/fracture propagation processes. Slight dynamics change in structure relaxation during unloading compared to constant strain level is also observed. Subsequently, the overall strain rate effect is not considered being significant.

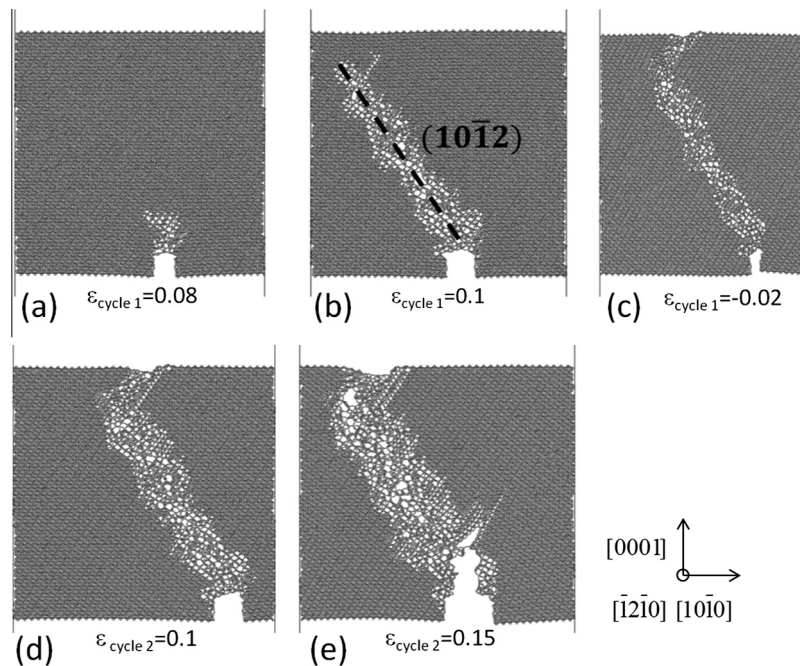


Fig. 5. Configuration snapshots for a $[10\bar{1}0]$ strained α -Al₂O₃ slab at 300 K.

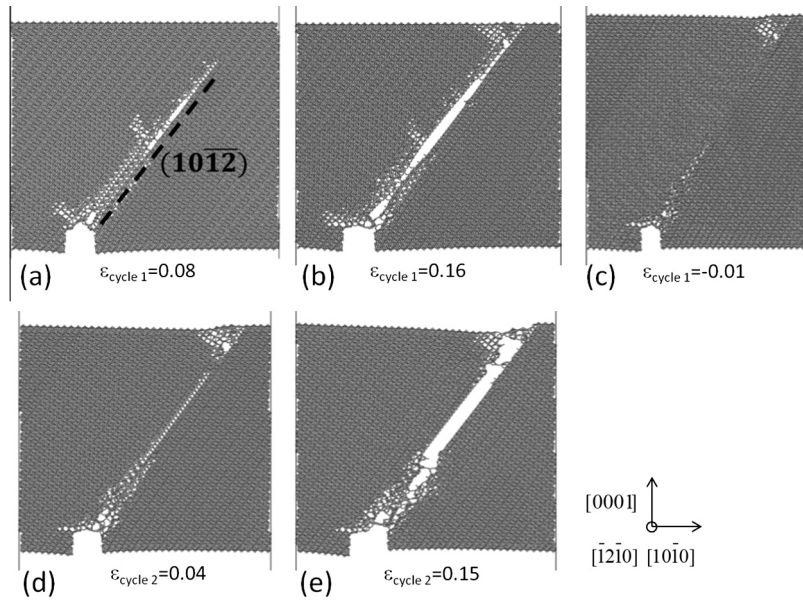


Fig. 6. Configuration snapshots for a $[10\bar{1}0]$ strained $\alpha\text{-Al}_2\text{O}_3$ slab at 0 K, $\epsilon_0 = 0.07$.

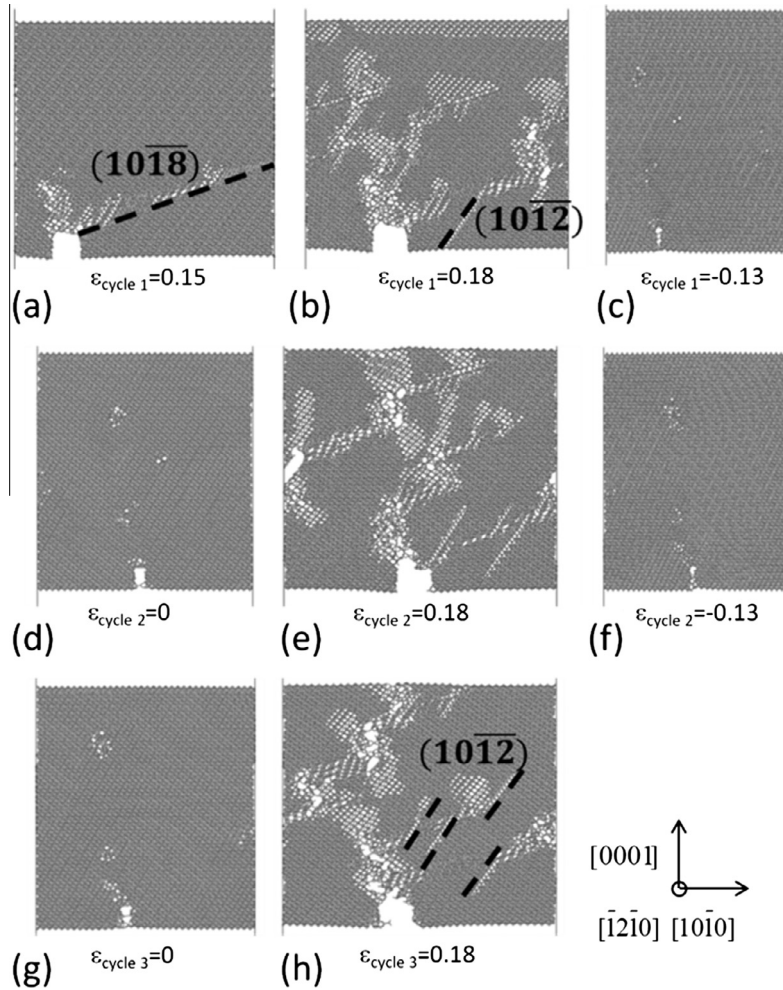


Fig. 7. Configuration snapshots for a $[10\bar{1}0]$ strained $\alpha\text{-Al}_2\text{O}_3$ slab at 0 K, $\epsilon_0 = 0.0$.

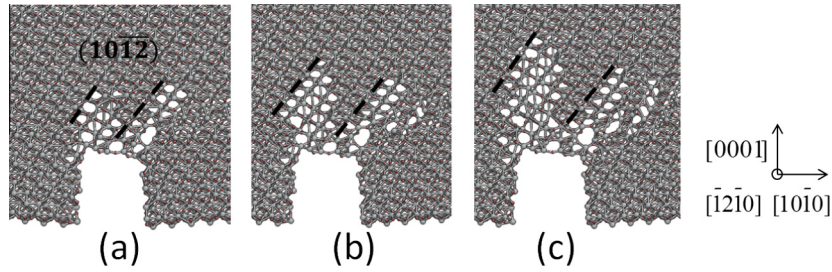


Fig. 8. Phase transition facilitated amorphization mechanism for a $[10\bar{1}0]$ strained α - Al_2O_3 slab.

It is worth indicating that the volume distributed crack pattern of the volume-minimized static structure is notably different from the pre-expanded static or 300 K volume-minimized systems, which indicate a single crack propagating along a $\{10\bar{1}2\}$ plane and a lower density band formation along a $\{10\bar{1}2\}$ plane (Figs. 5–7), respectively. Both are experimentally detected fracture planes [17,44]. In the case of the 300 K system we suggest that a fracture mechanism at room temperature could be $\{10\bar{1}2\}$ slip initiated layer-wise phase transition and subsequent amorphization (Fig. 8), in agreement with the unit cell $[10\bar{1}0]$ deformation results (Fig. 9) and experimentally detected slip planes [31]. We also observed that repeated loading in the volume-minimized static system may reduce $\{10\bar{1}8\}$ dislocation emission probability, instead favoring $\{10\bar{1}2\}$ dislocations with a higher resolved normal stress (Fig. 7) and cleavage probability [17].

A comparison of total ($\sum\gamma dA$) and surface-normalized (γ) surface energies, corresponding to the Griffith criterion for brittle fracture [51] at equivalent loading conditions (lateral strains $\epsilon_{\text{lateral}}$ and temperatures), and critical energy releases (ΔE_{crit}) during the stretching simulations was motivated by the observed differences in failure behavior in the $\{10\bar{1}2\}$ and $\{10\bar{1}2\}$ planes. The results of it are summarized in Tables 3 and 4.

For the pre-relaxed structure at 300 K (Table 3), the similarity of critical reduction in energy and Griffith criterion suggests that transition to a lower density phase instead of brittle fracture could

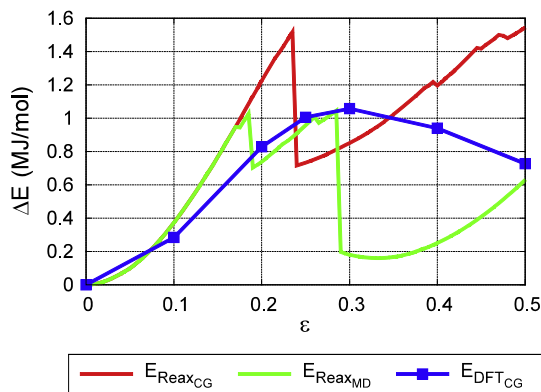


Fig. 9. $[10\bar{1}0]$ expansion equation of state a hexagonal α - Al_2O_3 unit cell (CG – conjugate gradient, MD – damped dynamics based minimization).

Table 3
Comparison of surface energies and critical strain energy releases during α - Al_2O_3 slab $[10\bar{1}0]$ expansion.

ΔE_{crit} (MJ/mol)	$\sum\gamma dA$ (MJ/mol)	$\epsilon_{\text{lateral}}^a$	T (K)	Damage planes
37.7	30.0	0	300	$\{10\bar{1}2\}$, $\{10\bar{1}2\}$
104.6	154.1	0.07	0	$\{10\bar{1}2\}$

^a $[\bar{1}2\bar{1}0]$ direction strain.

be energetically marginally favorable, which is partially supported by unit cell calculations (Fig. 9). For the pre-strained structure at 0 K (Table 3), the significantly lower critical reduction in energy, as compared to the Griffith criterion, is being attributed to the slab thickness size effect related (0001) surface relaxation prior to fracture, presumably facilitated by the relatively high accumulated potential energy (Table 2). The absence of $\{10\bar{1}2\}$ fracture despite the latter being significantly lower in energy at strained state (Table 4) is being attributed to the blunting by formation of lower density phase bands – two small bands along $\{10\bar{1}2\}$ planes and a single band along a $\{10\bar{1}2\}$ plane (Fig. 6). The band formation in both planes instead of $\{10\bar{1}2\}$ only is ascribed to the reduced energy barrier for laterally strained bulk material (Fig. 10). In distinction to the 300 K simulation, a transition to brittle fracture along the $\{10\bar{1}2\}$ plane where a lower density band was formed occurs immediately after the occurrence of the second small lower density band along a $\{10\bar{1}2\}$ plane. Subsequently, we attribute the difference in behavior from purely brittle bulk behavior predictions (Table 4) to the energetic feasibility of phase transitions, which also explains the comparatively high accumulated strain energy before fracture (Table 3), and geometry/size effects.

Furthermore, the difference in crack distribution evidently correlates with the potential energy and stress responses after yielding, which indicate a gradual discontinuous reduction for the volume-minimized static structure and a sharp drop for the other two structures (Fig. 3). The volume distributed pre-cracks in the volume-minimized static structure grow by void coalescence (Fig. 7), which is in agreement with experimental observations from fatigue studies of alumina coatings [8]. The crack healing, which was observed for this structure (Fig. 7), is in agreement with earlier DFT results [9]. According to these, such crack healing can be expected for structures with zero or negative lateral pre-strain levels [9], which explains the negligible amount of healing for the pre-expanded structure (Fig. 6). Subsequently, we concluded that processing technologies which favor compressive residual stress formation, hence a reduced stress triaxiality, would be recommendable for large polycrystalline or single crystal α - Al_2O_3 structures under cyclic loading.

Table 4
 α - Al_2O_3 surface energy comparison.

surface	Termination	γ (J/m ²) ^a	$\epsilon_{\text{lateral}}^b$	T (K)
$\{10\bar{1}2\}$	Al	3.15	0	0
		3.45	0.07	0
		3.19	0	300
$\{10\bar{1}2\}$	mixed	2.33	0	0
		15.63	0.07	0
		2.81	0	300
(0001)	Al	1.94	0	0

^a Potential energy based.

^b $[\bar{1}2\bar{1}0]$ direction strain.

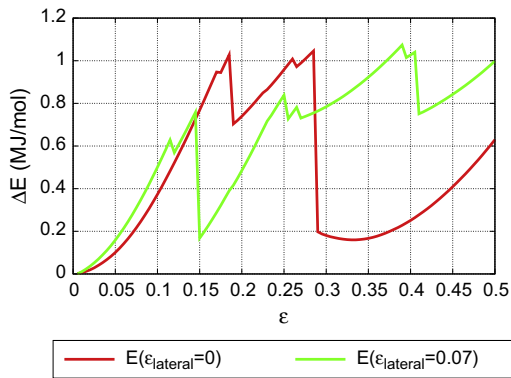


Fig. 10. $[10\bar{1}0]$ expansion equation of state a hexagonal α - Al_2O_3 unit cell at different lateral ($[\bar{1}2\bar{1}0]$) strain levels, using MD – based minimization.

In order to validate the suggested phase transition facilitated fatigue and compression induced healing mechanisms prior to crack opening, a comparison was done using DFT calculations. Analogous deformation in $[10\bar{1}0]$ with lateral dimensions fixed was applied to a hexagonal α - Al_2O_3 unit cell. It indicates (Fig. 9) that a phase transitions occur for both methods at around $\varepsilon = 0.25$, with a discontinuous barrier of between 1.0 and 1.5 MJ/mol for ReaxFF, depending on the minimization method used, and a continuous plastic deformation barrier of about 1.0 MJ/mol for DFT. Furthermore, we also found that upon compression both methods yield transition back to the α phase. It occurred at about $\varepsilon = -0.11$ for ReaxFF and between $\varepsilon = -0.18$ and $\varepsilon = -0.10$ for DFT, starting from a phase obtained at $\varepsilon = 0.70$ expansion in the latter case. Subsequently, we concluded that, despite minimization related differences in energy responses after the first phase transition in tension, the behavior of phase transitions was compatible for both methods below local strain levels of $\varepsilon = 0.5$.

4. Conclusion

We have performed a molecular dynamics study of fatigue initiation processes in α - Al_2O_3 nanoslabs. The results indicate that finite temperature and strain rate result in lower failure strains, as compared to static relaxation calculations. However, low strength enhancement of ductility with kinematic strain hardening upon repeated loading for the former case may occur. We suggest that the latter enhancement facilitates a shakedown mechanism.

Positive pre-straining results in increased stress triaxiality, which significantly reduces crack healing probability, due to single brittle crack propagation. Volume pre-relaxation results in multiple crack branching and/or amorphous band formation, which facilitates crack healing and shakedown possibility.

Amorphization, which manifests as small strain plasticity enhancement, may occur ahead of propagating or initiating cracks due to multiple dislocation mechanism as a low energy barrier quasi-plastic low density phase transition, both at static and finite temperature/strain rate conditions. Additional fatigue degradation contribution may be due to a change in dominant fracture planes upon repeated loading.

Acknowledgements

We acknowledge funding from the National Energy Technology Laboratory, US Department of Energy, under Award No. DE-EE0005867.

We also would like to thank D. Warner for the helpful discussions.

References

- [1] S.M. Barinov, N.V. Ivanov, S.V. Orlov, V.Y. Shevchenko, *Refract. Ind. Ceram.* 37 (1996) 375–377.
- [2] T. Okabe, M. Kido, T. Miyahara, *Eng. Fract. Mech.* 48 (1994) 137–146.
- [3] B. Shi, W.Y. Chu, Y.J. Su, K.W. Gao, L.J. Qiao, *J. Am. Ceram. Soc.* 88 (2005) 353–356.
- [4] C.P. Chen, W.J. Knapp, in: *Fatigue fracture of an alumina ceramic at several temperatures*, Plenum, New York, NY, USA, 1974, pp. 691–707.
- [5] H.E. Attiaoui, M. Saâdaoui, J. Chevalier, G. Fantozzi, *J. Am. Ceram. Soc.* 88 (2005) 172–178.
- [6] C.J. Gilbert, R.N. Petrany, R.O. Ritchie, R.H. Dauskardt, R.W. Steinbrech, *J. Mater. Sci.* 30 (1995) 643–654.
- [7] X. Hu, Y.W. Mai, *J. Am. Ceram. Soc.* 75 (1992) 848–853.
- [8] O. Kovarik, J. Siegl, J. Nohava, P. Chraska, *J. Therm. Spray Technol.* 14 (2005) 231–238.
- [9] E.A.A. Jarvis, E.A. Carter, *Nano Lett.* 6 (2006) 505–509.
- [10] M. Li, F. Guiv, *Acta Metall. Mater.* 43 (1995) 1871–1884.
- [11] L. Hanlian, T. Xinying, H. Chuazhen, *Mater. Sci. Amp. Eng. A (Struct. Mater.: Prop. Microstruct. Process.)* 452–453 (2007) 545–551.
- [12] E.A.A. Jarvis, R.L. Hayes, E.A. Carter, *ChemPhysChem* 2 (2001) 55–59.
- [13] J.-F. Li, R. Watanabe, *JIM* 40 (1999) 508–513.
- [14] J. Koike, H. Oikawa, S. Wakiya, T. Takeda, K. Maruyama, in: *11th International Conference on the Strength of Materials: 25–29 August 1997*, Elsevier, Switzerland, 1997, pp. 529–532.
- [15] H. Tomaszewski, M. Boniecki, H. Weglarz, *J. Eur. Ceram. Soc.* 20 (2000) 2569–2574.
- [16] Q. Ma, D.R. Clarke, *J. Am. Ceram. Soc.* 77 (1994) 298–302.
- [17] H. Matsuo, M. Mitsuhara, K. Ikeda, H. Nakashima, *Int. J. Fatigue* 32 (2010) 592–598.
- [18] D. Sherman, I. Be'ery, *J. Mater. Sci.* 35 (2000) 1283–1293.
- [19] P.L. Swanson, C.J. Fairbanks, B.R. Lawn, Y.W. Mai, B.J. Hockey, *J. Am. Ceram. Soc.* 70 (1987) 279–289.
- [20] C. Sklarczyk, *J. Eur. Ceram. Soc.* 9 (1992) 427–435.
- [21] V. Swamy, A. Kuznetsov, L.S. Dubrovinsky, P.F. McMillan, V.B. Prakapenka, S. Guoyin, B.C. Muddle, *Phys. Rev. Lett.* 96 (2006) 135702–135701.
- [22] L. Wang, W. Yang, Y. Ding, Y. Ren, S. Xiao, B. Liu, S.V. Sinogeikin, Y. Meng, D.J. Gosztola, G. Shen, R.J. Hemley, W.L. Mao, H.-K. Mao, *Phys. Rev. Lett.* 105 (2010).
- [23] C. Zhang, R.K. Kalia, A. Nakano, P. Vashishta, *Appl. Phys. Lett.* 91 (2007) (1911) 121911.
- [24] N. Kawai, Y. Harada, M. Yokoo, T. Atou, K.G. Nakamura, K. Kondo, *Int. J. Impact Eng* 35 (2008) 1612–1615.
- [25] E. Ma, *Scripta Mater.* 49 (2003) 941–946.
- [26] J. Wang, J. Li, S. Yip, D. Wolf, S. Phillpot, *Physica A* 240 (1997) 396–403.
- [27] I.A. Ovid'ko, *Scripta Mater.* 66 (2012) 402–405.
- [28] J.C. Barbour, J.A. Knapp, D.M. Follstaedt, T.M. Mayer, K.G. Minor, D.L. Linam, in: *10th International Conference on Radiation Effects in Insulators: 18–23 July 1999*, Elsevier, Netherlands, 2000, pp. 140–147.
- [29] A.S. Gandhi, V. Jayaram, *Acta Mater.* 51 (2003) 1641–1649.
- [30] S. Kumar, K.L. Joshi, A.C.T. van Duin, M.A. Haque, *Nanotechnology* 23 (2012) 095701. 095708 pp.
- [31] T.E. Mitchell, K.P.D. Lagerlof, A.H. Heuer, *Mater. Sci. Technol.* 1 (1985) 944–949.
- [32] D. Frenkel, B. Smit, *Understanding Molecular Simulation - From Algorithms to Applications*, Second ed., Academic Press, 2002.
- [33] LAMMPS Users Manual. <<http://lammmps.sandia.gov>>, 2014.
- [34] E. Bitzek, P. Koskinen, F. Gahler, M. Moseler, P. Gumbsch, *Phys. Rev. Lett.* 97 (2006) 170201.
- [35] S. Plimpton, *J. Comput. Phys.* 117 (1995) 1–19.
- [36] A.C.T. Van Duin, S. Dasgupta, F. Loran, W.A. Goddard III, *J. Phys. Chem. A* 105 (2001) 9396–9409.
- [37] F.G. Sen, Y. Qi, A.C.T. Van Duin, A.T. Alpas, *Appl. Phys. Lett.* 102 (2013).
- [38] Q. Zhang, T. Çağın, A. van Duin, W.A. Goddard III, Y. Qi, L.G. Hector Jr., *Phys. Rev. B* 69 (2004) 045423.
- [39] J.G.O. Ojwang, R.A. van Santen, G.J. Kramer, A.C.T. van Duin, W.A. Goddard, *J. Chem. Phys.* 131 (2009) 044501 (044513 pp.).
- [40] A.C.T. Van Duin, V.S. Bryantsev, M.S. Diallo, W.A. Goddard, O. Rahaman, D.J. Doren, D. Raymond, K. Hermansson, *J. Phys. Chem. A* 114 (2010) 9507–9514.
- [41] M. Russo, R. Li, M. Mench, A.C.T. van Duin, *Int. J. Hydrogen Energy* 36 (2011) 5828–5835.
- [42] J.C. Boettger, *Phys. Rev. B: Condens. Matter* 55 (1997) 750.
- [43] Y. Mitamura, Y. Wang, *J. Biomed. Mater. Res.* 28 (1994) 813–817.
- [44] R.A. Schults, M.C. Jensen, R.C. Bradt, *Int. J. Fract.* 65 (1994) 291–312.
- [45] P. Hohenberg, W. Kohn, *Phys. Rev.* 136 (1964) B864–B871.
- [46] G. Kresse, J. Hafner, *Phys. Rev. B* 47 (1993) 558–561.
- [47] P.E. Blöchl, *Phys. Rev. B* 50 (1994) 17953–17979.
- [48] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865–3868.
- [49] J.A. Koenig, *Shakedown of Elastic-Plastic Structures*, Elsevier, 1987.
- [50] M. Zhou, in: *44th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference: April 7, 2003–April 10, 2003*, American Institute of Aeronautics and Astronautics Inc., Norfolk, VA, United states, 2003, pp. 3368–3383.
- [51] N.E. Dowling, *Mechanical Behavior of Materials: Engineering Methods for Deformation, Fracture, and Fatigue*, Third ed., Prentice Hall, 2006.