A Nanoscale Mechanism of Fatigue in Ionic Solids

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ABSTRACT

We employ periodic density functional theory to explore the effect of cyclic tensile loading on the behavior of alumina in the threshold region of crack formation. We find evidence for nanoscale fatigue when the alumina lattice is subjected to uniaxial tensile loading and unloading and tensile stresses normal to the applied load. It is possible that such atomic-scale fatigue impacts the durability of ceramics, since the highly ionic bonding requires near-ideal lattice structures in order to maintain cohesive strength.

Advanced design and applications of materials require specification of the ideal material properties as well as an appreciation for how these properties are modified through physical and chemical degradation. In particular, as the pursuit of novel properties associated with nanodevices drives length scales ever smaller, an atomic-level understanding of materials properties becomes essential. Interestingly, some properties that have been well-characterized for decades at the macroscopic level become much more elusive at the microscopic level. The competing mechanisms associated with materials failure make it particularly challenging to characterize over a variety of length scales.

The cause and impact of fatigue processes in materials have been of interest to engineers and materials scientists for decades. The impact of fatigue properties in ceramics is critical in a variety of advanced structural applications. Fracture and fatigue behavior of alumina, Al₂O₃, have been investigated as they relate to a variety of pertinent properties and conditions such as impact strength,¹ temperature dependence,² static and cyclic loading,³-⁴ grain size,⁵-⁷ crack closure,⁸ and formation of dislocations and twinning due to abrasion.⁹ Similar fracture properties have been explored for oxide scales,¹₀ aluminum/alumina interfaces,¹¹ and other ceramics such as silicon carbide,¹² silicon nitride,¹³ and partially stabilized zirconia.¹⁴ Recently, studies of glass fracture via atomic force microscopy have shown similarities between ductile and brittle fracture, with the primary difference being order of magnitude length scale differences rather than fundamental mechanisms of failure,¹⁵ potentially opening a wealth of understanding from the extensive literature of fatigue in metals for application to brittle ceramics. Although significant contributions have been made in terms of analytical modeling of fatigue and fracture as well as some atomistic and ab initio dynamics, such as those detailed in refs ²⁰-³⁴, a detailed atomic-level understanding of the many competing factors in such materials failure remains far from complete.

Previously, we discussed the effects of oxidation on atomic-level mechanisms of crack formation in aluminum.³⁵ We showed how local changes to the electron density arising from aluminum oxidation hold significant implications for materials properties. Namely, the highly localized electron density of the large band gap oxide Al₂O₃ leads to nanocrack formation at considerably smaller tensile strains than required for irreversible crack formation in aluminum. Furthermore, the ionic bonding in Al₂O₃ results in significant relaxations of the surface upon crack formation, potentially inhibiting healing of small cracks. This feature, whereby alumina experiences dramatic surface relaxations due to the ionic nature of its bonding, is critical to our present discussion.

Here we show that the ionic bonding of the alumina crystal may lead to atomic-scale fatigue-type processes. Using periodic density functional theory (DFT)³⁶ within the generalized gradient approximation (GGA) (PW91)³⁷ for the electron exchange and correlation potential as implemented in the Vienna Ab Initio Simulation Package (VASP),³⁸ we investigate the “threshold” region of crack formation in α-Al₂O₃, i.e., where introduced nanocrack defects are small enough that it is energetically favorable for a crystal with

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an equilibrium bulk structure to heal the void rather than create two surfaces. Crack formation perpendicular to the c-axis of the α-Al₂O₃ hexagonal cell was investigated for three distinct cases: (1) with in-plane (a and b) lattice vectors fixed to ideal bulk values, (2) with compression of these lattice vectors by ≈5%, and (3) with expansion of these lattice vectors by ≈5%, corresponding to a local change of 0.1 Å in Al–O bond lengths. These local bonding defects, introduced through compression or expansion of the periodic cell, are designed to approximate a locally strained region at a crack tip rather than global crystal strain.

Our calculations employed the standard VASP ultrasoft pseudopotentials (VASP, version 4.4.4) to replace the core electrons plus nuclei; a nonlinear core correction to the exchange-correlation functional was included for Al. We tested total energy convergence with respect to k-point sampling density and kinetic energy cutoff of the plane wave basis for bulk α-Al₂O₃. As a result, we employed a k-point sampling of 3 × 3 × 1 for the hexagonal unit cell of Al₂O₃, kinetic energy cutoffs of 338 eV for the plane-wave basis, and 554 eV for the augmentation charge basis needed for the ultrasoft pseudopotentials. The chosen cutoffs and k-point density resulted in total energies converged to within the meV/atom range.

We optimized the volume of the primitive crystals by performing a series of single point energy calculations uniformly scaling the lattice vectors within ≈5% of the equilibrium value and fitting to the Murnaghan equation of state. For the ideal bulk crystal cases, the optimized cell equilibrium value and fitting to the Murnaghan equation of uniform scaling the lattice vectors within performing a series of single point energy calculations in the meV/atom range.

To simulate crack formation, we introduce tensile strain for α-Al₂O₃ and allow the ionic coordinates to relax so as to minimize the energy using a conjugate gradient relaxation from the initial bulk ionic coordinates. We introduce successively wider nanocracks until the relaxed coordinates can no longer heal the crack, as evidenced by a lack of sufficient electron density percolating across the two surfaces. We then investigate possible fatigue-type processes due to cyclic (tensile) loading and unloading in this threshold region of crack formation. Surfaces with relaxed ionic coordinates are brought back together to mimic unloading of a sample, i.e., the nanocrack thickness is decreased, to replicate the values of strain at which the defect site would have healed when starting from bulk ionic coordinates.

Figure 1 displays the bulk hexagonal α-Al₂O₃ with aluminum represented by black spheres and oxygen by red spheres. The dashed line indicates the location between adjacent Al planes parallel to (0001) where nanocracks are introduced.

Figure 1. Bulk hexagonal cell of α-Al₂O₃ with aluminum represented by black spheres and oxygen by red spheres. The dashed line indicates the location between adjacent Al planes parallel to (0001) where nanocracks are introduced.
brittle alumina is highly localized relative to aluminum metal, oxides bears significant implications for nanoscale mechanisms of materials failure. The electron density of the ionic, highly ionic bonding in alumina and other metal oxides has been discussed previously.\textsuperscript{46,47} Contrary to the cases with the ideal or compressed lattice, a clear hysteresis is apparent when the lattice is subject to in-plane expansion. This is shown in Figure 2b. In this case, the relaxed ionic coordinates in the crystal depend sensitively on the initial coordinates of the ions near the nanocrack region. When a nanocrack defect is introduced between the bulk ionic positions of the adjacent aluminum planes, the crystal heals the defect for the cases along the lower curve of the hysteresis loop. The resulting structure is uniformly strained when healing the local defect. However, when similar nanocrack defects are introduced to a crystal with relaxed surface ionic coordinates at the defect site, a local minimum is accessed upon relaxation. In these cases, the defect remains localized at the original site of the nanocrack instead of uniformly straining the crystal, thereby producing a higher energy structure. Thus, if the initial crack formed upon tensile loading exists long enough for the crack surfaces to adopt their preferred surface structure (with Al\textsuperscript{3+} ions buried in the oxygen ion layer beneath it), it will not heal properly upon unloading. This may very well occur upon unloading of a crack tip, where strains are likely to be tensile. Thus the “healed” crack may end up with a defective structure that is weakened, ultimately resulting in fatigue.

Figure 3 presents a qualitative display of the hysteresis shown quantitatively in Figure 2b, by depicting the ionic coordinates adopted during a tensile loading/unloading cycle. The upper section of the loop, accessed during unloading, shows nanocracks persisting after relaxation to a local minimum. These structures correspond to the higher energy curve of the hysteresis loop. The lower section of the loop, accessed during loading, initially contained ideal ionic coordinates for the expanded lattice for all ions on either side of the nanocrack. This lower section of the loop exhibits relaxed structures where the nanocrack heals. Although the surface relaxations of the expanded in-plane lattice are broadly similar to those with a compressed or ideal lattice, the moderate expansion of the lattice perpendicular to crack formation permits even greater relaxation to shield the “bare” surface ions. These surface stabilization effects are not as readily reversed upon decreasing nanocrack thickness, hence a local minimum is accessed upon relaxation of these surface structures. Accordingly, a nanoscale stress-strain hysteresis corresponding to atomic-level fatigue is observed.

The highly ionic bonding in alumina and other metal oxides bears significant implications for nanoscale mechanisms of materials failure. The electron density of the ionic, brittle alumina is highly localized relative to aluminum metal,
resulting in crack formation with much smaller tensile loads. Additionally, this ionic bonding may lead to large local relaxations at a defect site, resulting in irreversible crack formation at nanocracks which otherwise would not represent a failure defect in the crystal. This atomic-level mechanism of materials failure may contribute to fatigue crack growth. Similar mechanisms, whereby locally strained ionic bonding leads to large relaxations at defect sites, could be at work in the degradation of grain (boundary) bridging more commonly associated with fatigue in certain ceramics, including alumina. While our idealized parallel plane structure for a crack is of course only a crude approximation to a crack tip, we expect the qualitative trends to hold for an actual tip with crack propagating occurs. Providing an atomic-scale understanding of how such local changes in the oxide bonding modify the macroscopic materials properties represents an area of ongoing research.

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