



Original Article

Energetic design of grain boundary networks for toughening of nanocrystalline oxides

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ABSTRACT

Improving the mechanical performance of nanocrystalline functional oxides can have major implications for stability and resilience of battery cathodes, development of reliable nuclear oxide fuels, strong and durable catalytic supports. By combining Monte Carlo simulations, experimental thermodynamics, and in-situ transmission electron microscopy, we demonstrate a novel toughening mechanism based on interplay between the thermo-chemistry of the grain boundaries and crack propagation. By using zirconia as a model material, lanthanum segregation to the grain boundaries was used to increase the toughness of individual boundaries and simultaneously promote a smoother energy landscape in which cracks experience multiple deflections through the grain boundary network, ultimately improving fracture toughness.

1. Introduction

The mechanical performance of many functional oxides is limited due to the intrinsic brittleness resulting from the relatively fast crack nucleation and propagation through the material, which causes failure even at low impact energies. An effective mechanism designed to increase toughness in oxides is the transformation toughening in zirconium dioxide (ZrO₂) [1]. Crack propagation in this material triggers a suppressed phase transition, causing a local volumetric expansion and arresting crack motion. While being quite efficient, this mechanism only exists in ZrO₂-based materials or others few oxides that show similar phase stability diagrams. As for the rest of the oxides, a possible solution to increase toughness is the design of composite materials, such as host matrices with a random distribution or layered arrangement of reinforcing species. The former relies on the crack-bridging effect of some compounds with superior tensile strength, such as SiC nanoparticles or carbon nanotubes [2,3]. The latter uses layered configurations to resist fracturing since cracks can experience multiple deflections going from one layer to another [4]. Although the formation of composites is a flexible approach, a significant amount of secondary compounds strongly affects functional properties of the host, such as light transmission and mobility of charged species [5,6].

As the grain size decreases to the nanoscale, new opportunities for functional oxide materials emerge, such as increased charge-discharge rates in lithium battery cathodes [7–9], and improved radiation

tolerance in nuclear materials [10,11]. Some theoretical works have also predicted new mechanisms of toughening based on sliding of nanosized grains. As a result of new deformation modes [12–14], stress fields would potentially compensate external stresses near the crack tips and hinder their movement. However, those effects have not been experimentally observed in oxides, implying the validity of the alternate hypothesis, in which the lack of perfect atomic arrangement at the grain boundaries leads to weaker bonding and imperfect coordination. A large number of interfaces therefore defines the overall (limited) mechanical strength of nanocrystalline oxides by acting as regions of easy crack nucleation and propagation [15,16].

While the increase in bond strength and bonding coordination at the grain boundaries could potentially increase toughness [17], similarly to what has been proposed for thermal creep [18]; crack deflection could of course lead to much larger improvements. In this approach, the angle of crack deflection directly dictates the increase in toughness. If one can induce cracking on directions of non-maximum energy dissipation, then an apparent increase of the fracture toughness will be achieved [19]. Since deflection can be induced by any discontinuity, one may observe an inherent crack deflection pathway in the context of nanomaterials (without the need for a composite), which is the existing grain boundary network itself. Such network is, however, generally ineffective for deflection because of the random grain boundary distribution found in typical polycrystalline materials, i.e. co-existence of high energy and low energy boundaries. The high excess energy

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Table 1
List of all grain boundaries simulated in this study.

Geometry of grain boundary/misorientation angle	Size of simulation box $l_x/l_y/l_z$ (Å)	Number of atoms in simulation box Zr / O / Y / La substituting Y (if any)
[001] tilt axis		
$\Sigma 13(510) / 22.62^\circ$	26.08 / 104.26 / 30.77	7192 / 2024 / 4720 / 448
$\Sigma 5(310) / 36.9^\circ$	32.35 / 64.56 / 30.75	5446 / 1532 / 3574 / 340
[110] tilt axis		
$\Sigma 11(332) / 50.48^\circ$	24.07 / 102.73 / 28.90	6144 / 1728 / 4032 / 384
$\Sigma 3(111) / 70.53^\circ$	35.44 / 76.12 / 28.86	6703 / 1886 / 4399 / 418
$\Sigma 3(112) / 109.47^\circ$	37.54 / 71.49 / 28.90	6703 / 1886 / 4399 / 418
$\Sigma 11(113) / 129.52^\circ$	33.96 / 98.73 / 28.92	8286 / 2332 / 5438 / 516
$\Sigma 9(114) / 141.06^\circ$	21.69 / 97.41 / 28.57	5120 / 1440 / 3360 / 320
$\Sigma 19(116) / 153.47^\circ$	22.34 / 126.85 / 28.96	7029 / 1978 / 4613 / 438

boundaries tend to be mechanically weaker than the low energy ones due the existing large density of uncompensated chemical bonds and coordination [20]. It is therefore intuitive to say that low excess energies correspond to mechanically stronger (or more accurately, tougher, as one is talking about the energy till failure) boundaries because of their intrinsic stability. Likely intuitive, if the network is a combination of both, crack-tips will more easily propagate along boundaries with higher excess energy and “avoid” the ones with low excess energy, resulting in fairly straight and unbranched cracks typical of brittle behavior [21].

To induce crack deflection in the existing grain boundary network, we propose the hypothesis that all grain boundaries should be similar in terms of their excess energies. As a result, a stochastic deflection of crack path will be achieved – ultimately increasing fracture toughness. Such mechanism, however, would only work if grain boundaries were generally made stronger rather than the opposite [22]. This can minimize the energetic discontinuities that grain boundaries constitute in the system, and thus disabling low critical strain-energy release boundaries.

Leveling off the energy landscape in the grain boundary network has just become achievable based on recent advancements on the control of the thermodynamics of interfaces [23,24]. Grain boundary energies (γ_{gb}) can be chemically modified through segregation of dopants, following the simplified Gibbs adsorption equation for low concentrations:

$$\gamma_{gb} = \gamma_0 - \Gamma_B (RT \ln X_B^{bulk} - \Delta H_{seg}) \quad (1)$$

Here, γ_0 is the grain boundary energy of the undoped grain boundary, Γ_B is the solute excess at the grain boundary, ΔH_{seg} is the enthalpy of segregation, and X_{bulk} the bulk solute content [24]. If the enthalpy of segregation is favorable, the grain boundary energy decreases, becoming more energetically stable. Such favorable segregation enthalpy has been observed in oxides, for instance, when doped with rare-earth elements or transition metals [25,26]. Noteworthy, the segregation enthalpy is a function of grain boundary orientation and its intrinsic (dopant free) energy. High energy boundaries typically demonstrate a more favorable enthalpy of segregation, while low energy boundaries are inherently more stable and not prone to accommodate dopants [27]. This natural anisotropic interaction of dopants and boundaries could be directly used to homogenize the energetic landscape across the grain boundary network.

2. Methods and materials

2.1. Monte Carlo simulations

In this study, the potential effect of ion segregation in a model oxide system was investigated using Monte Carlo (MC) simulations. The simulations were performed for cubic ZrO_2 stabilized by 10 mol.% of Y_2O_3 (10YSZ), commonly used for solid electrolytes or thermal barrier

coating due to the absence of phase transformations in a wide range of grain sizes, temperatures, and stresses [28]. The grain boundaries of this material were modeled in different crystallographic orientations with and without La as a dopant, which was previously shown to decrease the average grain boundary energy in zirconia [29].

Initially, the structures of the pure ZrO_2 were built and relaxed using a gradient descent algorithm implemented in the LAMMPS code [30]. Then, the formation of a solid solution of ZrO_2 with Y_2O_3 as well as the doping with La were performed by random substitution of cations and following equilibration using the TOWHEE software [31]. The interaction between anions and cations was treated as fully ionic, modeled by a short-range Born-Mayer-Buckingham potential with the cutoff distance of 10 Å, and the long-range Coulomb potential. This potential model has been proven to reasonably reproduce the cubic structure of YSZ as well as other oxide compounds [32].

The MC simulations were carried out under NVT conditions (constant atom number, constant volume and constant temperature, $T = 300$ K) for 10^8 steps to ensure fully equilibration. Two modes of motion were considered: swapping for cations only, and translation for all ions. For each simulation step, the energy of the configuration was calculated and the new configuration accepted with probability of the minimum value in $(1, \exp(-\Delta E/k_B T))$. Here ΔE is the energy difference before and after MC trial moves, k_B is the Boltzmann’s constant and T is temperature.

The scope of this simulation part in this study was limited to the most common grain boundaries found in YSZ ceramics (Table 1). For instance, the experimental investigations are reported for $\Sigma 5$ and $\Sigma 13$ boundaries with [100] tilt [33,34] as well as for $\Sigma 3$, $\Sigma 9$ and $\Sigma 11$ with [110] tilt [35]. For each boundary geometry and composition, 3 independent configurations were simulated. The composition of the pristine boundary was set to $ZrO_2 + 10$ mol.% Y_2O_3 (10YSZ), while 1.5 mol.% of Y_2O_3 was substituted by La_2O_3 in the doped case, i.e. $ZrO_2 + 8.5$ mol.% $Y_2O_3 + 1.5$ mol.% La_2O_3 (1.5La8.5YSZ). Although $\Sigma 19$ boundary has not been experimentally studied in the literature, this geometry was also found stable in our simulations. The grain boundary structures were formed by rotating two grains about the tilt direction set as z axis so that x and z axes form the grain boundary plane with y axis perpendicular to this plane. Overlapping atoms (< 0.3 Å) due to rotation were not taken into account. Periodic boundary conditions were applied in all three directions, and the length of simulation box was set in such a way that ensures an integer multiple of the lattice constant.

Additionally, the reference structures without grain boundary were simulated for both compositions. The values of grain boundary energy were calculated as difference in internal energy between the grain boundary configurations and the reference structures without boundary. Each value represents the average of 20 data points uniformly sampled at different times of the equilibration process. The obtained values were additionally averaged with other independent configurations. The entropy contribution to the grain boundary energy was negligible due to adopted low temperature of simulations. The

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