Nanoindentation of ZrO_2 and ZrO_2/Zr Systems by Molecular Dynamics Simulation

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Abstract

The deformation behaviors of cubic zirconia and a cubic zirconia thin film on top of an hcp zirconium substrate are investigated using molecular dynamics nanoindentation simulation. Interatomic interactions are described by the previously developed Charge Optimized Many Body (COMB) potential for the $\text{Zr-ZrO}_2\text{-O}_2$ system. The load-displacement curves, deformation processes and hardnesses of zirconia and the zirconia/zirconium systems are characterized. In addition, by comparing with a previous nanoindentation simulation on zirconium, the effects of the zirconia layer on top on the mechanical properties of the zirconium substrate are determined.

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I. Introduction.

The fuel clad for light-water reactors (LWRs) is made from zirconium alloys. Under reactor operating conditions, the cladding experiences extremes of temperature, stress, radiation and corrosion. One of the major products of the corrosion process is zirconia. The three zero pressure phases of zirconia display monoclinic, tetragonal and cubic symmetry; the tetragonal phase and monoclinic phase are derivatives of the cubic fluorite phase [1]. At ambient pressure, the monoclinic phase is stable at room temperature, transforming to the tetragonal phase at 1205°C, which transforms to the cubic phase at about 2370°C [2]. The cubic phase of zirconia can be stabilized at room temperature by doping, most prominently with Y_2O_3 at concentrations of 8-10 mol% [3, 4]. This work was motivated by the appearance of zirconia on top of Zr clad. Zr can also be alloyed with uranium; ZrO_2 can also be used as the base for inert matrix fuel. [5, 6] In addition, however, zirconia itself is also used as a ceramic biomaterial [7, 8], a dental material [9], a reinforcing component in composite materials [10], a fuel cell electrolyte [11, 12], and as a thermal barrier coating [13]; in each of these applications its mechanical properties are important. The martensitic tetragonal to monoclinic phase transformation is the source of transformation toughening around crack tips in zirconia [14-18]. Under high pressure, zirconia transforms to an orthorhombic phase [1, 19, 20].

The structure of the oxide layer formed on clad has been studied extensively using Raman spectroscopy [21-25], in which the tetragonal and monoclinic phases of zirconia are found. The tetragonal phase is located close to the interface, while the outer part of the oxide layer consists of the monoclinic phase [23, 24]. The compressive stress at the interface helps to stabilize the tetragonal phase [22, 25, 26]. The cubic phase is extensively observed on zirconium surfaces by electron diffraction [27-30].

Since the mechanical integrity of the cladding is essential, it is important to understand its properties under high mechanical loads. In previous works we have elucidated the

mechanical response of Zr under tension [31] and under nanoindentation (to understand hardness) [32]. It is also important to understand the effects of oxidation on the mechanical integrity of the clad. Therefore in this work, we first analyze nanoindentation simulations of zirconia, representing an oxide layer; we then examine nanoindentation of a zirconia film on a zirconium substrate, representing the oxidized clad. Nanoindentation is an effective tool to extract mechanical properties [33, 34]. In situ nanoindentation technology has been developed to observe individual dislocation activity [35, 36]. Molecular dynamics (MD) simulation is capable of identifying deformation processes at the atomic level [31, 37-41], as has been demonstrated in studies on fcc [42-45], bcc [46, 47] and hcp [48] metals. Nanoindentation simulations of ceramics using MD have also been carried out [49-52]. This paper contains the first MD nanoindentation simulation of a metal-ceramic system: in this case ZrO_2/Zr .

The objective of this paper is to characterize the deformation processes associated with nanoindentation of zirconia at the atomic level; to rationalize the simulated macroscopic response in terms of experimental data and Hertz Law; and to characterize the deformation in a zirconium oxide layer on zirconium, including the load transfer through the interface.

The rest of this paper is organized as follows. Section II contains a brief description of the potential used to describe the interatomic interactions, the structure of cubic zirconia, the simulation setup, the crystallographic orientations used in the nanoindentation simulation, the effects of temperature and indentation speed, method used to rescale MD data to compare to the experiment, and analyses of the elastic and plastic deformation during nanoindentation simulation. Section III contains the results and discussions of nanoindentation of ZrO_2 . Section IV describes the ZrO_2/Zr system. Section V contains the results and discussions of nanoindentation of the ZrO_2/Zr system. Our conclusions are in Section VI.

II. Background and Methods

a. Interatomic potentials

There are several potentials for ZrO_2 in the literature [53-59]. Six interatomic potentials based on the Buckingham potential form for yttria-stabilized zirconia (YSZ) were assessed by Yin et al. [60]. For example, the Schelling potential, using a Buckingham type short-ranged potential and a Coulomb electrostatics term, can describe both the cubic and tetragonal phases; this potential was also able to describe yttria-stabilized zirconia (YSZ) [53]. However the Buckingham potential is a fixed charge formalism and thus cannot describe zirconium or oxygen separately or be used to describe the Zr/ZrO_2 system. The ReaxFF formalism, a variable charge reactive potential, has been parameterized to simulate reactive oxygen migration in YSZ [55]. However the ReaxFF potential does not currently include the ZrH_x system formed by hydrogen diffusion into the Zr cladding.

The third-generation Charge Optimized Many Body (COMB3) potential is a variable-charge reactive-potential formalism. It is capable of describing the creation and dissociation of chemical bonds [61, 62] and allows dynamic charge adjustment according to the local environment [62-64]. The COMB3 potential is capable of describing the Zr-O-H system [30, 65]; that is, it can describe zirconium, zirconia, zirconium hydride, as well as molecule oxygen, hydrogen and water interacting with zirconium. The details of the COMB3 formalism and other examples of its applications are described elsewhere [66, 67]. The development of a potential for such a wide range of materials inevitably requires some compromises with regards to the fidelity of any specific system. In particular, the ground state structure of ZrO_2 as described by the COMB3 potential is the cubic fluorite phase; while this is a clear limitation, the observed presence of the cubic fluorite on the Zr surface by electron diffraction [27-30] indicates that it can provide valuable information of such systems. In this paper MD simulations of nanoindentation of cubic ZrO_2 and the ZrO_2/Zr heterogeneous interface are performed to study their deformation behavior.

Here we only summarize the key properties of the potential with regards to representation of the c-ZrO₂; other properties are described elsewhere [30]. The elastic constants except for C₄₄ (and shear modulus) match well with DFT results [68], as shown in Table 1 [30]. As in a previous nanoindentation study [32], the reduced moduli have been calculated to be 370 GPa for the [110] orientation and 468 GPa for the [100] orientation. The reason for choosing the [110] and [100] orientations is discussed in the orientation section below. One of the compromises made in developing the potential is the fidelity of the defect formation energies listed in Table 2: the O vacancy, Zr vacancy and Zr interstitial formation energies predicted by the COMB3 potential are higher than the DFT calculations, while the formation energy of the O interstitial is underestimated significantly [30]. However, since the deformation associated with nanoindentation does not involve point-defect production, this limitation should not significantly influence the deformation behavior.

Table 1. Comparison of properties of cubic zirconia obtained by experiment, DFT and COMB.

Property	Experiment [69, 70]	DFT [68]	COMB3 [30]
a ₀ (Å)	5.0858	5.116	5.1247
C ₁₁ (GPa)	417	520	486
C ₁₂ (GPa)	82	93	94
C ₄₄ (GPa)	47	61	98
B (GPa)	194	235	228
G (GPa)	95	122	134

Table 2. Point defect formation energies predicted in cubic zirconia by DFT and COMB3.

Point defect	DFT (cubic phase) [30]	COMB3 (cubic phase) [30]
O vacancy (eV)	6.15	11.2
O interstitial (eV)	3.46	0.37
Zr vacancy (eV)	15.00	27.9

Zr interstitial (eV)	1.78	4.17
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b. Crystallography and slip systems in cubic ZrO₂

The crystal structure of cubic zirconia is fluorite, as illustrated in Fig. 1. Its dominant slip system is $\frac{1}{2}\langle 110 \rangle \{100\}$; however at high temperatures, or if the primary slip is suppressed, the secondary slip systems $\frac{1}{2}\langle 110 \rangle \{110\}$ and $\frac{1}{2}\langle 110 \rangle \{111\}$ can be activated [4, 71].

Fig. 1 The fluorite structure of cubic zirconia and schematic of edge dislocation in the fluorite structure. The glide plane is (001) and the Burgers vector is $(1/2) [110]$. [72]

c. Simulation setup

The nanoindentation MD simulations were performed using the LAMMPS software tool [73]. For the ZrO_2 system, the simulated system consists of three regions; from top to bottom: an active region, a thermostat region and a fixed region, as shown in Fig. 2. The force exerted by the spherical indenter is applied to the active region; this is achieved by using the “fix indent” fix style in LAMMPS.

$$\begin{aligned}
 F(r) &= -K(r - R)^2 & r < R \\
 F(r) &= 0 & r \geq R
 \end{aligned} \tag{1}$$

Here, $K = 10 \text{ eV/\AA}^3$ is the force constant, r is the distance from the atom to the center of the indenter and R is set to be $45 \text{ \AA}$, representing the radius of the indenter.

A Langevin thermostat [74] is applied to the thermostat region in order to control the system temperature. The bottom layer of the system is fixed in space in order to provide rigid support. Periodic boundary conditions are applied in the x-y plane.

Fig. 2 Schematic of the simulated [110] oriented ZrO_2 system.

d. Orientation

Both the [110] and [100] orientations of cubic zirconia have been observed in oxidized Zr by electron diffraction [27-30]; thus, these are chosen for our simulation study. The comparison of the [110] and [100] orientations can also probe the anisotropy of ZrO_2 . Our simulation results may also be compared with those of indentation experiments on the [110] and [100] orientations of YSZ [75]. The (110) plane is the charge neutral plane in the fluorite structure, as indicated in Fig. 3(a). The structure in the [100] direction consists of alternating planes of Zr and O and thus has a dipole moment normal to the surface. Charged planes can be expected to reconstruct [76, 77]. For example, for the (001) surface of the rock-salt structure, the octopolar reconstruction considerably lowers

the energy and reduce the surface stress [76]. In order to minimize the effect of the charged, the top and bottom surface (100) planes are reconstructed by hand. First the top and bottom surfaces are selected to be Zr planes. As a result, there is an extra Zr plane in the system. Then the atoms in the face center position of the top and bottom Zr planes are removed. Thus, after this modification, the (100) surface has a pyramid shape with (110) charge neutral facets, shown in Fig. 3 (c); this preserves the overall stoichiometry of the system. This method was developed for the rocksalt structure by Tasker [77].

Before nanoindentation, the two surface systems are fully relaxed using Isothermal-isobaric (NPT) ensemble. In subsequent discussions we denote the initial structures built purely from crystallographic understanding as ‘unrelaxed’; the system structures after the forces, as appropriate, the stresses have been minimized, to very low values and the charges optimized, are denoted ‘relaxed’. For the charge neutral (110) plane, the surface structure after relaxation is provided in Fig. 3(b). The surface oxygen layer splits into two layers separated by approximately $0.7\text{\AA}$, while the Zr atoms remain in their perfect-crystal lattice sites after relaxation. The charge of the surface Zr atoms is less positive than that of the Zr atoms in the bulk, while the charge of the surface oxygen atoms is less negative than in the bulk. For the reconstructed (100) charged plane, the Zr and oxygen atoms at the surface leave their original positions to form a relatively low energy configuration. For the (100) plane, the charge of the Zr atoms at the surface also becomes less positive, while the charge of the O atoms at the surface becomes less negative than in the bulk.

Fig. 3. Side view slice through the zirconia surface; the surface plane is at the top. (a) (110) plane before relaxation. (b) (110) plane after relaxation. (c) Reconstructed (100) plane before relaxation. (d) Reconstructed (100) plane after relaxation. (a) and (c) are color coded by atom type. Red (large) atoms are Zr and blue (small) atoms are O. (b) and (d) are color coded by charge, according to the color bar at right.

For the (110) surface, the Zr and O atoms are in the same plane, which is perpendicular to the plane containing the image. In the (100) surface the Zr and O are separated by a quarter of a lattice parameter into the image. For the [100] orientation, the bottom of the system has been reconstructed in the same way as the surface; thus the stoichiometry is preserved.

e. Effect of indentation speed and temperature

The possible effects of indentation speed and temperature are addressed first. Because it involves charge equilibration, the COMB3 potential is more computationally demanding than standard fixed-charge empirical potentials [78]. Thus, choosing an appropriate indentation speed that can both give physically reasonable results and minimize the computational time of the simulation is particularly important. MD simulations of nanoindentation have to use faster indentation speeds than experiments because of the inherent timescale limitations of the method. Nanoindentation MD simulations on CaCO_3

minerals using 10ms^{-1} and 30ms^{-1} indentation speeds generated almost the same load-displacement curve [79]. Indentation simulations at 10ms^{-1} and 50ms^{-1} are considered here. As illustrated in Fig. 4 for the (110) orientation, the load-displacement curves for the two speeds almost overlap at 300K. Most importantly, the load drops related to plastic deformation both occur at approximately the same displacement of $13\text{ \AA}$.

Examining the effect of temperature using an indentation speed of 50ms^{-1} , the load-displacement curves almost overlap for temperatures of 300, 800 and 2000K, especially before the first load drop. There is a small amount of elastic softening as the temperature increases; however, the load drops related to the plastic deformation takes place at an indentation of $13\text{ \AA}$ for all temperatures.

The results indicate that the effects of variation in temperature and indentation speed on the indentation simulation results are not that significant. In the subsequent simulations described below, we thus use an indentation speed of 50ms^{-1} to minimize computing time, and a temperature of 300K.

Fig. 4. (a) Load-displacement curve for [110] orientation at (a) indentation speeds of 50ms^{-1} and 10ms^{-1} at 300K, (b) 300K, 800K and 2000K at 50ms^{-1} indentation speed.

f. Using Hertz Law to rescale MD simulation data

Hertz continuum elastic contact analysis has been widely used to describe the elastic deformation behaviors for a spherical indenter. Here, the Hertz Law will be used to rescale the MD data to the time and length scale of the nanoindentation experiments to

allow a more direct comparison with experiment. Within Hertz theory, the load applied by the indenter, P , is given by [80, 81],

$$P = \frac{3}{4} E^* R^{\frac{1}{2}} h^{\frac{3}{2}} \quad (2)$$

where R is the radius of curvature of the indenter and h is the indentation depth. E^* is the reduced modulus, defined as [80, 81],

$$E^* = \left\{ \frac{1-v_s^2}{E_s} + \frac{1-v_i^2}{E_i} \right\}^{-1} \quad (3)$$

where E_s and v_s are Young's modulus and Poisson's ratio of the sample, and E_i and v_i are Young's modulus and Poisson's ratio of the indenter. For the case of a hard indenter $E_i = \infty$ and $v_i \neq 0$.

According to Eqn. 2, the reduced modulus E^* is the only materials related property. The relationship between loads from different nanoindentation tests using different indenter sizes (R_1 and R_2) and indentation depths for the same material can be expressed as

$$\frac{P_1}{P_2} = \sqrt{\frac{R_1}{R_2}} \left(\frac{h_1}{h_2} \right)^{\frac{3}{2}} \quad (4)$$

where P_1 and P_2 are load responses; h_1 and h_2 are the indentation depths. In this work, P_1 is at the nN scale, while R_1 and h_1 are at Å scale. For the experiments we compare with, P_2 is at μN scale, while R_2 and h_2 are hundreds of nms.

III. Nanoindentation of Zirconia

At the beginning of the indentation test, the system deforms elastically. As shown in Fig. 5, the load vs. $h^{3/2}$ curves obtained from the simulation are linear, which represents elastic behavior in the Hertz Law. The reduced modulus calculated using the COMB3 potential predicted elastic constants for the [110] and [100] orientations are 370 GPa and 468 GPa,

respectively. According to Eqn. 2, the slope of the load-displacement in the elastic region of the [100] orientation should be steeper than that of the [110] orientation. The slope of the [100] orientation from simulation is initially slightly steeper than that of the [110] orientation, which is consistent with the order predicted by the Hertz law. However the [100] orientation exhibits a softening with increasing load. The slope of the load vs. $h^{3/2}$ curves calculated from the Hertz Law is steeper than those from the simulations. The above difference may be caused by the effects of system size observed in the Zr nanoindentation simulations [32].

Having established that the elastic part of the indentation obeys Hertz Law, we can rescale the length scale of the MD system size to allow for direct comparison with experimental results that are obtained for much larger indenters (350nm) and indentation depths at the micrometer scale, according to Eqn. 4. Our simulation results for ZrO_2 are compared to the nanoindentation experiments carried on YSZ with 10 mole% yttria [75]. According to an experimental study of YSZ with yttria doping ranging from 11% to 18% mole%, the Young's modulus and shear modulus decreases as the mole% of yttria increases, while the anisotropy factor increases as the mole% of yttria increases [82].

As illustrated in Fig. 6, the rescaled load-displacement curves from the MD simulations match quite well with those from the indentation experiments on single crystal YSZ. The simulation results for the [110] orientation show the better match with the experimental data. For the [100] orientation, the simulation results agree well with the experiment for low loads prior to the softening discussed above. This softening could also be caused by system size effects, or could arise from the surface reconstruction.

The YSZ indentation experiments reveal that the slope of the load-displacement line of the [100] orientation is steeper than that of the [110] orientation, which is reflected in the MD results and the Hertz Law prediction. The difference between the load-displacement lines of the [110] and [100] orientations in our simulations is smaller than that in the experiments, which can be understood in terms of the increased anisotropy from the yttria doping in the experimental samples [82].

Fig. 5 Load vs. $h^{3/2}$ in the elastic region for [110] and [100] orientations.

Fig. 6 Comparison of load-displacement curves from rescaled MD data and experimental data. The experimental data shown were obtained from reference [75].

The first load drop typically represents the initiation of plastic deformation. As indicated in Fig. 7, the first load drop for the [110] orientation takes place at an indentation depth of $\sim 13\text{\AA}$, while for [100] orientation, the first load drop is at $\sim 10\text{\AA}$. After rescaling, the first load drop should be at $\sim 10\text{nm}$ for the [100] orientation and $\sim 13\text{nm}$ for the [110] orientation. The earlier yield for the [100] orientation simulation agrees reasonably well with the indentation experiments on YSZ, for which the first load drop for the [100] and [110] orientations occurs at 14nm and 22nm , respectively [75]. The simulated yield strength of the [110] orientation ($\sim 800\text{nN}$) is twice as much as that of the [100] orientation ($\sim 400\text{nN}$). This is also consistent with the experimental results [75] where the yield strength of the [110] and [100] orientations are $\sim 500\mu\text{N}$ and $\sim 250\mu\text{N}$, respectively.

Fig. 7 Load-displacement curves for [110] and [100] orientation under indentation at 300K for indentation speed of 50ms^{-1} .

The deformed atomic structures at an indentation depth of $25\text{\AA}$ are provided in Fig. 8. The atomic pileups represented by the miscoordinated atoms in Fig. 8 are seen in both the [110] and [001] orientations. It is evident that the shapes of the deformed regions are very

different for the two orientations. The origin of this difference resides in the anisotropy and the limited slip systems available in ZrO_2 . For the $[110]$ orientation, as we can see from the side view (001) plane, Fig. 8(a), and from the side view (110) plane, Fig. 7(b), the boundaries between the deformed and the un-deformed regions lie along the $\langle 110 \rangle$ direction. The boundary between the deformed region and un-deformed region in the $[100]$ orientation is also along the $\langle 110 \rangle$ direction, as shown in Figs. 8(c) and (d). This preference for deformation along the $\langle 110 \rangle$ direction during nanoindentation is consistent with $\langle 110 \rangle$ being the dominant slip direction for the ZrO_2 system. The Dislocation Extraction Algorithm (DXA) [83-85] can be used to capture dislocation structures. The DXA is applied to the Zr fcc sublattice, but captures no dislocations. By contrast indentation simulations of fluorite-structured CaF_2 did show the generation of dislocations as the first plastic event took place [51].

Because no dislocation structures can be observed in the deformed structure, more detailed analysis of evolution of the atomic structure is necessary in order to understand how the structure transforms around the first load drop. First, the volume change during indentation at different places in the atomic pile up region (miscoordinated atoms) is analyzed. To do this, four nearest neighbors of Zr atoms in the fcc lattice defined in Fig. 8 are chosen from different deformed regions. In the pile up region, the volume of the system decreases significantly at the load drops in the load-displacement curve. As shown in Fig. 9, the volume of the tetrahedron in the blue circle region shows no significant change through the indentation process. The volume of the tetrahedron in the purple region starts to decrease significantly at an indentation depth of $\sim 14 \text{ \AA}$, which corresponds to the first drop in the load-displacement curve. Furthermore, starting at $\sim 18 \text{ \AA}$ indentation depth, the volume of the tetrahedron in the red circle region exhibits a significant decrease, which corresponds to the second load drop in the load-displacement curve. The volume of the tetrahedron in the green circle region starts to decrease at $\sim 16 \text{ \AA}$. The tetrahedra inside the pile up region all experience significant volume decreases at very well-defined indentation depths, which confirms that the system undergoes significant structural change at the load drop.

Next, we analyze the evolution of the atomic structure of $[110]$ orientation at the load drop. We first examine representative (100) and (110) planes in the deformed region for the $[110]$ orientation simulation. For the (100) planes in Figs. 10(a) and (b), the atomic positions in the deformed area only change slightly along the $[100]$ direction, even though the force is applied along the $[100]$ direction by the indenter. For the (110) plane in Figs. 10(c) and (d), the atomic planes deform along the $[110]$ direction. We thus conclude that zirconia prefers to deform along the $[110]$ direction rather than the $[100]$ direction. For the spherical indenter used here, the forces applied along $[110]$ (x-axis) and $[100]$ (y-axis) are equal. By the comparison shown in Figure 9, we conclude that the structure prefers to deform along the $[110]$ direction with the $[100]$ direction being the hard direction. This is consistent with the fact that $[110]$ is the primary slip direction for the fluorite structure as discussed in Section II. b.

The Zr atoms in ZrO_2 lie on an fcc sub-lattice and thus have 12 Zr neighbors. Close to the indenter, there are a number of 13-coordinated Zr atoms, identified as red atoms Fig. 8. The structural change in the 13-coordinated atoms region is illustrated in Fig. 11. The xz- (100) plane deforms along $[110]$ to transform to a closed packed plane with 13 coordination numbers during indentation; the distance between nearest neighbors is ~ 2.8 Å. The structure of the xy- (100) plane stays unchanged during the indentation. Thus, the highly deformed region can be regarded as a closed pack structure with an AAA stacking sequence along the y- $\langle 100 \rangle$ direction. The transformation of the O sub-lattice is similar to that of Zr as shown in Fig. 11. On the xz- (100) plane, the O atoms squeeze along $[110]$ direction. The O atoms also form a higher density structure comparing with the original structure before indentation. The structure of the highly deformed region cannot be identified as any specific crystallographic phase; rather it appears to result from the original structure deforming along the $\langle 110 \rangle$ direction.

The charge distribution of the $[110]$ and $[100]$ orientation after nanoindentation is provided in Fig. 13. The pile up region and the boundaries between the deformed and undeformed region can also be represented by the charge distribution. As we can see the

charge of Zr atom becomes less positive in the deformed region, while the charge of the O atoms becomes less negative.

Fig. 8 Side views of deformed structures of ZrO_2 at indentation depth of $25 \text{ \AA}$. (a) [110] orientation side view of (001) plane. (b) [110] orientation side view of (110) plane. (c) [001] orientation side view of (001) plane. (d) [001] orientation side view of (110) plane. The color scheme represents the coordination number. Only Zr atoms are shown in the figure.

Fig. 9 Volume change of a zirconium tetrahedron in the deformed area during nanoindentation simulation for [110] orientation. Atom 1, 2, 3 and 4 form the tetrahedron.

Fig. 10 Analysis of indentation in $[110]$ orientation (a) One (100) plane before nanoindentation simulation. (b) The same (100) plane after nanoindentation simulation. (c) One (110) plane before nanoindentation simulation. (d) One (110) plane after nanoindentation simulation. Both planes lie under the indenter.

Fig. 11 The transformation of the highly deformed region for the $[100]$ orientation. Only Zr atoms are shown. Yellow atoms represent 12 coordination; red atoms represent 13 coordination.

Fig. 12 The transformation of highly deformed region for the $[100]$ orientation. The atoms are color coded by atom: Red for Zr and blue for O.

Fig. 13 Charge profile in side view of deformed structure of ZrO_2 at indentation depth of 25 Å. (a) [110] orientation side view of (001) plane. (b) [001] orientation side view of (001) plane. The atoms are color coded by charge.

The hardness for the two orientations is calculated using the method used in [32]. Briefly, as shown in Fig. 14, the hardness keeps increasing with indentation depth until the first load drop. After the first load drop, the hardness value stays relatively constant. We take as a representative hardness the average between the two dashed lines. The quoted error represents the standard deviation within the two red dotted lines region. The nanoindentation simulation yields a hardness value of 19.8 ± 0.6 GPa for the [110] orientation and 14.6 ± 0.3 GPa for the [100] orientation.

Fig. 14 Load vs. indentation depth and hardness vs. indentation depth for the [110] orientation.

IV. Zirconia/Zirconium Interface.

Under nuclear reactor working condition ZrO_2 forms on top of zirconium alloy cladding. In a previous study, the deformation processes and hardness of different orientations of single crystal Zr were characterized by MD nanoindentation simulation [32]. After illustrating the deformation process and hardness of single crystal cubic zirconia during nanoindentation simulation in the previous sections, nanoindentation simulations will be

carried out for the ZrO_2/Zr system. Then the comparison of the Zr, ZrO_2 and ZrO_2/Zr systems can help us to understand how the zirconia overlayer influences the mechanical properties of the substrate zirconium. First, however, the zirconia/zirconium interface has to be built and characterized. The [110] orientation of ZrO_2 has been observed in oxidized Zr by electron diffraction [27-30]; the (110) plane is charge neutral plane without dipole moment normal to the surface plane. The [0001] orientation is one of those commonly observed in Zircaloy [86]. While the surface formed by a 30° of the [0001] orientation around the c-axis is also commonly observed, it is not computationally convenient. Therefore, the Zr-[0001] orientation with ZrO_2 -[100] orientation on top is chosen for these simulations. A schematic of the simulated system is shown in Fig. 15. In order to reduce the lattice mismatch between Zr and ZrO_2 , the number of unit cells of Zr and ZrO_2 along x and y directions has been chosen such that total strain is less than 1% along the x direction and less than 3% along the y direction; reduction of the strain in the y-direction below this value would necessitate the use of a prohibitively large simulation cell. The work of adhesion of our simulated system is 2.31 Jm^{-2} , which is comparable to the DFT results, 1.96 Jm^{-2} for the Cu-(001)/ ZrO_2 -(110) interface [87].

After building the interface structure, the whole system is relaxed using constant number, pressure and temperature (NPT) conditions at 300K. The atomic structure of the system before and after relaxation is illustrated in Fig. 16. The O atoms diffuse to the second layer of the Zr substrate as shown in Fig. 16(b). The charge of the O atoms in the interface area become less negative compared to the bulk. As indicated in Fig. 16(c), the structures of three layers of Zr atoms in Zr substrate and two layers of Zr atoms in ZrO_2 at the interface rearrange after relaxation. The charge of the Zr in ZrO_2 becomes less positive at the interface while the charge of the Zr atoms at the interface region of the substrate becomes more positive compared to the bulk. The oxygen density is provided in Fig. 17 and the shear strain map at the interface is illustrated in Fig. 18. The O atoms move away from their perfect lattice sites during relaxation, which corresponds to the broadening of the O density peak in Fig. 17. The first two peaks in Fig. 17 at the ZrO_2 surface correspond to the splitting of the first O layer at the ZrO_2 surface, which is also seen at the surface of pure ZrO_2 after relaxation. The O density peaks decrease in height

and broaden close to the interface. The O atoms diffuse across the interface to the second layer of the Zr metal substrate. After relaxation, a strain field exists at the interface, as shown in Fig. 18. Two layers of ZrO_2 and three layers of Zr at the interface are ultimately strained. The structures of the first layer of Zr, Fig. 18(b), and the first layer of ZrO_2 are distorted in Fig. 18(c), but do not transform to different structures. At the interface, the Zr substrate experiences higher shear strain than the ZrO_2 layer. The magnitude of the charges on the Zr and O in ZrO_2 decrease close to the interface, as shown in Fig. 19(a). This charge transfer at the interface results in the formation of a dipole moment at the interface seen in Fig. 19(b) between 25 Å and 30 Å. The total charge inside the ZrO_2 layer and in the Zr substrate is zero.

For the ZrO_2/Zr interface after relaxation, oxygen atoms diffuse across the interface and charge transfer takes place at the interface. After building and relaxing the interface, the system is ready for the nanoindentation simulation.

Fig. 15 Schematic of the simulated ZrO_2/Zr system.

Fig. 16 ZrO₂ and Zr interface. (a) ZrO₂/Zr system before relaxation. Red atoms represent Zr and blue atoms represent O. (b) Charge map of O atoms after relaxation. (c) Charge map of Zr atoms after relaxation.

Fig. 17 O density profile in ZrO₂/Zr system. Position $z=0$ Å corresponds to position of the ZrO₂ surface.

Fig. 18 Shear strain map at the interface of ZrO_2/Zr system after relaxation; see the color scale bar. Only Zr atoms are shown. (a) Side view of ZrO_2/Zr system. (b) Top view of the first layer in Zr at the interface. (c) Top view of the first layer in ZrO_2 at the interface.

Fig. 19 Charge profile across the ZrO₂/Zr interface. (a) Average charge of Zr and O across the ZrO₂/Zr interface. (b) Total charge density across the ZrO₂/Zr interface.

V. Nanoindentation of Zirconia/Zirconium

The nanoindentation simulation set up for the ZrO₂/Zr system is similar to the setup for ZrO₂; the system parameters are shown in Fig. 15. The simulation is performed at 300K with a 10ms⁻¹ indentation speed. This slower speed is chosen to ensure stability of the system throughout the simulation.

The load-displacement curve and the hardness vs. indentation depth are provided in Fig. 20. In the load-displacement curve, no significant yielding takes place until an indentation depth of 18 Å, at which point the load and the calculated hardness start to decrease. The hardness first increases with the indentation depth, then becomes stable with small fluctuations between 13 Å and 18 Å.

The comparison of the load-displacement curves for Zr-(0001), ZrO₂-(110) and ZrO₂-(110)/Zr-(0001) is shown in Fig. 21, where it is clear that the ZrO₂ is harder than Zr, while the ZrO₂/Zr system lies between them. As a metallic system, it is reasonable that the Zr system yields at the shallowest indentation depth of around 5 Å. However, the harder ZrO₂ yields at around 13 Å, while the intermediate hardness ZrO₂/Zr system yields at 18 Å. This raises the question as to at what depth the Zr substrate in ZrO₂/Zr system starts to yield, and what plastic processes are associated with the load drop at the 18 Å

indentation depth. The above questions are addressed by the deformation analysis that follows.

Fig. 20 Load-displacement curve and hardness vs. indentation depth for the ZrO_2/Zr system

Fig. 21 Load-displacement curves of [0001] Zr, [110] ZrO₂ and [110]/[0001] ZrO₂/Zr systems

The deformed structure during the nanoindentation simulation (with oxygen atoms removed from the image for clarity) is illustrated in Fig. 22. The Zr atoms are in an fcc environment in the ZrO₂ layer and in an hcp environment in the Zr substrate. Thus, common neighbor analysis (CNA) [88, 89] has to be applied separately in Zr and ZrO₂ to identify fcc-like atoms, hcp-like atoms and disordered atoms. DXA is then used to identify dislocation lines. Pyramidal $\langle a+c \rangle$ dislocations start to nucleate in the Zr substrate at an indentation of ~ 12 Å as revealed by Fig. 22(a). This 12 Å indentation depth corresponds to point *b* in the load-displacement curve in Fig. 20. It answers the question raised previously, showing that the Zr substrate starts to deform plastically at 12 Å, before the yield point *c* in Fig. 20 at 18 Å. However unlike the pure Zr system [32], no significant load drop is predicted in the load-displacement curve for the ZrO₂/Zr system when plastic deformation takes place in Zr substrate. That is, the presence of the ZrO₂ layer delays the plastic deformation in the Zr substrate relative to the pure Zr system.

The dislocation lines in the top ZrO₂ layer are captured by DXA at an indentation depth of 18.5 Å as shown in Fig. 22(b). The green dislocation line in Fig. 22(b) is a $1/6\langle 110 \rangle$

Shockley partial, while the Burgers vector of the red dislocation cannot be identified by the DXA. The deformed structure corresponds to point *c* in Fig. 20. This answers the other question raised previously: the load drops at around 18 Å is caused by the plastic deformation in the top ZrO₂ layer. Before the formation of dislocations in ZrO₂ at around 18 Å, the ZrO₂ layer deforms the system along the [110] direction in the same way as in the ZrO₂ simulation (see Fig. 8). In addition, DXA shows that there are dislocation lines in the ZrO₂ layer of ZrO₂/Zr system, but not in the pure ZrO₂ system. This dislocation generation might be caused by the presence the heterogeneous interface and the fact that the ZrO₂ layer in ZrO₂/Zr system is especially thin (much thinner than in the ZrO₂ simulation).

The hardness of the ZrO₂/Zr system increases as the indentation depth increases up to 13 Å, at which point the plastic deformation begins. Then the hardness fluctuates between 13 Å and 18 Å; this is similar to the pure Zr case [32]. The hardness starts to decrease after 18 Å where the load starts to drop and the dislocations start to form in the ZrO₂ layer. We thus speculate that if we indent deeper than 24 Å, the hardness might become stable. However, when we do actually indent deeper than 24 Å, the ZrO₂/Zr system fails and the ZrO₂ fragments in an explosive manner as it is not able to absorb more energy, even at the relatively slow indentation speed used here; the failed system is shown in Fig. 23. In Fig. 23, the indenter presses down by moving from top to bottom. The failure of the ZrO₂ layer at 24 Å indentation depth might be a result of the thinness of the oxide layer, much less than that of the pure ZrO₂ system analyzed above. Moreover, stress can accumulate at the ZrO₂/Zr interface. This interface can impede the transmission of stress from the ZrO₂ thin film to Zr substrate. As a result, the ZrO₂/Zr system tends to fail at shallower indentation depth comparing to ZrO₂ system. In summary, before plastic deformation takes place in the ZrO₂ layer, the relationship between hardness and indentation depth matches that of the pure Zr system. After plastic deformation takes place in the ZrO₂ layer, the relationship between hardness and indentation depth is similar to the situation in the pure ZrO₂ system.

The evolution of the volumetric strain, calculated by the method found in [90, 91], is provided in Fig 24. The reference configuration for calculation of the atomic strain tensor is chosen to be the relaxed ZrO_2/Zr system before indentation. The first highly strained region is located at the interface right under the indenter in Fig. 24(a). The stress first passes to the Zr substrate at the interface. In the above strained region, a dislocation starts to nucleate in the Zr substrate, which correspond to point *a* in the load-displacement curve in Fig. 20. In Fig. 24(b), as the highly strained region continues to grow in the Zr substrate, the Zr surface that contacts the indenter becomes highly strained. Then the highly strained region starts to appear inside the ZrO_2 layer as shown in Fig. 24(c). This region works as a dislocation nucleation site in the ZrO_2 , which corresponds to the point *b* in the load-displacement curve in Fig. 20. The strain does not accumulate at the interface except for the area right under the indenter.

Fig. 22 Deformed structure of ZrO_2/Zr system after nanoindentation. (a) Deformed structure at 12.4 Å indentation depth. The red atoms represent disordered atoms. Atoms in fcc and hcp environment have been removed. (b) Deformed structure at 19 Å indentation depth. The atoms in ZrO_2 layer have been removed. Only dislocation lines are shown. Green lines represent the Shockley partials. Red lines represent other dislocations types. The dislocation lines are captured using DXA.

Fig. 23 The failure of the ZrO₂ layer. Red atoms represent Zr atoms. Blue atoms represent O atoms.

Fig. 24 Evolution of volumetric strain during nanoindentation simulation. Atoms with volumetric strain value smaller than 0.02 are removed. (a) Volumetric strain map at indentation depth of 12 Å. (b) Volumetric strain map at indentation depth of 15.3 Å. (c) Volumetric strain map at indentation depth of 18.6 Å. (d) Volumetric strain map at indentation depth of 21.2 Å.

VI. Conclusions

This work addresses the deformation process of cubic ZrO_2 in both the [110] and [100] orientations. In the elastic deformation regime, the MD simulation results agree with Hertz Law. After rescaling, the MD data is comparable to experimental data for similar systems. Furthermore, the anisotropy predicted by MD simulation matches experiment and the classical theory. Yield behaviors are seen in both the [110] and [100] orientations. The earlier yielding for the [100] orientation is consistent with experiment. All of the above agreement with experiment demonstrates the fidelity of COMB3 ZrO_2 potential used in this work. In the plastic deformation regime, the structural transformation indicates that the structure tends to deform along [110] direction. As the COMB3

potential is a variable charge potential, the charge evolution is also analyzed. When Zr and O atoms are at surface area or in the deformed region, both of their charges tends to decrease in magnitude. These findings for ZrO_2 build the foundation to investigate the ZrO_2/Zr system.

The comparison of Zr, ZrO_2 and ZrO_2/Zr systems provides insights into how the deformation behaviors change as each system forms a heterogeneous structure. The presence of the zirconium oxide layer on top of zirconium substrate significantly delays the plastic deformation in the zirconium substrate, as was also predicted for the pure zirconium system. In addition, this investigation of the ZrO_2/Zr system is, to the best of our knowledge, the first classical MD simulation of the mechanical response of an ionic/metallic heterogeneous system.

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