Nanoindentation of Zr by Molecular Dynamics Simulation

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Abstract

Molecular dynamics simulations of nanoindentation are used to study the deformation behaviors of single crystal Zr for four different surface orientations. The comparison of results for two different potentials, an embedded atom method potential and a charged optimized many body potential, reveals the influence of stable and unstable stacking fault energy on dislocation behaviors under nanoindentation. The load-displacement curve, hardness and deformation behaviors of the various surface orientations Zr are compared and the elastic and plastic deformation behaviors are analyzed.

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I. Introduction.

Due to their very low cross-section for absorption of thermal neutrons, good mechanical properties at elevated temperatures and corrosion resistance, zirconium alloys have been widely used as cladding material in nuclear reactors [1, 2]. Most of these alloy are actually almost all Zr. For example Zircaloy-2 is Zr with Sn(1.2-1.7%), Fe(0.07-0.20%), Cr(0.05-0.15%), and Ni(0.03-0.08%). Zircaloy-4 was developed from Zircaloy-2 with the principal aim of reducing the tendency to pick up hydrogen [3, 4]; this was accomplished by reducing the Ni content and slightly increasing the Fe content [5]. The behaviors of Zircaloy-2 and Zircaloy-4 are very similar except that during high-temperature water corrosion, Zircaloy-4 absorbs less hydrogen than Zircaloy-2 does [1]. Because zirconium clad alloys contain more than 95% zirconium, much of their mechanical response can be expected to be similar to that of pure zirconium. In the reactor, the cladding experiences extremes of temperature, stress, radiation and corrosion. The intense radiation environment will cause radiation defect structures in the cladding material [6-8]. The cladding can react with steam to form hydrogen and ZrO_2 [9]. This hydrogen can diffuse into Zr cladding to form zirconium hydrides.

A Better understanding of the basic deformation behaviors of Zr (and of zirconia-coated zirconium, and zirconium hydride in zirconium) can be expected to help to improve the design and ultimately performance of clad. Nanoindentation is now an important and widely-used method used to probe the mechanical properties of materials at the nanoscale. In particular, it is commonly used for measuring basic mechanical properties such as hardness and elastic modulus [10]. With further development, other mechanical properties can also be determined using nanoindentation [11, 12]. To observe the nucleation and propagation of dislocations and evolution of defect structures, nanoindentation has been combined with electron microscopy to characterize deformation processes at the nanoscale in real time. Nili et al. have discussed the application and development of in situ nanoindentation technology to several different

materials system [13]; opportunities and challenges of in situ nanoindentation and scratch testing combined with SEM have also been reviewed [14]. Despite the development of in situ nanoindentation, full observation of the nucleation and propagation of dislocations at the atomic level remains challenging.

Molecular dynamics (MD) simulation has been used as an effective tool to study the deformation process of metals [15-20] at the atomic level. For example, Van Swygenhoven and coworkers have shown that the stable and unstable stacking fault energies have a strong influence on deformation behavior in fcc metals[18]. Work on Zr by Lu using polycrystalline models discussed the relationship between deformation behaviors and the stable and unstable stacking fault energies [20]. The nanoindentation process has been studied using molecular dynamics in fcc [21-24], bcc [25, 26] and hcp [27] metals. Indeed, computational methods have played a very important role in elucidating the atomic-level mechanisms of dislocation nucleation and propagation under nanoindentation [11].

In this work, we perform molecular dynamics simulations of nanoindentation of a Zr single crystal. Two different empirical potentials are used in the simulation: a Charge Optimized Many Body (COMB) potential [28] and the Mendelev and Ackland Embedded Atom Method (MA EAM) potential [29]. The nucleation and propagation of dislocations are analyzed from the atomistic point view. The effects of four different surface orientations are discussed. The influence of stable and unstable stacking energies on deformation behavior is revealed from the comparison of the results of the two potentials. In future work, we will use the extension of the COMB potential to the Zr-H-O system [30] to analyze the effects of oxidation and hydriding on the deformation behavior under nanoindentation, and the hardness of Zr.

II. Background and Methods

a. Crystallography and slip systems in Zr

The hcp system has an ABABAB close-packed stacking sequence. The crystallography and low-index planes of hcp system are shown in Fig. 1. The ideal c/a ratio for hcp metals is 1.633 [31]. The c/a ratio of Zr is 1.593 [32], which is lower than the ideal value; as a result the prismatic plane is the most densely packed plane in Zr metal and thus prismatic $\langle a \rangle$ is the primary slip system. The experimentally observed deformation modes of Zr are shown in Table. 1.

Fig. 1 (a) Basal and prismatic planes in hcp. (b) First and second order pyramidal planes.

Table 1. Slip and twinning systems of Zr [32].

Properties	Zr
Slip system	Predominant prismatic $\langle a \rangle$
	Secondary basal $\langle a \rangle$, pyramidal $\langle c+a \rangle$
Twin system	Tensile twin $\{1\bar{1}02\} \{11\bar{2}1\}$
	Compressive twin $\{11\bar{2}2\}$

b. Interatomic Potentials

Two empirical potentials will be used in the nanoindentation simulation, the EAM potential developed by Mendeleev and Ackland (MA EAM) [29] and the charge optimized many body potential (COMB) potential [33]. The details of the zirconium COMB potential are presented elsewhere [28]. The pertinent properties of the MA EAM and COMB potentials are listed in Table 2. Both potentials yield very accurate lattice constants and elastic constants compared to experiments, as do DFT calculations. Comparing to the DFT results, both potentials also predict relatively accurate unstable and stable stacking fault energy. Most importantly, for both potentials the energy barrier for basal slip is higher than that of prismatic slip, ensuring that the potentials predict the prismatic slip to be the dominant slip mode [20].

c. Simulation setup

The LAMMPS MD simulator will be used to perform the nanoindentation simulations [34]. The simulation system consists of an active region, a thermostat region and a fixed region, as shown in Fig 2. The active region interacts with the indenter and the movement of atoms in this region is governed purely by the forces on them, with no constraints. The thermostat region helps to control the temperature of the whole system; a Langevin thermostat [35] is applied to this region to control the system's temperature. The fixed region is used to provide rigid support. Periodic boundary conditions are applied in the plane of the Zr film (x and y directions). Prior to the nanoindentation simulation itself, the system is equilibrated under NPT condition at 300K for 50ps. As shown in Fig. 2, the rigid spherical indenter interacts with the active region. The indentation simulation is performed using the “fix indent” command built in LAMMPS. The force exerted by the spherical indenter on each atom in the Zr film is described by:

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

Here, $K = 10 \text{ eV}/\text{\AA}^3$ is the force constant for interactions between the indenter and the film, r is the distance from the atom to the center of the indenter and $R (=45\text{\AA})$ is the radius of the indenter.

Regarding the use of a spherical indenter, the simulation results in the elastic region can be easily compared with the classical theory- Hertz Law. However, stress concentration at a sharper indenter tip could lead to stronger stress concentration and thus lower the stress needed for the first plastic event; for example, when using conical indenters, the both experiment and numerical results show that the hardness increases as the corner angle decreases. [36]. For the spherical indenter, the hardness depends on the radius of the indenter rather than the indentation depth; the hardness increases as the indenter size decreases [37]. Using the spherical indenter allows us to determine the hardness. In addition, the weaker stress concentration for spherical indenter can reduce the dislocation pile up, making it easier to analyze the individual dislocation behaviors.

Table 2. Properties of Zr described by the MA EAM and COMB potentials, compared with experiments and DFT.

Properties	Experiment [38, 39]	DFT [40]	MA EAM [29, 41]	COMB [28]
a (Å)	3.23	3.23	3.234	3.226
c (Å)	5.15	5.17	5.168	5.159
c/a	1.594	1.600	1.598	1.599
E _c (eV/atom)	-6.32	N/A	-6.635	-6.32
C ₁₁ (GPa)	155	156	147	154
C ₁₂ (GPa)	67	61	69	71
C ₁₃ (GPa)	65	62	74	62
C ₃₃ (GPa)	172	166	168	164
C ₄₄ (GPa)	36	26	44	32
Basal I ₂ stacking fault (mJ/m ²)		227	199	267
Prism I ₁ stacking fault (mJ/m ²)		197	145	215
Basal surface (mJ/m ²)		1600	1770	1770
Prism surface (mJ/m ²)		1660	1930	1740

Fig. 2 Schematic of the nanoindentation simulation.

d. Analysis

The load-displacement curves are extracted from the indentation simulation. Prior to the first plastic event, the load-displacement curve shows the characteristic features of elastic response. Hertz continuum elastic contact analysis has been used to determine the elastic deformation behaviors for spherical indenter. Within Hertz theory [42, 43],

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

where P is the applied load by the indenter, R is the radius of curvature of the indenter, h is the indentation depth, and E^* is the reduced modulus, defined as [42, 43],

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

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 hard indenter $E=\infty$ and $v=0$.

The Young's modulus E under a uniaxial stress

$\sigma_{[11\bar{2}0]}$, $\sigma_{[10\bar{1}0]}$, and $\sigma_{[0001]}$ is described in terms of components of the compliance tensor S [44-47],

$$E_{[11\bar{2}0]} = (S_{11})^{-1}$$

$$E_{[10\bar{1}0]} = (S_{11})^{-1} \quad (4)$$

$$E_{[0001]} = (S_{33})^{-1}$$

$$E_{30^\circ \text{ orientation}} = (S'_{33})^{-1}$$

$$S'_{33} = S_{11} \cdot \sin^2(30^\circ) + S_{33} \cdot \cos^2(30^\circ) + (2S_{13} + S_{44}) \cdot \cos^2(30^\circ) \cdot \sin^2(30^\circ)$$

Under a uniaxial stress $\sigma_{[11\bar{2}0]}$, $\sigma_{[10\bar{1}0]}$, and $\sigma_{[0001]}$, the average Poisson's ratio can be expressed as [44-47],

$$\nu_{[11\bar{2}0]} = \frac{-(S_{12}+S_{13})}{2S_{11}}$$

$$\nu_{[10\bar{1}0]} = \frac{-(S_{12}+S_{13})}{2S_{11}} \quad (5)$$

$$\nu_{[0001]} = \frac{-(S_{13}+S_{13})}{2S_{33}}$$

$$\nu_{30^\circ \text{ texture}} = \frac{-(S'_{13} + S'_{13})}{2S'_{33}}$$

$$S'_{13} = S_{13} \cdot [\sin^4(30^\circ) + \cos^4(30^\circ)] + (S_{11} + S_{33} - S_{44}) \cdot \cos^2(30^\circ) \cdot \sin^2(30^\circ)$$

The relationship between stiffness C and compliance S is [47, 48],

$$S_{11} + S_{12} = \frac{C_{33}}{C^2}, S_{11} - S_{12} = \frac{1}{C_{11} - C_{12}}, S_{13} = \frac{-C_{13}}{C^2}, S_{33} = \frac{C_{11} + C_{12}}{C^2}, S_{44} = \frac{1}{C_{44}}$$

$$C^2 = C_{33}(C_{11} + C_{12}) - 2C_{13}^2 \quad (6)$$

Through Eqn. 3 to Eqn. 6, the reduced modulus E^* of MA EAM and COMB potentials can be obtained, Table. 3.

Table. 3 The reduced modulus for MA EAM and COMB potentials.

	$E_{[11\bar{2}0]}^*$ (GPa)	$E_{[10\bar{1}0]}^*$ (GPa)	$E_{[0001]}^*$ (GPa)	$E_{30^\circ \text{ orientation}}^*$ (GPa)
MA EAM	114	114	133	129
COMB	125	125	141	121
Experiment [44]	109	109	138	106

The hardness, H, can also be extracted from the nanoindentation [49],

$$H = P/A \quad (7)$$

Where P is the load in the direction perpendicular to the surface of the indenter and A is the imprinted area of the indenter on the surface. Eqn. 7 will be used to calculate the hardness value of the nanoindentation simulation. The load value P is calculated directly from the simulation by the LAMMPS code. The area A is calculated using

$$A = \pi\delta(2R - \delta) \quad (8)$$

Where R is the radius of the indenter and δ is the indentation depth.

The method used to calculate hardness is shown in Fig. 3. In the elastic region, hardness as defined in Eqn. 7 is a strong function of the indentation depth, but once the plastic deformation begins, its value stabilizes and only fluctuates slightly, reflecting the various operant deformation processes. This is illustrated in the relationship between hardness and indentation depth in Fig. 4. The hardness is thus obtained by calculating the instantaneous simulated values of the hardness over the indentation depths greater than

about $9\text{\AA}$ shown in the red dot line region in Fig. 6. The reported error bars of the hardness are represented by the standard deviation from the average in this dataset.

Fig. 3 Method used to calculate hardness after reference [10, 12].

Fig. 4 Relationship between (a) load and (b) hardness and indentation depth for $[11\bar{2}0]$ orientation. The reported hardness and its uncertainty are obtained for depths bounded by the red dotted lines.

In order to analyze the deformation process, Common Neighbor Analysis (CNA) [50, 51] is used to distinguish atoms in hcp, fcc and other environments. With the help of CNA, the dislocation lines and stacking fault structures can be easily visualized. In addition, the visualization software OVITO is used to visualize the structures [52]. The Crystal Analysis Tool developed by Stukowski is capable of identifying lattice and defect

structures, identifying dislocation directions and their corresponding Burgers vectors, and computing the atomic-level elastic and plastic deformation gradient fields [53-55].

e. Indentation speed.

In indentation experiments, the velocity of the indenter ranges from tens of nm s^{-1} , to 1 mms^{-1} , [27]. Because of the computational cost of MD simulation, the velocity of the indenter has to be of the order of ms^{-1} , which is much faster than experiment. In order to explore the effect of the indentation speed on the nanoindentation results, simulations were performed under different indenter velocities, ranging from 2 ms^{-1} to 50 ms^{-1} .

Because simulations using the MA EAM potential are less time consuming than simulations with the COMB potential, this indentation speed test is performed using only the MA EAM potential and the [0001] orientation. A relatively small system size is used to perform the indentation speed test.

From Fig. 5, we can see that while the general shape and characteristics of the load-displacement curve are only weakly dependent on the indentation speed, the fine details are substantially different, especially for the fastest nanoindentation simulation of 50 ms^{-1} . These fine details are associated with the various dislocation nucleation and propagation processes, as we describe in detail below. In particular, the first peak in the load map before it drops takes place at the indentation depth of $\sim 5 \text{ \AA}$ for $2, 5, 10$ and 25 ms^{-1} speeds, but at somewhat deeper indentation depth for 50 ms^{-1} . In addition, the magnitude of this first load drop generally increases as the indentation speed decreases, with the $2, 5$, and 10 ms^{-1} drops being very similar. Similarly, the 2nd and subsequent peaks on load-displacement curves for $2, 5, 10, 25$ and 50 ms^{-1} are all at different indentation depths. Overall, for slower speeds, there are more peaks and the load drop for each peak is larger. Detailed comparison of the processes, however, which is presented in Fig. 6 for 5 and 50 ms^{-1} , clearly demonstrates that faster speed results in qualitatively different behavior, namely there are very few dislocation loops observed for 50 ms^{-1} , while they are present in all simulation with slower indentation speeds. For faster indentation speed, pyramidal

dislocations mainly form, while for slower indentation speed, pyramidal, basal and prismatic dislocations all form. The hardness obtained from different indentation speeds also varies systematically: 4.5 ± 0.2 GPa (50 ms^{-1}), 4.2 ± 0.2 GPa (25 ms^{-1}), 4.0 ± 0.2 GPa (10 ms^{-1}), 3.6 ± 0.3 GPa (5 ms^{-1}) and 3.5 ± 0.26 GPa (2 ms^{-1}). As the indentation speed decreases, the calculated hardness becomes smaller, becoming essentially independent of indentation speed at low speeds. In subsequent simulations, use 5 ms^{-1} as the indentation speed as providing a realistic representation of the dislocation behaviors in Zr at a reasonable computational load.

Fig 5. The loading and unloading curve of Zr using MA EAM potential at 2 ms^{-1} , 5 ms^{-1} , 10 ms^{-1} , 25 ms^{-1} and 50 ms^{-1} .

Fig. 6. Indentation at 24 Å indentation depth of MA EAM potential (a) 50 ms⁻¹ (b) 5 ms⁻¹. Red atoms represent disordered atoms. Atoms in hcp environments are not shown.

f. Substrate thickness effects

Systems used in MD simulations have dimensions of tens or at most a few hundred nanometers. The characteristics of the load-displacement curve can be influenced by the system size. In order to understand how the substrate's thickness influences the load-displacement curve in both elastic deformation and plastic deformation regime, MD nanoindentation simulations with different active layer sizes are tested for the $[10\bar{1}0]$ orientation, using the MA EAM potential. It can be seen from Fig. 7 that the thickness of the active layer has an effect on the load-displacement curve for small thicknesses of the active layer, converging for larger thicknesses, with the results for 168 Å and 190 Å being essentially identical. Further evidence that this system size is adequate come the fact that the slope of the load-displacement curve matches the Hertz law result. For thicker active layer as shown in Fig. 7, the first load drop related to the plastic deformation takes place at a smaller indentation depth. As for the characteristics of the dislocations, there are no fundamental structural differences for different active layer thickness, as shown in Fig. 8. The dislocation loop travels downwards and stops at the bottom of the active region. The strain field of the dislocation loop is different for different thickness active region; in particular, the dislocation loops in the thicker active region are larger in size. As for simulations with the COMB potential, no dislocation loops have been observed, so the substrate thickness effect is smaller for COMB than MA EAM.

Fig. 7. Load-indentation curves of $[10\bar{1}0]$ orientation using the MA EAM potential with the thickness of the active region ranging from 90Å to 190Å.

Fig. 8. Deformed structures of $[10\bar{1}0]$ orientation using the MA EAM potential at 22Å indentation depth. (a) 134Å (b) 168Å thick active regions.

III. Results and Discussion

a. Indentation with different orientations

In indentation of a single crystal, the crystallographic orientation of the indented surface will promote some deformation modes and hinder others, thus eliciting different mechanical responses [32]. Murty and Charit performed a detailed experimental study of the orientation development and deformation behavior in zircaloys. In this work, four different orientations as shown in Fig. 9 are chosen to perform the indentation tests: [0001], [11 $\bar{2}$ 0], [10 $\bar{1}$ 0] and the [0001] orientation rotated by 30° around the c-axis (“the 30° orientation”), commonly used in zircaloy [56]. From the crystallography point of view, the [11 $\bar{2}$ 0] and [10 $\bar{1}$ 0] orientations promote prismatic <a> slip and basal <a> slip. The [0001] orientation promotes pyramidal <a+c> slip. The 30° orientation promotes pyramidal <a+c> slip and basal <a> slip. The load-displacement curves for the two potentials in the elastic region are shown in Fig. 10, while complete load-displacement curves are shown in Fig. 11. The hardness values calculated from these data are shown in Fig. 12. The hardness value is obtained from experiment done on Zr-1Nb-0.05Cu zirconium alloy [57]. The polycrystalline zirconium alloy has grain boundary structures and more orientations of grains, which can make it easier for the dislocation to nucleate. So it is reasonable that the hardness value of the tested zirconium alloy is smaller than that of the simulation results.

Before the first dislocation activity, the characteristic of the load-displacement curve lies in the elastic regime. The MD results are consistent with the Hertz analysis; in particular, in the elastic regions shown in Fig. 10, the load does indeed vary as $h^{3/2}$ for both potentials and for all four surface orientations; the reduced modulus values, E^* shown in Table 3. These E^* values indicate that the slope of the load-displacement curve of [0001] orientation should be steeper than that of the [11 $\bar{2}$ 0] orientation and [10 $\bar{1}$ 0] orientation. From the classical theory, $E_{[11\bar{2}0]}^* = E_{[10\bar{1}0]}^*$; thus the load-displacement curves of [11 $\bar{2}$ 0] and [10 $\bar{1}$ 0] orientations should be the same in the elastic region. For the MA EAM, Fig. 10(a), they match exactly with each other while for the COMB potential, Fig. 10(c), there is a small deviation. In addition, the load-displacement curves of [11 $\bar{2}$ 0] and [10 $\bar{1}$ 0] orientations from the simulations also quite closely match the Hertz law for the two potentials, particularly for the MA EAM potential.

By contrast, the load-displacement curves obtained from the simulations for the [0001] orientation are steeper than the Hertz Law predictions for both potentials, with the disagreement being larger for the MA EAM potential than for the COMB potential. For the 30° orientation, the load-displacement curves predicted by the Hertz Law are steeper than the simulation results for both potentials. Although the deviation of the simulation results from the Hertz Law predictions for [0001] and the 30° orientation are slightly larger, the load-displacement curves still show elastic behavior. In summary, the overall elastic response can be quite well represented by Hertz theory.

The plastic deformation begins at the first load drop in the load-displacement curve. It is most pronounced for the [0001] orientation, and less so for the other orientations considered. As shown in Fig. 11(a) for the MA EAM potential, the 30° orientations support the largest load, while the $[10\bar{1}0]$ support the lowest load. As shown in Fig. 11(b) for the COMB potential, the $[11\bar{2}0]$ orientation supports the largest load, while the 30° orientation supports the lowest load. The load drops in the load-displacement curve represent the plastic deformation events throughout the indentation simulation. The magnitude of the load drop and the indentation depth where the load drop happens all varies slightly for different orientations of different potentials. One obvious similarity for both potentials is that the [0001] orientation has the largest first load drop at around $5\text{\AA}$ indentation depth. The details of the plastic deformation events are discussed later.

The comparison of hardness for the four simulated orientations of two potentials is shown in Fig. 12. The 30° orientation (MA EAM) and $[11\bar{2}0]$ orientation (COMB) have highest hardness value, while the $[10\bar{1}0]$ orientation (MA EAM) and the 30° orientation (COMB) have the lowest. However, as shown in Fig. 4, the hardness fluctuates with the indentation depth. So when taking into account the fluctuations represented by the errors bars in Fig. 12, the difference of the hardness value for different orientations of the two potentials is not significant.

The atomic-level details of the deformed structures combined with the elastic properties provide insights into these differences in the hardness and load-displacement curves. The

deformed atomic structures of the four orientations are shown in Fig. 13 (MA EAM) and Fig. 14 (COMB) where again atoms are color coded in accord with Common Neighbor Analysis (CNA) [50, 51]. The calculated total dislocation line length, dislocation density, dislocation segments and junctions of all the deformed structure using the Crystal Analysis Tool are listed in Table. 4 [53-55]. The Crystal Analysis Tool has some difficulties to capture the dislocation structure in the COMB simulations. So the dislocation density of the COMB simulations is not listed in Table. 4.

Fig. 9 Four different orientations of Zr used in the nanoindentation simulation, with the surface plane shown in blue. (a) $[0001]$ orientation. (b) $[11\bar{2}0]$ orientation. (c) $[10\bar{1}0]$ orientation. (d) The “ 30° orientation”. The exposed plane in (d) is perpendicular to c_1 .

Fig. 10 Load-displacement curves in the elastic region. (a) MA EAM $[11\bar{2}0]$ and $[10\bar{1}0]$ orientation, (b) MA EAM $[0001]$ orientation and 30° orientation, (c) COMB $[11\bar{2}0]$ and $[10\bar{1}0]$ orientation (d) COMB $[0001]$ orientation and 30° orientation. All the data from the MD simulations are fitted using a moving average method.

Fig. 11 Load-displacement curve of four different orientations for the nanoindentation simulation: (a) MA EAM potential, (b) COMB potential.

Fig. 12 Hardness of four orientations using MA EAM and COMB potential. The experiment value is from reference [57].

Table 4. Total dislocation line length, dislocation density, number of dislocation segments and junctions calculated by Crystal Analysis Tool.

	Total dislocation line length (Å)	Dislocation Density (m^{-2})	Segments	Junctions
MA EAM $[11\bar{2}0]$	1608	1.17×10^{16}	72	36
MA EAM $[10\bar{1}0]$	1315	0.96×10^{16}	51	23
MA EAM $[0001]$	1132	0.9×10^{16}	67	32
MA EAM 30° orientation	765	4.02×10^{15}	32	14
COMB $[11\bar{2}0]$	219		3	0
COMB $[10\bar{1}0]$	203		7	1
COMB $[0001]$	0		0	0
COMB 30° orientation	6.1		1	0

b. MA EAM analysis

From the deformed structures of four different orientations shown in Fig. 13, we can see that dislocation loops are commonly activated for the MA EAM potential. The dislocation loop consists of partial dislocations on the basal plane and dislocations on the prismatic planes. Dislocation loops are only been observed traveling along the $\langle a \rangle$ direction on prismatic plane inside the bulk or on the surface in this nanoindentation simulation. The dislocation loop observed in this nanoindentation turns out to be the most stable interstitial loop in Zr, and has been observed by de Diego and coworkers in their simulation work [58]. They found that the rectangular self-interstitial loop that consists of prismatic dislocations and basal partial dislocations has the lowest formation energy and highest binding energy [58].

For the $[10\bar{1}0]$ and $[11\bar{2}0]$ orientations, as shown in Figs. 13 (a) and (b), the dislocation loops form under the indenter and travel along the $\langle a \rangle$ direction on the prismatic plane. Despite their similar dislocation behaviors, there is a difference of hardness between the $[11\bar{2}0]$ orientation (5.27 GPa) vs. $[10\bar{1}0]$ orientation (4.65 GPa). When considering the elastic deformation contribution, as discussed in Section 4.1 the $[11\bar{2}0]$ orientation and $[10\bar{1}0]$ orientation have similar load-displacement curves due to the same reduced modulus. With regards to the plastic deformation contribution, the Schmid factors [59] for prismatic and basal slips are identical for these two orientations: 0.433 (prismatic planes neither parallel nor perpendicular to the indentation direction) and 0 (prismatic planes parallel or perpendicular to the indentation direction) for prismatic slips and 0 for basal slip. However, for the $[10\bar{1}0]$ orientation, the surface is one of the prismatic planes; therefore dislocation loops travelling along the $\langle a \rangle$ direction on the surface are commonly observed in these nanoindentation simulations. This dislocation loop motion on the surface may contribute to the lower hardness for the $[10\bar{1}0]$ orientation. In addition, the size and the detailed atomic structures of dislocations are different for these two orientations, with the dislocation loops formed in the $[11\bar{2}0]$ orientation being generally larger. The detailed atomic structures of one of the dislocation loops from each orientation are shown in Fig. 13. The sizes of the dislocation loop for $[10\bar{1}0]$ and $[11\bar{2}0]$ orientations are $42\text{\AA} \times 55\text{\AA}$ and $66\text{\AA} \times 55\text{\AA}$ correspondingly. The basal partial component

of the dislocation loop is longer for $[11\bar{2}0]$ (66 Å) than for $[10\bar{1}0]$ (42 Å). In addition, more jogs are formed in the basal partial component of the dislocation loop for the $[11\bar{2}0]$ orientation than for the $[10\bar{1}0]$ orientation. From the dislocation structures we conclude that more plasticity events take place in the $[11\bar{2}0]$ orientation than in the $[10\bar{1}0]$ orientation. This is confirmed by the calculation results from the Crystal Analysis Tool: the $[11\bar{2}0]$ orientation yields longer total dislocation line length (1608 Å vs. 1315 Å for $[10\bar{1}0]$), more segments (72 vs. 51) and more junctions (36 vs. 23). From the load-displacement curve, we can see that for the $[10\bar{1}0]$ orientation the large load drops happen at an early stage of the plastic deformation, while for $[11\bar{2}0]$ orientation the large load drops happen at a later stage of the plastic deformation. After 15 Å indentation depth, the load response for $[11\bar{2}0]$ orientation becomes obviously larger than for the $[10\bar{1}0]$ orientation. This leads to the result that the hardness of $[11\bar{2}0]$ (5.27 GPa) is higher than that of $[10\bar{1}0]$ orientation (4.65 GPa). However, when taking into account the uncertainties associated with the fluctuations shown in Fig.4 and Fig. 12, these values do not differ significantly. In summary, taking into account both of the contribution from elastic and plastic deformation, the $[11\bar{2}0]$ orientation yields similar hardness as $[10\bar{1}0]$ orientation does.

For the 30° and $[0001]$ orientations, as shown in Figs. 13 (c) and (d), dislocation loops form under the indenter. For both orientations, the dislocation loops only travel along the surface. The second basal partial dislocation cannot nucleate to form a full dislocation loop. It is thus not surprising that dislocation loops are not observed to leave the surface to travel inside the bulk. Pyramidal slip is observed along with the dislocation loops.

Considering the elastic deformation, the reduced modulus of the $[0001]$ orientation has the highest value among the four orientations. The reduced modulus of the 30° orientation (129 GPa) lies between those of the $[0001]$ orientation (133 GPa) and $[11\bar{2}0]$ orientation (114 GPa) but very close to $[0001]$ orientation. Thus, from the viewpoint of elasticity, the $[0001]$ orientation should have the highest load response and the steepest slope of the load-displacement curve in the elastic region, which agrees with the simulation results as shown in Fig. 11(a).

Comparing the details of the plastic deformation of these two orientations may give some insights to the difference in the magnitude of the load drop. As shown in Fig. 13 (c) and (d), the dislocation density is much higher for the [0001] orientation than for the 30° orientation. In addition, the calculations from the Crystal Analysis Tool show that the [0001] orientation has a total length of dislocation of 1132 Å compared to 765 Å for the 30° orientation, confirming that the 30° orientation has the lowest dislocation density. This lower dislocation density is consistent with the small load drop. The small dislocation density combined with the moderately reduced modulus results in the largest hardness value (5.68 GPa) for the 30° orientation among the four orientations. Although it has the largest reduced modulus, the [0001] orientation has a hardness of only 5.13 GPa due to the relative ease with which plastic events are nucleated. Furthermore, this ease of nucleation for [0001] orientation is consistent with the crystallography: the dislocation loop glides in the $\langle a \rangle$ direction on prismatic plane, which is parallel to the surface for the [0001] orientation.

Fig. 13 CNA analysis of Zr indentation at around 26 Å indentation depth using MA EAM. (a) $[10\bar{1}0]$ orientation (b) $[11\bar{2}0]$ orientation (c) 30° orientation along c-axis. (d) $[0001]$ orientation. Red atoms represent the disordered atoms. Green atoms represent the atoms in fcc environment. The atoms in hcp environment are not shown.

Fig. 14 CNA analysis of Zr indentation at around 26 Å indentation depth using the COMB potential. (a) $[10\bar{1}0]$ orientation (b) $[11\bar{2}0]$ orientation (c) 30° orientation along c-axis. (d) $[0001]$ orientation.

Fig. 15 Atomic structures of dislocation loop formed during indentation simulation using MA EAM potential. (a) $[10\bar{1}0]$, (b) $[11\bar{2}0]$

c. COMB analysis

As we saw in Fig. 12, the hardness values predicted from the COMB potential are similar to those predicted from the MA EAM potentials. Nevertheless, as we now discuss, the atomic-level details of the plastic response are somewhat different.

The deformed structures of four orientations are shown in Fig. 14 for the COMB potential. The prismatic $\langle a \rangle$ and pyramidal dislocation are the most prevalent; moreover, there are very few basal partial dislocations. In the absence of basal partial dislocations, the dislocation loop of basal and prismatic dislocations seen in MA EAM simulation is not observed in the COMB simulation. The reasons for this difference will be discussed in the following section.

For the $[10\bar{1}0]$ and $[11\bar{2}0]$ orientations, as shown in Figs. 14 (a) and (b), prismatic $\langle a \rangle$ dislocations and pyramidal dislocations are most commonly activated during the indentation test. In the elastic deformation regime, the $[10\bar{1}0]$ and $[11\bar{2}0]$ orientations

yield very similar load-displacement curves because they have same reduced moduli. In combination with their similar dislocation behaviors, this results in similar hardness values, 5.37 GPa for the $[10\bar{1}0]$ orientation and 5.46 GPa for the $[11\bar{2}0]$ orientation.

For the 30° and $[0001]$ orientations, as shown in Figs. 14 (c) and (d), pyramidal $\langle a+c \rangle$ dislocations predominate. For the $[0001]$ orientation, the load-displacement curve has the highest load response in the elastic regime, as shown in Fig. 11(b). Moreover, as in the case of the MA EAM potential, the load drop related to the first plastic event, at around 5 Å indentation depth, is the largest among the four orientations. The largest elastic deformation combined with the largest load drop leads to a moderate hardness value of 5.04 GPa, smaller than that of $[11\bar{2}0]$ and $[10\bar{1}0]$ orientations. For the 30° orientation, as a result of the smallest reduced modulus (121 GPa) among the four orientations, it has the lowest load response in the elastic regime, as shown in Fig. 11(b). The dislocation behavior of the 30° orientation is very similar to the $[0001]$ orientation. With the contributions from both elastic and plastic deformation, the 30° orientation yields the smallest hardness value of 4.79 GPa.

d. Comparison between MA EAM and COMB potential

In the elastic regime, both the MA EAM and COMB potential agree with the Hertz Law predictions especially for the order of the load response of four different orientations. In the plastic regime, the prismatic $\langle a \rangle$ dislocation and pyramidal dislocation are most commonly observed for both potentials. Among the four orientations, the $[0001]$ orientation has the largest first load drop for both potentials, which has a significant influence on the hardness value. And as we saw in Fig. 12, the hardness values predicted from the COMB potential are similar to those predicted from the MA EAM potentials when taking into account the uncertainties represented by the error bars. Nevertheless, the atomic-level details of the plastic response are different. In contrast with the MA EAM potentials, no dislocation loops are emitted for the COMB potential. The reason for this difference is discussed as below.

As is well known, the stacking fault and unstable stacking fault energies play an important role in determining the dislocation behaviors [18]. A comparison of the stacking fault energies of MA EAM potential and COMB potential was reported previously [20]. Summarizing these previously reported results, the stable and unstable stacking fault energies along the basal partial $\langle a \rangle$ path for the COMB potential are higher than for the MA EAM potential, while the most reliable DFT values are the lowest. This explains why basal partial dislocations and stacking fault structures are rare in COMB; in this regard the MA EAM potential should have higher materials fidelity than the COMB potential. Also the ratio of energy barriers for basal slip and prismatic slip, $\frac{\gamma_{basal}}{\gamma_{prismatic}}$, is 1.13 for MA EAM and 1.41 for COMB potential, while the DFT [41] value is 1.26. That is, for the MA EAM potential prismatic dislocations should be only slightly more prevalent than basal partial dislocations. This is consistent with dislocation loop consists of basal partial dislocation and prismatic dislocation being commonly observed for MA EAM potential. By contrast for the COMB potential, prismatic dislocations are more likely to form than basal partial dislocations. For all four orientations, the COMB nanoindentation simulations display prismatic dislocations rather than basal dislocations. Because the stacking fault energies for the COMB potential is higher than for the MA EAM potential[20], the dislocation density for MA EAM potential is higher than COMB potential.

DFT calculations generally offer higher materials fidelity than calculations with classical potentials; thus the DFT results should more closely match experiment. While nanoindentation with DFT is not computationally feasible, the fact that the energy barrier ratio for DFT lies between the values for COMB and MA EAM suggests that formation and propagation of dislocation loops in Zr metal should take place, but not to the same degree as predicted by MA EAM potential.

e. Microstructure evolution during nanoindentation for $[10\bar{1}0]$ orientation

The initial stages of dislocation evolution are shown in Fig. 16 (MA EAM) and Fig. 17 (COMB). When the dislocation starts to form in the area under the indenter, the deformed structures are similar for both potentials. The prismatic $\langle a \rangle$ dislocation and stacking fault on the basal plane are observed as shown in Fig. 16(a) and Fig. 17(a). For the MA EAM potential, a prismatic $\langle a \rangle$ dislocation form first with glide plane is parallel to the surface. This is followed by the basal partial $\langle a \rangle$ dislocation that connects with one end of the prismatic $\langle a \rangle$ dislocation. Then another basal partial $\langle a \rangle$ dislocation forms and connects with the other end of the prismatic $\langle a \rangle$ dislocation. Thus the formation of a dislocation loop that consists of two basal partial $\langle a \rangle$ dislocations and one prismatic $\langle a \rangle$ dislocations is completed. The dislocation loop glides on the $[10\bar{1}0]$ surface along the $\langle a \rangle$ direction. In contrast, for the COMB potential, as shown in Fig. 17, the prismatic $\langle a \rangle$ dislocation continues to glide on the initial prismatic plane when it forms. At higher stress the pyramidal dislocations form and glide in addition to prismatic ones; however, no basal dislocations are produced. This picture is consistent with the energy barrier ratios for the two potentials. In addition, pyramidal dislocations have only been observed for the COMB potential. Pyramidal $\langle a+c \rangle$ dislocation provides the needed deformation in $\langle c \rangle$ direction.

In addition, for the MA EAM potential, dislocation loops form under the indenter and glide into the bulk, as shown in Fig. 18. The first defect structure consists of a leading prismatic dislocation and two basal partials, as shown in Fig. 18 (a). This then evolves into a structure that consists of two basal partial dislocations and a prismatic dislocation gliding into the bulk along the prismatic plane, as shown in Fig. 18 (b) and (c). The defect structure then starts to break off from the two dislocations. A similar break-off behavior was also observed in MD simulations of nanoindentation of a bcc metal [25]. The break-off process of the defect structure is shown in Fig. 19 from a different direction. We can see that while the two basal partial dislocations and a prismatic dislocation defect structure glide into the bulk through the screw $\langle a \rangle$ component of two dislocations, the two dislocations appear to have edge $\langle a \rangle$ components. The two dislocations also move in the $\langle c \rangle$ direction, as shown in Fig. 19(b). When the dislocations moving along the $\langle c \rangle$ direction finally meet, as shown in Fig. 19(c), the break-off behavior takes place. The

final dislocation loop structure is shown in Fig. 19(d). Thus, while the COMB potential shows dislocation $\langle c \rangle$ component through pyramidal $\langle c+a \rangle$ slip, the MA EAM potential shows a dislocation $\langle c \rangle$ component in the dislocation loop formation process.

Fig. 16 Initial stage of dislocation behaviors for MA EAM potential in $[10\bar{1}0]$ orientation.

Fig. 17 Initial stage of dislocation behaviors for COMB potential in $[10\bar{1}0]$ orientation.

Fig. 18 Formation of dislocation loop that glides into the bulk of MA EAM potential in the $[10\bar{1}0]$ orientation.

Fig. 19 Dislocation loop formation process of MA EAM potential in $[10\bar{1}0]$ orientation.

f. Microstructure evolution during nanoindentation for $[0001]$ orientation

The initial dislocation behaviors of MA EAM and COMB potential for $[0001]$ orientation are shown in Fig. 20. For MA EAM, the basal partial dislocation and prismatic dislocation start to form under the indenter. The basal partial dislocation and prismatic

dislocation forming a dislocation loop glide on the surface (basal plane) along the $\langle a \rangle$ direction. For COMB, pyramidal $\langle a+c \rangle$ dislocations start to form under the indenter. While because of the higher energy barrier for basal partial dislocations compared to MA EAM, basal partial dislocations are not expected in the COMB potential, they are not observed in the MA EAM simulations either. It appears that the energy barrier for pyramidal $\langle a+c \rangle$ dislocation to form is relatively low since we observe pyramidal dislocations in all four orientations for COMB. Also for MA EAM, the basal partial dislocation and prismatic dislocation seem to facilitate each other, because basal partial dislocations and prismatic dislocations always connect with each other to form a loop. Thus the COMB potential displays deformation in the $\langle a \rangle$ and $\langle c \rangle$ direction by pyramidal $\langle a+c \rangle$ dislocation, whereas the MA EAM potential displays the deformation in $\langle a \rangle$ and $\langle c \rangle$ direction by forming dislocation loops. The detail of the formation of dislocation loops is shown in Fig. 21. First, the prismatic $\langle a \rangle$ dislocation forms connected with the basal partial dislocations as shown in Fig. 21(a). Then the basal partial dislocation grows with several jogs that contain a $\langle c \rangle$ component as shown in Fig. 21(b) and (c); the second prismatic dislocation then forms. The dislocation loop, consisting of two prismatic dislocations and one basal partial dislocation, moves along the surface (basal plane) as shown in Fig. 21(d). The movement of the dislocation loop along the surface is also seen in the $[10\bar{1}0]$ orientation. However due to the different orientation, the dislocation loop seen in $[10\bar{1}0]$ orientation consists of two basal partial dislocations and one prismatic dislocation.

Fig. 20 Microstructure evolution of [0001] orientation during nanoindentation. (a) and (b) MA EAM. (c) and (d) COMB.

Fig. 21 Details of dislocation loop formation in $[0001]$ orientation for MA EAM.

IV. Conclusions

In this work, nanoindentation MD simulation has been performed for four different orientations of single crystal Zr using MA EAM and COMB potentials. The load-displacement curves present the elastic characteristics in the elastic region for both

potentials. The factors that influence hardness value have been illustrated. Both elastic and plastic deformations contribute to the hardness value. Due to the small differences in the reduced modulus for different orientations of the tested four orientations, the plastic deformation plays a more important role in determining the hardness value. The load drop associated with dislocation behaviors has a direct impact on the hardness value, with larger load drops tending to lead to a relatively small hardness. Furthermore, the dislocation behaviors and the atomic structures of the dislocations during the nanoindentation largely depend on the stable and unstable stacking fault energy and the ratio of unstable stacking fault energies on different slip planes. The rather small difference in $\frac{\gamma_{basal}}{\gamma_{prismatic}}$ values leads to very different dislocation behaviors in the nanoindentation test. For MA EAM, dislocation loops consist of basal partial dislocation and prismatic $\langle a \rangle$ dislocation are extensively observed. In contrast, for COMB, no basal dislocations are produced; as it doesn't produce any dislocation loops either. The comparison of the two potential during nanoindentation shows that the competition between different types of dislocation on different planes under nanoindentation is mainly determined by the small difference of the unstable stacking energy on the gliding plane.

In summary, while we see that the specifics of the plastic response depend on the energetics of the stacking faulty, which differ for the two potentials, the overall responses for all four surface orientations and for both potentials are rather similar. We can thus expect that they reasonably well describe the experimental mechanisms of deformation in Zr.

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