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An interatomic potential for simulation of defects and phase change of zirconium

Yifang Ouyang [a,*], Jizheng Wu [a], Minghui Zheng [a], Hongmei Chen [a], Xiaoma Tao [a], Yong Du [b], Qing Peng [c,*]

[a] *Guangxi Colleges and Universities Key Laboratory of Novel Energy Materials and Related Technology, College of Physical Science and Technology, Guangxi University, Nanning 530004, China*
[b] *State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China*
[c] *Department of Nuclear Engineering and Radiological Science, University of Michigan, Ann Arbor, MI 48109, USA*

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ABSTRACT

We introduce a long-range interaction analytical embedded atom method (namely la-EAM) interatomic potential, which has been developed by fitting the lattice constants, cohesive energy, mono-vacancy formation energy and elastic constants of α-Zirconium. We validate this la-EAM potential by extensive investigation of the bulk, surface, and defect properties of Zirconium using molecular dynamics simulations compared with available experiments and theoretical results. We examine the lattice constants, cohesive energy, elastic constants, phonon dispersion curves of α-, β-, and ω-Zirconium and find a good agreement with available experiments. We have studied the 0D (zero-dimension) defects including vacancies and self-interstitial atoms, 1D defects (dislocations), 2D defects including surface and stacking fault, and 3D bulk properties. Furthermore, our phase transformation energy barrier of $\alpha \rightarrow \omega$ agrees with the experimental observation. The success of our potential could attribute to the correctly accounting for the long-range interactions of the Zr atoms. Our results suggest that the developed la-EAM potential of Zr is useful in molecular dynamics simulations of bulk, surface and defect properties and phase transitions of Zirconium at various temperatures and pressures.

1. Introduction

Zirconium is a fascinating *d*-orbital transition metal, which has extensive technical applications in aerospace, medical and nuclear fields due to its high strength, light weight, corrosion resistance, and small neutron absorption sections [1]. At ambient conditions, the crystalline structure of Zirconium is hexagonal close-packed (hcp) structure, or α phase. When the temperature rises, at zero pressure, Zirconium transforms from martensitic (a face-centered cubic, fcc) structure into the body-centered cubic (bcc) structure, or β phase, at 1136 K, and then eventually melts. When the pressure is increased while temperature kept at room temperature, a martensitic phase (fcc) transformation into the ω phase is observed [2,3]. The ω phase is widely accepted as the strengthening phase in Zr and its alloys due to its higher hardness over α phase [4].

The phase transformation of Zirconium may be explained by its anomalism of the phonon dispersion curves. One of the aims of this work is the anomalous phonon properties for Zirconium, which might be a hint to the various martensitic transformations. Furthermore, it could provide some hint in understanding the anomalous self-diffusion of Zirconium. In the hcp structure, the zone center of the [0 0 1] LO branch substantially softens and exhibits a dip at low temperature [5]. This may lead to the superconducting transition. The phonon dispersion curves of bcc phase show that there is a large low-energy dip in the high-symmetry longitudinal phonon branch L $[\xi\xi\xi]$ for ξ=2/3. This dip appears at high temperature, and it is temperature-dependent. This soft mode is believed to cause the $\alpha \rightarrow \omega$ phase transformation. The entire T_1 $[\xi\xi 0]$ phonon branch with $[1\ \bar{1}\ 0]$ polarization is of low energy and is overdamped, which is related to the transformation of $\beta \rightarrow \alpha$. There is inconsistency of phonon-dispersion curves of bcc phase between the theoretical predictions and experiments. At ambient pressure, the theoretical predicted soft modes of T_1 N-point phonon and an unstable bcc structure [6], while, experiments confirmed the phase transformation occurs at a finite frequency [7].

From experimental aspect, the orientation relationship of phase transformation between the parent and the product phases may be determined. However, such an approach may result in multiple transformation pathways for a given set of orientation relationships. As a consequence, one has to guess the possible

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* Corresponding authors.
E-mail addresses: ouyangyf@gxu.edu.cn (Y. Ouyang), qpeng.org@gmail.com (Q. Peng).

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transformation pathway by calculating the energy barrier of phase transformation to unravel the mechanism of phase transition [8,9].

Molecular dynamics (MD) and Monte Carlo (MC) methods are powerful techniques for atomistically investigating the phenomena relevant to temperature and time dependence in large scales, which in general are impractical for first-principles methods. The force field potential describes the atomistic interactions between atoms, which plays an essential role in MD and MC simulations. However, the accuracy of atomistic simulation ultimately depends on the force field potentials, which is generally generated by fitting with experiments or first-principles calculations. Plenty of empirical potentials have been developed in the past six decades (refer to [10,11]).

Zirconium has been the subject of many theoretical studies. There have been quite a lot of attempts to develop many-body interatomic potentials for the hcp structures of various materials, especially for Zr. These potentials, most of them if not all, aim to reproduce the experimental values of elastic constants and c/a ratio of hcp structures. There are five independent elastic constants of hcp structures. The *c*/*a* ratio of an "idea" hcp structure is 1.633. The lattice constants and elastic constants are critical important in determine many other related physical properties including modulus, strength, and hardness. It turns out that force field generated in this way can be reliable in studying the bulk, surface and defects properties. Same strategies are employed in the development of the embedded atom method (EAM) [12], as well as the *n*-body potential [13]. Following the schedule of EAM, Oh and Johnson [14,15] proposed an analytical EAM (AEAM) by fitting the Voigt bulk and shear moduli, with ideal *c*/*a* ratio for Mg, Zr and Ti [14] and a more realistic *c*/*a* ratio for Zr [15]. Igarashi et al. [16] presented EAM type potentials for a number of hcp metals by attempting to exactly match those properties. Hu et al. proposed an analytic modified EAM for hcp metals by including a modified term [17]. Baskes and Johnson [18,19], Kim et al. [20] presented so called modified EAM (MEAM). As for hcp structure metals, other potentials [21–23] have been developed by different means. These developed potentials have been applied to study the bulk, surface, defect and thermodynamic properties. Despite extensive efforts, an accurate force field for Zr is still lacking to describe defective structures and phase transitions. For example, the investigations of stacking fault energy in α Zirconium indicate that the long-range interaction potential is needed for exactly description of anomalous behavior of Zirconium, which, however, are missing for currently available force fields of Zr.

In this work, we develop a long-range interaction analytical EAM potential, namely la-EAM, for Zirconium by fitting the physical properties of α-Zr from experiments. The presented potential is employed to study the bulk (3D) properties, point defects (0D) properties, line defects (1D) properties, stacking fault (2D) properties, of α-Zr. In addition, we have calculated the phase transformation energy barriers. Our results are compared with literature to validate our la-EAM potential. The uniqueness of this newly developed potential is the capability to accurately model the phase transitions and various defective structures of zirconium. The organization of this work is as follows: Section 2, we introduce the la-EAM potential and details of our models and simulations. The results and discussion are presented in Section 3, followed by the conclusions in Section 4.

2. The formula of long-range analytical EAM potential

Within the framework of Embeded Atom Model (EAM), the energy of an atom in a system can be expressed as [12]

$$E_i = F_i(\rho_i) + \frac{1}{2}\sum_{j(\neq i)} \phi(r_{ij}) \tag{1}$$

where $F_i(\rho_i)$ is the embedding energy required to place an atom at site *i* with electron density ρ_i. $\phi(r_{ij})$ is the pair-potential between atoms *i* and *j*, and r_{ij} is the separation distance related to the specified pair of atoms *i* and *j*. ρ_i denotes the host electron density at the site of atom *i* which has the pair-wise contributions from each of all other atoms. This host electron density is the sum of the electron density $f(r_{ij})$ of the individual atom *j* with the linear superposition approximation, as

$$\rho = \sum_{j\neq i} f(r_{ij}) \tag{2}$$

Following the la-EAM scheme [24], we have fixed analytical from of $F(\rho)$, $\phi(r)$ and $f(r)$ as following.

$$F(\rho) = \begin{cases} \sum_{i=0}^{4} F_{1i}(\rho-\rho_1)^i & \rho \leqslant \rho_1 = 0.85\rho_e \\ \sum_{i=0}^{4} F_{2i}(\rho-\rho_2)^i & \rho_1 < \rho \leqslant \rho_2 = 1.0\rho_e \\ \sum_{i=0}^{3} F_{3i}(\rho-\rho_2)^i & \rho > \rho_2 \end{cases} \tag{3}$$

$$\varphi(r) = \begin{cases} -\varphi_e\left[1+\alpha\left(\frac{r}{r_1}-1\right)\right]\exp\left[-\delta\left(\frac{r}{r_1}-1\right)\right] & r \leqslant r_1 \\ \sum_{i=0}^{8} \lambda_i\left(\frac{r}{r_2}-1\right)^i & r_1 < r \leqslant r_b \\ \sum_{i=0}^{5} \kappa_i(r-r_b)^i & r_b < r \leqslant r_c \end{cases} \tag{4}$$

$$f(r) = f_e\left(\frac{r}{r_1}\right)^2 \exp\left[-\beta\left(\frac{r}{r_1}-1\right)\right] \tag{5}$$

Having specified the functions of $F(\rho)$, $\phi(r)$ and $f(r)$, the parameters were determined by fitting to experimental data. The experimental thermodynamic data including the equilibrium lattice constants *a* and *c*, elastic constants C_{11}–C_{12}, C_{44} and bulk modulus *B*, cohesive energy E_c, the mono-vacancy formation energy E_f were used in the present model. The parameters of pair potential are obtained by fitting the vacancy formation energy, equilibration condition, elastic constants C_{11}–C_{12} and C_{44}.

With the developed la-EAM potential, we do further investigations using molecular static and molecular dynamics simulations using the program GULP [25]. In the calculations, the lattice parameters, elastic properties are obtained in three-dimensional (3D) periodic crystal cells. The surface energies are calculated with 15 layers with more than 10 Å vacuum layer. The formation energies were calculated using supercells $15a \times 15a \times 10c$ (α), $15a \times 15a$ (β) and $15a \times 15a \times 20c$ (ω). The melting temperature was obtained by NPT with supercell of $30a \times 30a \times 20c$ and the atomic displacement of edge dislocation by NVT with supercell of $100a \times 3b \times 100c$ ($b = \sqrt{3}a$). The time step is 1.0 fs. The cutoff for force is 5.984 Å.

3. Results and discussion

3.1. Parameters of la-EAM potential

The la-EAM potential by fitting the formula to the experimental data. The atomic density distribution function, β is taken from Reference [26] and f_e is determined from atomic volume Ω, bulk modulus *B* and cohesive energy E_c as $(9\Omega B/E_c)^{0.6}$ [24]. And then the parameters ρ_1 and ρ_2 are determined from ρ_e using Eq. (2) including the 5th neighbors. The embedding function was divided into three segments, and the second segment was fitted to