An embedded atom method interatomic potential for the zirconium-iron system

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ABSTRACT

We present a new interatomic potential suitable for molecular dynamics and Monte Carlo simulations of crystalline Zr-Fe alloys, specialized for the Zr rich side of the phase diagram. To provide input data for developing the potential, *ab initio* calculations were performed. We show that the potential accurately predicts the formation energy and the lattice parameter of both stable and metastable intermetallic compounds. In addition, predictions of the potential regarding the stability of self-interstitials are in agreement with first principle method calculations. Finally, the capability of the potential in dynamic simulations is examined by employing variance-constrained semi-grand-canonical ensemble to study the segregation of Fe atoms at a vacancy dislocation loop for Zr-2 at.%Fe. We observe phase stability in agreement with the Zr-Fe phase diagram, in addition to the experimentally observed segregation of dissolved Fe atoms in the dislocation loop.

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1. Introduction

Zirconium and zirconium alloys are known for their excellent corrosion- and radiation-resistant properties [1], and are therefore good candidates for use in nuclear reactor cores as fuel cladding and guide tubes. In order to ensure cladding integrity and material longevity throughout component lifetime, a comprehensive understanding of the effect of radiation on the mechanical properties and related radiation-induced microstructure is essential. The effects of radiation are appreciable on an atomic scale; for example, we can note the effect of radiation on the density of prismatic dislocation loops [2], which results in a significant reduction in dislocation glide, and therefore yields a significant increase in strength and reduction in ductility [3]. A common alloying element in industrial standard alloys, for example Zircaloy-4, is iron, the presence of which results in postponing radiation-induced embrittlement [4]. It has been hypothesized that iron segregates at the strain fields of these defects and consequently stabilizes the dislocation loops [5,6].

Experimental studies of these phenomena are limited due to the associated technical difficulties. In addition, the time and size scales of radiation events are in a range that make instantaneous observation almost impossible. Therefore, simulations with appropriate scales offer an alternative way to study the mechanisms involved and a route to interpreting experimental results collected at longer timescales.

Atomic scale simulation methods, such as molecular dynamics (MD) and Monte Carlo (MC) can provide important insights into interfacial properties and atomistic kinetic processes, such as the excess free energy, mobility of solid-liquid interfaces [7–9], grain boundaries [10,11], interphase boundaries [12,13], the structure and kinetics of faceted crystal-melt interfaces [14–16], and solute segregation phenomenon [17,18]. A more recent technique, variance-constrained semi-grand-canonical (VC-SGC), has successfully combined these techniques in order to generate faster and more precise atomistic-scale simulations [19].

Central force embedded atom method (EAM) and its modified versions have been widely used in the study of pure and multicomponent metallic systems [20]. Such studies have provided a satisfactory characterization of many important properties in Zr and its alloys [21–23]. However, it should be noted that the results of classical MD simulations rely on the quality of the interatomic potentials. It has been shown that employing different potentials for simulation of a particular phenomenon in the same system can generate very different results. Consequently, developing a potential that can be used for all purposes seems impossible. One solution to this problem is to identify those properties that are related to the processes of interest and use them as target values with which to fit the parameters of the potential [22]. This is

why there exist many different potentials, even in the case of pure elements.

The phase diagram of the binary Zr-Fe system shows the stability of two different intermetallic compounds and allotropy for both components. The number of intermetallic compounds has even been reported as many as five [24]. These stoichiometric compounds exhibit extraordinary anisotropy. Therefore, considering their formation energy and lattice parameter in the fitting process is essential. In addition, when studying the effect of radiation, formation energy of point defects plays an important role; this is another target value to consider.

In the present study, for the first time we construct an interatomic potential of the EAM type for the Zr-Fe system. For pure Zr we chose potential 3 from [22], which is more appropriate for radiation damage studies, whereas for pure Fe the potential was taken from [25]. In this manuscript we describe the development procedure for a potential. The formation energy of the intermetallic compounds as well as the stability and energy of the point defects are presented. The level of solubility of Fe in Zr-HCP is also calculated. At the end, the VC-SGC ensemble is employed to ensure the coexistence of Zr with the first stable intermetallic compound at the Zr-rich side of the phase diagram, Zr_3Fe. As a case study, possible segregation of Fe atoms at a dislocation loop according to experimentally observed cases during irradiation is examined for Zr-2at.%Fe, the results of which suggest that the potential is suitable for radiation damage studies.

2. Zr-Fe cross interaction potentials

We employed the EAM [20], equivalent to the Finnis-Sinclair (FS) [26] potential, to describe the interatomic interactions in the Zr-Fe system. The EAM model consists of two parts to describe the energy of an atom, E: the pair interaction, ϕ, and embedding energy function $F(\rho)$:

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

where r_{ij} is the distance between atoms i and j, and ρ is the density contribution. Based on the EAM model, the density contribution is the summation of the partial density contributions, f_{ij}, which is another pairwise potential:

$$\rho_i = \sum_{j \neq i} f_{ij}(r_{ij}) \tag{2}$$

For developing an EAM potential, one needs to optimize the $F, f(r)$ and $\phi(r)$ functions; this is true for binary systems, where optimization for pairwise functions is required for both similar and cross interactions.

As mentioned above, for pure Zr and Fe we chose the potential from [22,25], respectively. However, the scaling of the density contribution used in the original development of these potentials is different. One solution to this problem is rescaling the embedding functional in the EAM scheme. This method has been used in previous studies for the development of potentials in binary systems [27]. Based on this approach [28], the energy and forces in the EAM formalism was found to be invariant to the following transformations:

$$f_{ij}(r_{ij}) \rightarrow \eta f_{ij}(r_{ij}) \tag{3}$$

$$F(\rho) \rightarrow F\left(\frac{\rho}{\eta}\right) \tag{4}$$

where η is an arbitrary scale factor. The advantage of this transformation is that the properties of the pure system are able to remain unchanged, while the properties of the alloy do change. For the next step we introduce the equation that describes the pair energy term as follows:

$$\phi_{ij}(r_{ij}) = \left[A \exp\left(-\alpha\left(\frac{R_M}{r_{ij} - R_M}\right)\right)\left(\frac{r_{ij}}{\sigma}\right)^{-P} - B \exp\left(-\beta\left(\frac{R_M}{r_{ij} - R_M}\right)\right)\left(\frac{r_{ij}}{\sigma}\right)^{-Q}\right]\prod_{k=1}^{2}\Gamma_{\phi_k}(r_{ij}) \tag{5}$$

where $A, B, \alpha, \beta, \sigma, P, Q$ and R_M are fitting parameters. The formalism for pair energy has two parts: the first part is similar to the one that is used by Dongare et al. [29], and the second part is multiplication of two modifying functions, $\Gamma_{\phi_k}(r_{ij})$, which apply local and smooth variations to the main form of the pair potential formulation and achieves another degree of freedom. $\Gamma_{\phi_k}(r_{ij})$ is defined as:

$$\Gamma_{\phi_k}(r_{ij}) = \begin{cases} 1 & r_{ij} < R_{\phi_k}^{min} \\ 1 + C_{\phi_k}\left(1 - \cos\left(2\pi\left(\frac{r_{ij} - R_{\phi_k}^{min}}{R_{\phi_k}^{max} - R_{\phi_k}^{min}}\right)\right)\right) & R_{\phi_k}^{min} < r_{ij} < R_{\phi_k}^{max} \\ 1 & r_{ij} > R_{\phi_k}^{max} \end{cases} \tag{6}$$

where $C_{\phi_k}, R_{\phi_k}^{min}$ and $R_{\phi_k}^{max}$ are constants and subscript k is the counter for the modification function. In this study, the partial electron density contributions from Zr to Fe and Fe to Zr are considered equal. Summarily, we define $f_{ij}(r_{ij})$ based on the type of bonds and not the type of neighboring atom.

$$f_{ij}(r_{ij}) = f_{ji}(r_{ij}) = f_0 \exp\left(-\gamma r_{ij}^m\right) \tag{7}$$

where f_0, γ and m are fitting parameters.

Based on the Zr-Fe phase diagram, several intermetallic compounds are thermodynamically stable and can form at $T = 0$ K. In addition, the formation energy of the point defects, especially interstitials, plays an important role in radiation studies; consequently, lattice parameters, formation energies of intermetallic compounds and of interstitials, are included in the fitting procedure of the cross-functions of the potentials. The corresponding *ab initio* values for intermetallic compounds are taken from [30]. The calculation of the formation energy of interstitial configurations were computed through spin-polarized density functional theory (DFT) using the plane-wave DFT code, VASP [31–33]. We employed standard PAW potentials with Perdew-Wang91 parameterization in the generalized gradient approximations (GGA), that are distributed with VASP [34], with Vosko-Wilk-Nusair interpolation [35]. The plane wave energy cutoff was 270 eV, which is sufficient for convergence of energy differences between our systems. Brillouin zone sampling was performed using $2 \times 1 \times 1$ meshes in the Monkhorst-Pack scheme [36] for a rectangular system containing 108 atoms. We used first order Methfessel-Paxton smearing with the smearing width of 0.2 eV [37].

The formation energy E_f of a simulation box consisting of atoms with stoichiometry of Zr_nFe_m is calculated using:

$$E_f = E_{Zr_nFe_m} - nE_{Zr} - mE_{Fe} \tag{8}$$

where E_{Zr} and E_{Fe} are the energies per atom of equilibrated Zr and Fe systems.

Finally, in order to measure the displacement of the atoms from the original HCP structure as a result of the now occupied interstitial sites, the root mean square deviation (RMSD) of atomic positions is determined using:

$$RMSD = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\delta_i^2} \tag{9}$$

where δ_i is the displacement of atom i as a result of the interstitial formation, which is measured for N atoms in the initial structure.