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A modified embedded atom method potential for interstitial oxygen in titanium

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ABSTRACT

Modeling oxygen interstitials in titanium requires a new empirical potential. We optimize potential parameters using a fitting database of first-principle oxygen interstitial energies and forces. A new database optimization algorithm based on Bayesian sampling is applied to obtain an optimal potential for a specific testing set of density functional data. A parallel genetic algorithm minimizes the sum of logistic function evaluations of the testing set predictions. We test the transferability of the potential model against oxygen interstitials in HCP titanium, transition barriers between oxygen interstitial sites, and oxygen in the titanium prismatic stacking fault. The potential predicts that the interaction between oxygen and a screw dislocation core is weak and short-ranged.

1. Introduction

Titanium alloys have good strength-to-weight ratios, high toughness, high melting temperature, and excellent corrosion resistance, which make them promising candidates for many structural applications especially in aerospace and aviation [1]. The introduction of O in Ti increases the yield strength but reduces the ductility [2,3]. In-situ transmission electron microscopy compression tests on Ti nanopillars with different O concentrations suggest that the strength increase comes from an interaction between the O interstitial atoms and the screw dislocation core [4]. Previous experiments along with crystallographic models also show that oxygen interstitials impede $(10\bar{1}2)$ Ti twin growth, indicating that O could affect the deformation properties of Ti [5,6]. Wu and Trinkle used density functional theory (DFT) to calculate oxygen diffusion in HCP Ti, where they found a new stable crowdion site—in addition to the known octahedral and hexahedral sites—that also contributes to O diffusion in HCP Ti [7]. Moreover, Ghazisaeidi and Trinkle DFT calculations of O interaction with the $(10\bar{1}2)$ Ti twin boundary and the $(10\bar{1}0)$ prismatic stacking fault showed that some oxygen interstitial sites at the twin boundary are attractive while others are repulsive, and that oxygen increases the prismatic stacking fault energy [8]. DFT also predicts that oxygen will decrease the Ti basal stacking fault energy [9]. Efficient and accurate empirical potentials that capture all the Ti-O interaction effects are not present, which is essential for large molecular dynamics simulations of oxygen interaction with "large" Ti defects such as dislocations, grain and twin boundaries, crack tips, and other defects that are difficult to simulate from first-principles.

Modified embedded-atom method (MEAM) potentials have been widely used to predict structural properties for metals. Baskes [10,11] extended the embedded atom method [12,13] to include the angular dependent three-body term in the electron density. Joost et al. recently developed an analytic MEAM potential to model Ti oxides; however, the potential was not optimize to modeling O interaction with defects in Ti [14]. Spline-based MEAM potentials offer enhanced flexibility and efficiency over analytic MEAM potentials [15]. Three successful single-element implementations on Si [15], Ti [16] and Mo [17] have been published, but multicomponent MEAM models are still difficult to optimize. For our situation, the spline-based Ti MEAM potential developed by Hennig et al. [16] to study the martensitic phase transition between α, β and ω Ti phases also predicts a similar Ti screw dislocation core structure as DFT [18]. We build on this model to include Ti-O interactions within MEAM formalism to study O near dislocations in Ti.

We start with the development of the binary MEAM potential functional form. The Ti MEAM potential [16] parameters are unchanged for Ti-Ti interactions, and we introduce Ti-O interactions. We construct a DFT database of structural energies and forces, and use the force-matching method [19] to optimize oxygen interaction functions. We expand the potential fitting problem to the optimization of the fitting database itself, by using an objective function based on testing errors, and optimized using our new database optimization algorithm [20]. The objective function

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consists of quantitative assessments of the testing set predictions of the potential model given by the logistic function. A parallel genetic algorithm minimizes the objective function and provides optimal weights for each entry in the fitting database. We test the transferability of the Ti-O potential for O interstitial sites in HCP Ti, transition barriers between the interstitial sites, and O in the Ti prismatic stacking fault. Finally, we use our Ti-O potential to study O interacting with a Ti screw dislocation: exploring the stable sites near the dislocation core, and the oxygen-induced changes in the Ti dislocation core structure.

2. Optimization of the binary MEAM potential for titanium-oxygen

2.1. Potential functional form

We develop a spline-based binary MEAM potential for Ti-O. The MEAM potential functional form is [15],

$$E = \sum_{i<j} \phi_{ij}(r_{ij}) + \sum_i U_i(n_i), \tag{1}$$

where $\phi_{ij}(r)$ is the pair interaction between atoms i and j, $U_i(n_i)$ is the embedding energy, and the density n_i at atom i is,

$$n_i = \sum_{j\neq i} \rho_j(r_{ij}) + \sum_{\substack{j<k,\\ j,k\neq i}} f_j(r_{ij}) f_k(r_{ik}) g_{jk}(\cos\theta_{jik}). \tag{2}$$

The indices i and j range over all atoms in the system. The angle θ_{jik} is the bond angle between atoms j, i, and k, centered on i. We employ the idea from the embedded atom method, where the density of the impurity atom i only depends on the other "host" atoms. Therefore, the functions ρ, f and g are selected based on the neighbors of i, but do *not* depend on the chemical identity of atom i. We use the Ti MEAM potential [16] for Ti-Ti interactions and neglect O-O interactions due to the dilute limit assumption. We fit the cubic spline functions for the Ti-O pair interaction $\phi_{\mathrm{TiO}}(r)$, the O density function $\rho_{\mathrm{O}}(r)$, the O embedding function $U_{\mathrm{O}}(n)$, and the functions $f_{\mathrm{O}}(r)$ and $g_{\mathrm{TiO}}(\cos\theta)$ which comprise the three-body contributions to the density n_i. The MEAM potential calculations are done using the molecular dynamics code LAMMPS [21].

Our new database optimization algorithm [20] offers a quantitative and automated way of optimizing an empirical potential. A conventional potential fitting process uses weighted least-squares minimization to find the best set of parameters with numerous manual trial and error attempts to "tune" the weights appearing in the squared error. Multiple local minima of the squared errors can also make the development of empirical potential model time-consuming and heavily guided by individual perception. We formulate the optimization of the empirical potential model into a two-step optimization problem. First, we minimize the weighted least-squared error against a fitting database to optimize the potential parameters. We can also define an objective function for a fitting database, with its optimal potential parameters based on errors against a larger testing set to measure the "transferability" of the potential model. Second, we optimize the *fitting database* by minimizing the objective function to find the optimal weight values as the input of the next iteration. This two step process repeats in a cycle to find the best potential parameters *and* fitting database that produces those parameters. Following Ref. [20], we use a Bayesian statistical framework with weighed least-squares fitting; the likelihood of the potential parameters θ for a given fitting database F,

$$L(F|\theta) \propto \exp\left(-\frac{1}{W}\sum_{\alpha\in F} w_\alpha \epsilon_\alpha^2(\theta)\right), \tag{3}$$

where w_α is the relative weight for entry α in the fitting database, $W = S(\theta^{\mathrm{MLE}}, F)$, and θ^{MLE} is the maximum likelihood estimation (MLE) of the likelihood function. The objective function of a fitting database F given a testing set T (consisting of structural energies, forces, or other potential predictions) is,

$$O(F|T) = \sum_{\beta\in T} C(\langle\epsilon_\beta^2(\theta)\rangle_F, \epsilon_{\beta 0}), \tag{4}$$

where the $C(x, \epsilon_0)$ is the *cost function* of a prediction of the potential for ensemble average error $\langle\epsilon_\beta^2(\theta)\rangle_F$ and "decision boundary" value $\epsilon_{\beta 0}$ (see below). The ensemble average $\langle\epsilon_\beta^2(\theta)\rangle_F$ is calculated using Bayesian sampling in the neighboring domain of the θ^{MLE} to account for the MLE errors and the flexibility of the model under small variations in parameters [22], the so-called "sloppiness" of the model.

We choose the logistic function [23],

$$C(x, \epsilon_0) = \frac{1}{1 + \exp(-m((x/\epsilon_0) - 1))}, \tag{5}$$

for our cost function as it mimics the evaluation process of predictions for a classical potential. We wish to balance errors, where the ideal outcome is all the testing set errors are below acceptable thresholds. Once a prediction falls below the threshold, decreasing the error of the same entry does not significantly improve the transferability of the potential. On the other hand, if a prediction error is very large, making worse predictions does not affect the transferability of the potential (with obvious caveats about the introduction of artificially low energy structures). The logistic function captures these two key features in potential fitting, which makes it a good candidate for the objective function. The derivative of the logistic function is not zero, which maintains the improvement by error reduction compared to a step function. The smooth functional form is also straightforward to calculate and couple with optimization algorithms such as gradient descent and genetic algorithms [24] (GA). The stiffness of the logistic function is determined by m. As $m \to \infty$, the logistic function becomes the step function. We identify ϵ_0 as the "decision boundary" in classification regression analysis, which determines the "acceptable" error threshold for each entry in the testing set. The decision boundary for the energy entries and force entries in this work are 0.2 eV and 0.5 eV/Å, respectively. The energy error boundary denotes the threshold of the error in total energy differences between two structures. The force error boundary denotes the threshold for the root of sum of squared errors for all force components on all atoms in a structure. We represent the optimal fitting database as the optimal weight set and the set of parameters with the least squared-errors in the fitting database. The decision boundaries are chosen to produce errors of less than 0.2 eV in activation barriers for diffusion (c.f. Table 3).

2.2. Ab initio database and optimization algorithm

We perform density functional theory (DFT) calculations using the planewave basis code VASP [25,26] for various Ti-O configurations to build the fitting database and the testing set for the potential fitting process [27]. The fitting database consists of DFT energies and forces for O in HCP Ti at the octahedral (o), hexahedral (h) and crowdion (c) interstitial sites, and for the transition state configurations, oh, oc, hc and oo, between these sites evaluated using the nudged-elastic band method (NEB) [28]. While these geometries are relaxed in DFT, they will not be relaxed during the evaluation of errors for the likelihood function; instead, the energies and forces will be evaluated, and the target value for the forces will be zero. The testing set includes the fitting database structures as well as configurations with O displaced from interstitial sites by a fixed distance (0.1 Å and 0.05 Å) in random directions, and prismatic stacking fault configurations with O in