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Interaction between oxygen interstitials and deformation twins in alpha-titanium

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ABSTRACT

Twinning is an important deformation mechanism in many hexagonal close packed metals, including α-titanium (Ti) alloys. However, the mechanisms for twin nucleation, growth, and interaction with other defects are not completely understood. In this study we interrogate the behavior of oxygen (O) interstitials near a $(10\bar{1}2)$ twin boundary using a combination of density functional theory (DFT) and modified embedded atom method (MEAM) calculations. The presence of the twin boundary significantly affects both interstitial formation energy as well as the activation barriers for diffusion between sites. We demonstrate that a tetrahedral interstitial is stable in the twin boundary, despite being unstable in bulk Ti, while the formation energies of the octahedral, hexahedral, and crowdion interstitials are all modified by a nearby twin. Further, the activation barriers for diffusion in the region near the twin are uniformly lower than in the bulk. An atom diffusing across the twin boundary moves through several paths with peak energies more than 0.3 eV lower than for comparable diffusion far from the twin, suggesting that the $(10\bar{1}2)$ twin is a fast diffusion pathway and movement of oxygen interstitials across the twin during twin growth is possible.

1. Introduction

Titanium (Ti) alloys exhibit excellent specific strength, toughness, high temperature stability, and corrosion resistance, among other characteristics [1]. This unique set of properties enables use in applications as varied as jet engines [2], artificial hip joints [3], offshore oil drilling equipment [4], and suspension components for the Spirit and Opportunity Mars rovers [5]. Deformation of Ti alloys, whether hexagonal close packed (hcp) α-phase, body centered cubic (bcc) β-phase, or a combination thereof, can occur via twinning; understanding the effects of alloy chemistry and impurity content on deformation twinning is therefore an important step towards improved mechanical performance and reliability.

Oxygen (O) has up to 33 at% solubility in α-Ti [6] and is a common impurity and alloying element. Interstitial O is also believed to interact with deformation twins, and may result in time-dependent twinning by obstructing the shearing/shuffling process associated with twin growth [7]. Early work by Biget & Saada identified that the shuffle distances for interstitial impurities in Zr (an hcp metal with a similar structure to Ti) are larger than the shuffle distances for Zr atoms during $(10\bar{1}2)$ and $(11\bar{2}1)$ twinning, although the possibility for O–Zr interference during shuffling was not described [8]. More recent experimental measurements combined with a crystallographic model suggest that O interstitial sites interfere with the shuffle of Ti atoms during twin growth in bcc Ti, requiring O interstitial diffusion away from or across the twin to enable further twin growth [9]. In addition, a decrease in $(10\bar{1}2)$ twin growth rate during creep in α-Ti may be associated with the presence of O interstitials based on a similar crystallographic model [10,11]. The width of $(10\bar{1}2)$ twins decreases with increasing strain rate during quasi-static loading, providing further evidence of time dependence of twin growth in α-Ti [12]. The measured activation energy for twin growth in α-Ti, calculated using the diffusion coefficient for O diffusion in the bulk, is approximately 0.684 eV during creep loading [11]; the activation energy for O diffusion in bulk α-Ti was recently measured as 1.75±0.52 eV using high purity samples and the nuclear resonance technique [13], while DFT calculations yield an activation barrier of 2.08 eV [14]. Historical measurements with reasonable results indicate activation energy for diffusion between 1.45 eV and 2.68 eV [15]. Should O interstitials interact with twin growth as crystallographic modeling suggests, the difference between the bulk diffusion activation

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barrier and the activation barrier for twin growth indicates that twin growth and O diffusion mechanisms interact in a complicated way. The length and time scales of these interactions make experimental measurement very difficult, while atomistic modeling provides an excellent tool set for gaining an improved, mechanistic understanding of the processes. Density functional theory (DFT) calculations by Ghazisaeidi and Trinkle demonstrate that a $(10\bar{1}2)$ twin boundary affects the formation energy of octahedral oxygen interstitials in the immediate vicinity of the twin [16], however the effect of the twin on formation energy of other sites and the activation barriers for diffusion between the sites is not known. Recent DFT calculations reveal that O diffuses readily along the core of a prismatic edge dislocation in α-Ti and that the presence of O increases Peierls stress and modifies dislocation core geometry [17], providing further indication of complicated interactions between Ti deformation mechanisms and O interstitials. In this study we interrogate the effect of $(10\bar{1}2)$ twin boundaries on the formation energies, activation barriers, and diffusion pathways for O. We report that the presence of a $(10\bar{1}2)$ twin boundary has a significant effect on the thermodynamics and kinetics of nearby O interstitials.

2. Computational techniques

Investigating material behavior often requires multiple computational techniques to properly address the range of relevant time and length scales. Directly simulating interactions of O defects with a crystallographically complicated planar defect such as a twin requires atomistic modeling, however many such techniques exist. In this study, we employ a combination of DFT and modified embedded atom method (MEAM) calculations to leverage the benefits and offset the disadvantages of each tool. DFT is an *ab-initio* technique that offers excellent predictive power but is limited to simulation of relatively few atoms for relatively brief periods. The MEAM is an empirical potential method that trades a loss of rigorous physical modeling for capability to simulate substantially larger systems for longer periods of time when compared to DFT. Our DFT calculations are performed in the Vienna Ab-initio Simulation Package (VASP) [18–21], employing projector augmented wave (PAW) psuedopotentials [22,23] and the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) [24]. The cut-off energy for all calculations was held at 520 eV. We apply Methfessel-Paxton smearing of 0.2 eV and use a $2\times1\times6$ Monkhorst-Pack *k*-point mesh. Relaxation calculations were stopped when the force on each atom in the system was <5 meV/Å. Our MEAM calculations are performed in LAMMPS [25] using published MEAM potentials for Ti [26], O [27], and Ti–O [28], noting that the Ti–O potential was fit specifically to study the interaction between O interstitials and twins in Ti alloys. Among several variations of the MEAM, we use the second nearest neighbor (2NN) technique as outlined by Lee et al. [29,30], following the earlier work by Baskes [31–34]. Activation barriers for diffusion are calculated using the climbing imagine nudged elastic band (CI-NEB) approach with three to seven intermediate images [35–37]. Creation of the supercells for these calculations, visualization of results, and production of several figures was accomplished using the Open Visualization Tool (OVITO) [38]. The data used to produce Figs. 5, 7 and 8 are archived and available [39].

3. Structural model

3.1. $(10\bar{1}2)$ twin in pure Ti

We produced several supercells in order to investigate of the effects of distance between twins and oxygen interstitials on the behavior of the system. Fig. 1 shows our “short” and “tall” twin

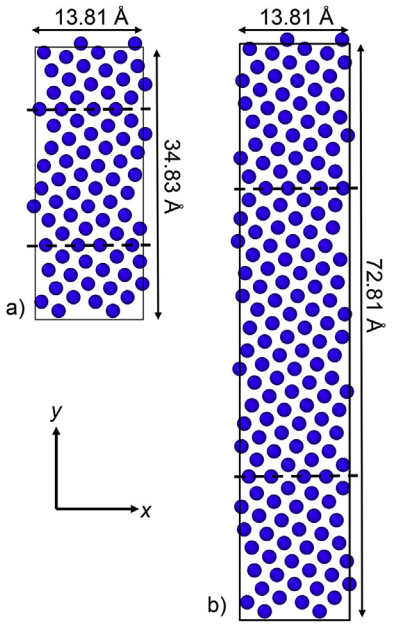

Fig. 1. Front view of the a)“short” and b) “tall” twin supercells along with the coordinate system used in this study. The twin boundaries are indicated with dashed lines. The supercells vary in depth along the *z*-direction (out of the page), which corresponds to $[1\bar{2}10]$.

supercells, which differ in size along the *y*-direction, along with the coordinate system used in this study. Each cell contains two $(10\bar{1}2)$ twin boundaries as required in order to maintain periodicity in the *y*-direction. Cell depth in the *z*-direction (which corresponds to $[1\bar{2}10]$) varies in intervals of the lattice parameter of α-Ti, *a*, which is equal to 2.95 Å [40]. To create a supercell containing a $(10\bar{1}2)$ twin we first rotate the hcp titanium unit cell such that the $[1\bar{2}10]$ direction is aligned with the *z*-direction. One side of the twin is rotated so that the normal to the $(10\bar{1}2)$ plane is aligned with the *y*-direction, while the second side of the twin is rotated so that the normal to the $(\bar{1}012)$ is aligned with the *y*-direction. Volumes of atoms rotated for each side of the twin are combined into a single supercell and trimmed in the *x*- and *z*-directions for periodicity. Relaxation of the initial twin structure is accomplished in two steps: first, the cell is relaxed in the *y*-direction only while the atoms are allowed to relax completely, after which the cell and atoms are free to relax in all directions, although the cell is prevented from shear distortion.

We first compare the experimentally measured twin boundary structure [41] with the results of our DFT and MEAM calculations with $z = 2a$. Fig. 2 compares the DFT, MEAM, and experimental structures, with the structure motif superimposed for clarity; the calculated $(10\bar{1}2)$ structures relax to a planar twin as found experimentally, while the angle between basal planes across the twin boundary, θ, is also correctly captured. The $(10\bar{1}2)$ twin energy is 0.301 J/m^2 calculated using DFT, in good agreement with previous reports [42,16], and 0.410 J/m^2 calculated using the MEAM. The relaxed structure and twin boundary energy is identical for the short and tall twin supercells and is not affected by changes to supercell depth in the *x*- or *z*-directions. While the MEAM overestimates the twin boundary energy by comparison to DFT, the formation energies of the many oxygen interstitials studied here are not significantly affected.