FIRST PRINCIPLES STUDY OF METASTABLE
BETA TITANIUM ALLOYS
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The high temperature BCC phase (\(\beta\)) of titanium undergoes a martensitic transformation to HCP phase (\(\alpha\)) upon cooling, but can be stabilized at room temperature by alloying with BCC transition metals such as Mo. There exists a metastable composition range within which the alloyed \(\beta\) phase separates into \(\alpha+\beta\) upon equilibrium cooling but not when rapidly quenched. Compositional partitioning of the stabilizing element in as-quenched \(\beta\) microstructure creates nanoscale precipitates of a new simple hexagonal \(\omega\) phase, which considerably reduces ductility. These phase transformation reactions have been extensively studied experimentally, yet several significant questions remain: (i) The mechanism by which the alloying element stabilizes the \(\beta\) phase, thwarts its transformation to \(\omega\) and how these processes vary as a function of the concentration of the stabilizing element is unclear. (ii) What is the atomistic mechanism responsible for the non-Arrhenius, anomalous diffusion widely observed in experiments, and how does it extend to low temperatures? How does the concentration of the stabilizing elements alter this behavior? There are many other \(\omega\) forming alloys that such exhibit anomalous diffusion behavior. (iii) A lack of clarity remains on whether \(\omega\) can transform to \(\alpha\) -phase in the crystal bulk or if it occurs only at high-energy regions such as grain boundaries. Furthermore, what is the nature of the \(\alpha\) phase embryo? (iv) Although previous computational results discovered a new \(\omega \rightarrow \alpha\) transformation mechanism in pure Ti with activation energy lower than the classical Silcock pathway, it is at odds with the \(\alpha/\beta/\omega\) orientation relationship seen in experiments.
First principles calculations based on density functional theory provide an accurate approach to study such nanoscale behavior with full atomistic resolution, allowing investigation of the complex structural and chemical effects inherent in the alloyed state. In the present work, a model Ti-Mo system is investigated to resolve these fundamental questions. Particular attention is paid to how Mo- (i) influences the bonding in Ti, (ii) distorts the local structure in the Ti lattice, (iii) impacts the point and interfacial defect formation and migration energies, and (iv) affects the mechanism and energetics of $\beta \rightarrow \omega$ and $\omega \rightarrow \alpha$ transformations. Our results are correlated with appropriate experimental results of our collaborators and those in open literature.

The modification of Ti bonding by Mo solutes and the attendant distortion of the lattice hold the key to answering the diverse questions listed above. The solutes enhance electron charge density in the $<111>$ directions and, consequently, stiffen the lattice against the displacements necessary for $\beta \rightarrow \omega$ transformation. However, Ti atoms uncoordinated by Mo remain relatively mobile, and locally displace towards $\omega$ lattice positions. This effect was further studied in a metastable Ti-8.3 at.% Mo system with an alternate cell geometry which allows for either $\beta \rightarrow \omega$ or $\beta \rightarrow \alpha$ transformation, and it was found that after minimization Ti atoms possessed either $\alpha$ or $\omega$ coordination environments. The creation of this microstructure is attributed to both the disruption of uniform $\beta \rightarrow \omega$ transformation by the Mo atoms and the overlap of Ti-Mo bond contractions facilitating atomic displacements to the relatively stable $\alpha$ or $\omega$ structures in Mo-free regions. The vacancy migration behavior in such a microstructure was then explored.
Additionally, several minimized configurations were created with planar interfaces between Mo-stabilized β region and its adjacent α- or ω- phases, and it was found that the positioning of Mo at the interface strongly dictates the structure of the adjacent Mo depleted region.
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CHAPTER 1

INTRODUCTION

1.1. A Brief History and Motivation

Titanium is renowned as an extremely versatile material, with exceptional strength and fracture related properties, low density, and enhanced corrosion resistance. In the past several decades, largely fueled by exacting demands of the rapidly growing aerospace industry, commercial output in U.S. has gone from virtually nonexistent to over 25 million kg/yr. However, the inherent versatility and chemical modifiability of titanium has its own drawbacks, requiring careful control of chemistry and microstructure throughout processing to optimize material performance, which causes the price of commercial alloys to stay elevated and restricts their use in less cost-intensive applications. Despite this, titanium alloys have made inroads in biomedical, chemical production, and sporting goods applications, where they provide superlative advantages over conventional materials.

Titanium alloys for structural applications are generally categorized as near $\alpha$, $\alpha + \beta$, and $\beta$ alloys, where $\alpha$ and $\beta$ refer to the hexagonal close packed (HCP) and body centered cubic crystal structures, respectively. $\alpha + \beta$ alloys, specifically Ti-6Al-4V, have been traditionally most widely used, accounting for nearly 60% of all output due to it’s specific development for aerospace implementations, but beta alloys are increasingly being researched due to advantages in processing, namely cold deformability, and higher yield stresses after aging. However, within metastable composition ranges, where the beta phase is expected to transform to either $\alpha'$ or $\alpha + \beta$, a low temperature simple hexagonal phase, $\omega$, may be retained upon fast quenching. This phase has attracted interest from both a metal physics and metallurgical processing perspective. While the $\omega$ phase has been predicted to be the thermodynamically stable phase at low temperatures and high pressures for pure Ti and the other Group IV transition metals (Zr and Hf), it hasn’t been observed even at extremely fast quenching rates due to the intermediate transformation to the $\alpha$ phase. However, the addition of beta stabilizing elements lowers the $\beta \leftrightarrow \alpha$ transus
temperature, and can bypass the $\alpha$ phase regime if cooled fast enough. At these temperatures, the concentration fluctuations will nucleate a nanoscale dispersion of $\omega$ precipitates. These precipitates are undesirable from a mechanical perspective, as they induce significant brittleness into the material, and can occupy a substantial volume fraction when relatively low amounts of stabilizing additions are used. However, upon annealing, the $\omega$ can transform to $\alpha$, yielding a very fine $\alpha$ reinforced microstructure, opening up new potential processing routes.

The $\omega$ that forms upon quenching is termed athermal $\omega$, as it seemingly forms independent of diffusion. The atomistic mechanisms that are present in this state are of considerable interest, and form the basis of the research presented in this work. Density functional theory is well suited for application for this material system, as it provides the requisite chemical accuracy in addressing the electronic transfer inherent to alloying which modifies bonding behavior, while allowing study of system sizes tractable on current computational resources. An important caveat inherent to the study of thermally allotropic materials such as titanium is that in the absence of vibrational effects, the stability of the high temperature phases, BCC in this case, will always be under-predicted. As such the metastable compositions and structures studied with the DFT method represent an idealized scenario where a system is instantaneously quenched to 0 K. However, the results are still relevant to experimental observations, as there is no further transformation expected below the room temperature quenched state. Furthermore, in most cases where the modeled results and previous experimental work diverge, the known effect of vibrational stabilization can qualitatively accommodate for discrepancies.

1.2. Scope and Outline

The dissertation is organized according to several classes of behavior relevant to the evolution of metastable $\beta$ titanium alloys upon quenching. Modelling efforts were primarily focused on the $\beta$-isomorphous binary Ti-Mo system, with some extension to related isomorphous forming Nb and V systems. The overarching objective addressed
in this work is to reveal the incipient processes expected to occur either during or after quenching related to the formation of the \( \omega \) (or \( \alpha \)) phase. The work is outlined as follows:

Chapter 2 provides a brief overview of the origins and occurrence of the \( \omega \) phase in titanium, as well as relevant studies related to understanding it’s properties. Commonly observed orientation relationships are reviewed, as well as observed and proposed \( \beta \leftrightarrow \omega \) and \( \omega \leftrightarrow \alpha \) transformation paths.

Chapter 3 explains the details of the computational methodology used throughout the work, specifically the theory behind density functional theory (DFT) calculations and the nudged elastic band (NEB) method.

Chapter 4 investigates the effect of Mo addition to the BCC Ti lattice. The change in the \( \beta \rightarrow \omega \) pathway energy as a function of Mo concentration is calculated. The nature of bond contractions around Mo atoms is studied, and how the induced structural distortions lead to complex local atomic structures. Additionally, the interfaces that develop between Mo-enriched and Mo-depleted regions is investigated, as well as their relative energies and structural features.

Chapter 5 details the vacancy formation energy within pure Ti and near a Mo solute atom, as well in the alloyed system. The local structure of Ti atoms in the metastable alloy is a mixture of different coordination environments, and the vacancy formation energies are found to correlate well with the pertinent values of their reference structure. The energetics of select migration pathways between sites is also explored, and a overview of expected diffusion behavior is provided.

Chapter 6 revisits the Silcock pathway for \( \omega \) to \( \alpha \) transformation, which although correctly predicts the most common orientation relation seen between \( \alpha/\beta/\omega \), is considered improbable due to the high degree of reconstruction involved and high energy barrier. A revised description is proposed wherein the transformation has a thermally activated component and a glide component, with the former requiring a transformation to an intermediate BCC-like state. This is supported by the observation that the addition of Mo lowers the thermally active component of the barrier, while minimimally affecting the glide
component. The requirement of a glide component is explained in the context of observed transformation from elliptical $\omega$ precipitates to lathe and needle-like $\alpha$ and recent torsional studies of room temperature reversible $\alpha$-$\omega$ transformation.
2.1. The Omega Phase

The omega (ω) phase was first documented by Frost et al. in 1954 when x-ray diffraction analysis showed evidence of a second phase in aged body centered cubic (BCC) titanium alloys. It has since been observed to occur in all group IV transition metals (titanium, zirconium, and hafnium) under both elemental and alloyed conditions, and has been the subject of considerable research to better understand conditions of its formation, its effect on a range of mechanical, structural, and conductive properties, and how it evolves under pressure and temperature [8, 9].

Crystallography of Omega

The ideal ω phase has a hexagonal AlB$_2$-type crystal structure, with space group $P6/mmm$ and Wyckoff Positions 1a (A site) at (0,0,0) and 2d (B site) at ($\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$) and ($\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$). If the B atoms are deviated from their $\frac{1}{2}c$ positions, usually due to presence of solute atoms, then the symmetry reduces to a trigonal crystal structure, with space group $P\bar{3}m1$. A diagram of the ideal structure is depicted in Fig. 2.1. For titanium, the ω phase has experimentally measured lattice constants of $a = 4.62$ Å and $c = 2.81$ Å ($c/a = 0.61$) [9], and ab-initio (DFT) calculated lattice constants of $a = 4.58$ Å and $c = 2.83$ Å ($c/a = 0.619$), resulting in an error of < 1%. The details of relevant calculations are given in Chapter 3.

The A atom is coordinated by twelve B atoms in the $\langle 2023 \rangle$ directions and two A atoms in the [0001] directions, while the B atom is coordinated by six A atoms along $\langle 2023 \rangle$ directions, three B atoms along $\langle 10\overline{1}0 \rangle$, and two B atoms along [0001] directions. The [0001] direction has ABAB stacking, with all A planes having A atoms, and all B planes have B atoms. The coordination environment for each site is illustrated in Fig. 2.2 and Fig. 2.3, with respect to the [0001] and [11\overline{2}0] directions respectively. The latter is of interest since in the Silcock orientation relationship (OR) between ω and the α, the
Figure 2.1. Diagram of the ideal omega phase of titanium, lattice positions, and lattice constants.

$(1\bar{1}20)_\omega$ planes transform into $(0001)_\alpha$ basal planes, and maintains an ABAB stacking sequence in both structures in the normal directions. The in- and out-of-plane coordination environment is depicted in Fig. 2.3 for both A and B sites. The A atom in this orientation has six first nearest neighbor (1NN) atoms within the plane, and four 1NN atoms on either adjacent plane, while the B atom has five 1NN atoms within the plane, and three atoms on either adjacent plane. The A site has a nearly hexagonal in-plane coordination, but with small 1NN distance and angle deviations, as shown in the figure. After transformation, all of the A and B sites transition to six neighboring atoms in-plane, and three neighboring atoms above and below. This will be discussed in more detail in Chapter 6.

Omega Formation in Pure Metals

The $\omega$ phase was observed in pure Ti and Zr under static pressures by Jamieson et al. in 1963 [10], and has been studied extensively since under different stress states, impurity content, and temperature ranges [11, 12, 9, 13, 14, 15, 16, 17, 18, 19, 20]. Titanium at ambient temperatures has a hexagonal-close-packed crystal structure (HCP), known as the
Figure 2.2. The coordination environment of the A and B sites, shown with respect to the [0001] direction.

\( \alpha \) phase, and upon heating above 1155 K transforms to the BCC crystal structure, known as the \( \beta \) phase. Under sufficient pressure, the \( \alpha \) phase can also directly transform to the \( \omega \) phase, which has a simple hexagonal structure. Several experimental and theoretical studies have been done to characterize the phase boundaries between \( \alpha, \omega, \) and \( \beta \), though the low temperature regime has not been well characterized from experiment. In Fig. 2.4, the P-T phase diagram for titanium is depicted, with the most recent experimental evaluation provided by Young and Zhang et al. [21, 22], density functional theory (DFT) based theoretical calculations using the Debye model for the free energy of each phase [23, 24], and modified embedded atom method (MEAM) based theoretical calculations using molecular dynamics (MD) methods based on phase co-existence [17]. The diagram demonstrates good agreement between DFT based phase boundaries and experimental evaluations, and also confirms that \( \omega \) is indeed the lowest energy phase at low temperatures, with a \( \alpha \rightarrow \omega \) transformation temperature calculated to be 152 - 186 K at zero pressure. However, the \( \alpha \)
Figure 2.3. The coordination environment of the A and B sites, shown with respect to the [1120] direction. The approximately hexagonal nature of the central plane of the A site and the semi-hexagonal nature of the B site is depicted. The distances and angles are calculated from the DFT minimized $\omega$ structure. The A-site has a 4-6-4 stacking pattern with, while the B site has a 3-5-3 stacking pattern.

is not observed to spontaneously transform to the $\omega$ phase due to kinetic barriers, and nor can the $\beta$ phase be quenched fast enough to retain $\alpha$. The MEAM results are generated using a semi-empirical formalism fitted to first principles data, and generally captures the slope of the $\alpha/\omega$ phase boundary well, as well as correctly predicts the high temperature $\beta$ phase, but has pronounced errors in the position of the boundaries, as well as the slope of the $\alpha$ and $\beta$ phase.

Under dynamic loading conditions, the transformation is observed to begin between 10-15 GPa[15], and recent studies have shown a peak $\omega$ volume fraction at 15 GPa, after which point the heating induced from shock loading increasingly stabilizes the $\alpha$ phase [20]. The recovered microstructures usually retain a highly defected $\alpha + \omega$ microstructure, but due to the complex stress and temperature states during such conditions, multiple
reversible transformations, twinning, and extensive plastic deformation may be possible, making direct interpretation of $\alpha \rightarrow \omega$ transformation difficult to discern. Recent MD studies using the aforementioned MEAM interatomic potential have been able to elucidate some of the possible intermediate mechanisms, simulating shock loading on $\alpha$-Ti \cite{19}. In that work, it was shown that the transformation mechanism was loading direction dependent, as was the resulting orientation relationship. It was further found that non-hydrostatic components of stress play an important role in initiating the transformation, which may be why the lowest energy theoretical $\alpha \rightarrow \omega$ path is not observed citeTrinkle. The lowest reported transformation stress for $\alpha \rightarrow \omega$ was in shear deformation, giving a transformation stress of $2.0 \pm 0.3$ GPa \cite{25}.

There remains confusion about which conditions dictate the $\alpha \rightarrow \omega$ pathway. In diamond anvil cell studies (DAC) on Zr without a pressure medium, the effect of uniaxial strain was found to be significant in reducing the transformation pressure \cite{26}, and though they ruled out the Silcock mechanism for transformation due to the minimal cell shape change described in the original paper \cite{27}, the Silcock mechanism does still in fact hold if it is described with a glide component instead of with the reconstructive character. This
has been described recently in a combined experimental/MEAM-MD shock loading study of pure Ti observe the $\alpha \leftrightarrow \omega$ behavior, and in more depth using DFT in Chapter 6 of this work.

In fact, recent in-situ x-ray diffraction textures studies using DAC and Deformation DIA (an instrument which allows imposing uniaxial strain in addition to quasi-hydrostatic stress) showed that the Silcock OR between $\alpha$ and $\omega$ was maintained during deformation, and that the presence of large compressive strains (measured as $\sim 20\%$ in D-DIA, unquantified in DAC) reduced the transformation start stress to 3-4 GPa. Annealing the retained $\omega$ at 400 ° restored the original texture of the $\alpha$ phase, indicating a similar reversible transformation mechanism in both high pressure and high temperature conditions. This further confirms the strong role deviatoric and off-diagonal stress components play in the observed transformation mechanism.

Recent thin film studies have shown that the sputtering deposition of pure Zr targets on various substrates created either $\alpha$, $\alpha + \omega$, or completely $\omega$ microstructures in the absence of any high pressure conditions [28, 29]. Thin film compressive stresses were measured to be less than 1 GPa in both studies. These are some of the first studies of $\omega$ phase formation without a preceding phase transformation. While deposition on Si and SiO$_2$ gave either a mixture or pure $\alpha$, the behavior changed with a metallic layer, with XRD analysis demonstrating no detected $\omega$ for Fe, Cu, Ag, or ZrN, a mixture for Mo and steel, and purely $\omega$ for Cr. There are yet to be any studies using this method to study the $\omega$ phase, but it may be an effective method to characterize its properties in a more chemically and microstructurally controlled way. Analogous work on sputter deposition of titanium has not been performed.

**Omega Formation in Alloys**

In the alloyed condition, the $\omega$ phase has been observed in a wide range of Zr, Ti, and Hf alloys, primarily which have been $\beta$ stabilized by the addition of transition metals such as V, Mo, Nb, Cr, Cu, Ni, Fe, Co, Au, Ag, W, Pt, and Pd [30]. The formation of $\omega$ is classified as either athermal or isothermal. Athermal $\omega$ is typically found to occur in alloys
Figure 2.5. The metastable composition range of the Ti-Mo phase diagram is shown, for a) equilibrium conditions, b) moderate quenching to temperatures > 200° C, and c) fast quenching or isothermal aging conditions. The valence electron/atom ratio is correlated to the Mo composition, in order to qualitatively compare behavior for different β stabilizing elements. The 5-15 at.% Mo range is observed to nucleate ω precipitates.

quenched from the high temperature β phase, forming submicron ω precipitates in a β parent matrix. Isothermal ω is formed at higher temperatures via diffusional compositional partitioning followed by ω formation in the stabilizer depleted region. While each stabilizing element has distinct behavior within the alloy microstructure, the stabilizing effect can be considered equivalent in terms of a generalized valence electron/atom ratio, e/a.

For the prototypical Ti-Mo system studied in this work, the relevant Ti-rich regime of the phase diagram is shown in Fig. 2.5 for both equilibrium and non-equilibrium conditions as a function of both Mo concentration and the e/a ratio, reproduced from [31].

The equilibrium diagram is shown on top in (a), a non-equilibrium diagram denoting quenching to the >200° C temperature regime in (b), and a second non-equilibrium
diagram denoting the observed concentration range over which ω is formed in (c), depending on specifics of the thermal history. Quenching initiates the formation of the α’ martensite phase for concentrations < ~5 at.% ($e/a < 4.1$), and for concentrations between 5-15 at.% Mo ($e/a \sim 4.1-4.3$), ω is observed to form from the β phase either athermally or isothermally, depending on the temperature regime. The density and size of ω-phase precipitates increases as the concentration approaches the $M_s$ line, and characteristically increases hardness and strength while inducing brittleness. The temperature at which athermal ω forms also decreases with increasing Mo content [32, 33]. The maximum size of ω precipitates after coarsening is limited by the concentration of the stabilizer; for Ti-9 at.% Mo, ω precipitates were measured to reach a peak average diameter of ~ 80 nm after aging for 48 h at 475° C, while in Ti-12 at.% Mo the average diameter reached a maximum of 16 nm after aging for < 4 h at 450° C, and remained constant after aging for an additional 96 hours [34]. At Ti-20%, the maximum average diameter after aging decreases only slightly to 15 nm under similar conditions [35]. In the latter two higher concentration systems, the abnormal cease of coarsening was predicted to be an effect of elastic inhomogeneity, and thus the final precipitate reflected elastic stability between the two phases. This may not be the only contributing behavior however; as will be discussed in Chapter 5, the kinetics of vacancy diffusion change drastically with Mo enrichment. An example of an aged $\beta + \omega$ microstructure in Ti-9 at.% Mo is depicted in Fig. 2.6, showing both a dark-field HRTEM image and a 3D atom probe reconstruction, which depicts elemental isosurfaces to delineate the ω precipitates within β.

2.2. $\alpha \leftrightarrow \omega$ Transformation Mechanism

The pathways for $\alpha \to \omega$ and $\omega \to \alpha$ are often considered to be the same, with most of the prior research being focused on the $\alpha \to \omega$ transformation observed in shock-induced transformations at high pressures. The Rabinkin and Silcock mechanisms were proposed based on crystallographic considerations, but the actual atomistic behavior underlying the transformation could only be theorized as it is highly difficult to resolve in experimental conditions [36, 27]. Rabinkin commented that Silcock’s mechanism was unlikely due to
the 50% shear deformation required, and instead proposed a long range ordered process consisting of (1010) planar displacements, atomic shuffles, and linear deformations. Song and Gray generalized that these two mechanisms were closely related, and the Rabinkin pathway could be described as two opposing simultaneous Silcock-type transformations which eliminate the overall cell shear [14].

Other ORs have also been observed from shocked polycrystalline Ti and Zr samples under different loading conditions, and have been generally been categorized as one of four possible variants, summarized in Table 2.1.

Recent theoretical studies of the $\alpha \rightarrow \omega$ martensitic transformation used a novel search method to identify a new low energy pathway for $\alpha \rightarrow \omega$, referred to as TAO-1 [37, 38, 17]. Using first principles methods, it was observed that at 0K this mechanism had a barrier nearly one third of that corresponding to a homogeneous Silcock mechanism, and thus was expected to be the most favorable for $\alpha \rightarrow \omega$ transformation. A diagram comparing the TAO-1 and Silcock pathways is shown in Fig. 2.7. However, the
<table>
<thead>
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<th>Variant</th>
<th>Orientation Relationship</th>
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| I       | (0001)_{α} \parallel (10\bar{1}1)_{ω}  
          | [10\bar{1}0]_{α} \parallel [\bar{1}011]_{ω} |
| II      | (0001)_{α} \parallel (1\bar{2}10)_{ω}  
          | [1\bar{2}10]_{α} \parallel [0001]_{ω} |
| III     | (0001)_{α} \parallel (10\bar{1}0)_{ω}  
          | [10\bar{1}0]_{α} \parallel [11\bar{2}3]_{ω} |
| IV      | (0001)_{α} \parallel (1\bar{1}02)_{ω}  
          | [1\bar{1}00]_{α} \parallel [11\bar{2}0]_{ω} |

**Table 2.1.** Observed variants of α and ω orientation relationships.

**Figure 2.7.** Diagram of the lattice orientation relationship between α and ω produced by both the TAO-1 (Variant IV) and Silcock (Variant II) transformation pathways. The cross-section of the conventional cell for each lattice type is overlayed on the atomic positions to simplify identification. Atoms are shaded by coordination, with ω having 11- and 14-coordinated sites, and α uniformly having 12-coordinated sites.

OR resulting from the transformation, Variant IV, is unexpectedly never witnessed in experimental observations. The OR determined in these cases is primarily found to be of the Silcock-type (Variant II), and in some cases Variant I [39, 40]. Variant III, though
observed, was determined to likely be derived from the Variant I OR [14, 40]. Despite the variety of OR’s observed from shock studies, for the reverse case when isothermal \( \omega \) is annealed to transform to \( \alpha \), the Silcock OR is nearly uniformly observed to be maintained between \( \alpha/\omega \) during transformation, leading to the Burgers OR between the \( \beta \) matrix and the transformed \( \alpha \) particle [34, 41, 42, 43]. Whether this transformation originates within the \( \beta \) phase, at \( \beta/\omega \) interfaces, or within \( \omega \) still remains a open topic of discussion. These uniformly distributed fine scale \( \alpha \) particles cause considerable strengthening of \( \beta \) alloys.
CHAPTER 3

COMPUTATIONAL METHODS

In this chapter, a general overview of the computational and analysis methods used throughout the dissertation will be given. All atomistic modeling was performed using density functional theory with a planewave basis set as implemented in the Vienna Ab-Initio Simulation Package (VASP) [44, 45, 46, 47]. For transitional phenomena, a nudged elastic band algorithm was used to search for minimum energy pathways using the VTST package for VASP [48, 49, 50, 1]. Both of these methods are described at a cursory level below, though state-of-the-art implementations in modern computational software packages such as VASP are much more sophisticated and have been continuously improved for speed, scalability, transferability, and accuracy. While many complete texts on either of these subjects exist, useful reviews of the theory and practical applications can be found in Refs. [51, 52, 53].

3.1. Fundamentals of Density Functional Theory

Density functional theory (DFT) has been successfully applied to find accurate solutions to the otherwise numerically intractable many-body Schrödinger equation, and has provided a useful framework for understanding fundamental material physics and chemistry underlying a wide range of phenomena. At its core it is a method for solving for the total energy of a system of atoms in its ground state (specifically the electronic structure), and does so in an intrinsically ab-initio way; the minimum required information for a given material system is the positions of the atoms, their chemical identities, and in particular for condensed matter systems, a suitably chosen system cell which reflects the periodicity of the lattice. With knowledge of this energy, useful comparisons between different reference systems can be made, allowing a powerful way to explore the effect of various configurational changes. Additionally, quantities such as forces on atoms, system stress, band structures, spatial charge density distributions, can be obtained. Fundamental
aspects of the underlying theory, its inherent assumptions and its application in this work are given here.

Given that the wavefunction of a system \( \Psi \) contains all necessary information, this is the desired quantity for an ab-initio description of any atomic system. For a nonrelativistic, time-independant system of electrons in a crystal potential, the wavefunction \( \Psi \) can be described by Schrödinger's equation:

\[
\mathcal{H}\Psi = E\Psi, 
\]
and with the Hamiltonian operator \( \mathcal{H} \) expanded in reduced atomic units,

\[
\left( \sum_i \frac{-1}{2} \nabla_i^2 + \frac{1}{2} \sum_i \sum_j \frac{1}{|r_i - r_j|} + \sum_i \sum_I \frac{-Z_I}{|r_i - r_I|} \right) \Psi = E\Psi,
\]
where \( i \) and \( j \) are indices for the electrons, and \( I \) for the nuclei. The time-independant assumption is considered valid according to the Born-Oppenheimer approximation, which assumes the motion of electrons follows the nuclei adiabatically, i.e. the electrons reach a ground state instantaneously relative to any motion of the nuclei due to their significantly less mass. Additionally, within this approximation excited electron states are ignored, and only the ground state energy and corresponding wavefunction is of interest. Thus, the total energy is a unique function of the atomic nuclei positions, and the complexity of the coupled equations is drastically reduced.

The Hamiltonian shown above includes terms only relevant to the electronic wavefunction: the kinetic energy of the electrons

\[
\hat{T} = \sum_i \frac{-1}{2} \nabla_i^2,
\]
the potential energy arising from electron-electron interactions

\[
\hat{V} = \frac{1}{2} \sum_i \sum_j \frac{1}{|r_i - r_j|}.
\]
and the potential energy arising from the electrons and the external potential of the nuclei

\[ \hat{V}_{\text{ext}} = \sum_i \sum_j \frac{-Z_i}{|\mathbf{r}_i - \mathbf{r}_j|}. \]

However, even at this level of approximation, the Schrödinger’s equation is numerically exceedingly difficult to solve for all except the simplest wavefunction problems, and true many-body problems such as found in real materials and molecules remain well beyond reach.

One of the breakthroughs in further reducing the complexity of the many-body system came with the Hohenberg and Kohn theorems in 1964 [54]. The first theorem states that the ground-state energy is a unique functional of the electron density \( \rho(\mathbf{r}) \), i.e., there is a one-to-one mapping between the ground-state wave function and the ground-state electron density, and thus the electron density also contains all the information of a system’s ground state properties. Here, \( \rho(r) \) for a system of \( N \) electrons is defined as

\[ \rho(\mathbf{r}) = N \int \cdots \int |\Psi(r_1, r_2, ..., r_N)|^2 dr_1 ... dr_N. \]

This reduces the problem of solving for the 3N dimensions of the wavefunction \( \Psi(r_1, r_2, ..., r_N) \) to the 3 spatial dimensions of \( \rho(\mathbf{r}) \) (and an additional coordinate for spin, neglected in discussions here). Thus, if the ground state density is known, the ground state energy is a functional of it, i.e. a unique value can be calculated from it. Accordingly, the second theorem states that if the energy functional is known, it can be variationally minimized with respect to changes to the electron density, and will reach a minimum when the true ground state electron density is found, i.e. the one that would be obtained from solving Schrödinger’s equation.

Within this new framework of the problem, the total energy of the system, now written as the functional \( E[\rho] \) can be expressed as

\[ E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V[\rho(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}, \]
where the first two terms are also known as the Hohenberg-Kohn functional. This functional can be re-expressed with some rearrangement into the terms which are readily known, and those which capture the more difficult quantum effects, as

\[ E[\rho(r)] = T_s[\rho(r)] + V_{Hartree}[\rho(r)] + V_{XC}[\rho(r)] + V_{ext}[\rho(r)], \]

where \( T_s[\rho(r)] \) is the kinetic energy of a system of non-interacting electrons, \( V_{Hartree} \) is the Coloumbic interaction between a single electron and the total electron density, \( V_{XC} \) is the exchange-correlation functional, and \( V_{ext} \) is the interaction of the electrons with the nuclei. \( V_{XC} \) is a term which captures the complicated many-body effects, such as exchange energy required due to Pauli exclusion principle, self-interaction corrections to the Hartree potential, and correlation energy, which is the energy contribution from \( T - T_s \), i.e. the difference between the true kinetic energy of the electrons and the one calculated from the non-interacting system.

The Kohn-Sham equations soon thereafter provided a mathematical tool to actually solve for this density in a self-consistent way[55]. The Kohn-Sham method introduces an analogous quasiparticle system composed of non-interacting orbitals \( \psi_i(r) \), with which the exact ground state density is found according to the relation

\[ \rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2, \]

The Kohn-Sham equations then allow for the solution of each single-particle wavefunction according to

\[ [T_s + V_{Hartree}(r) + V_{XC}(r) + V_{ext}(r)]\psi_i(r) = \epsilon_i \psi_i(r) \]

These single particle wavefunctions \( \psi_i(r) \) are not the same as an actual electronic wavefunction, thus a direct physical interpretation is not strictly correct, but their solution allows a tractable way of determining the electron density. However, they require the density as an input for their solution, creating a circular problem. This is addressed by solving for
the density in a self-consistent way; an initial guess to the electron density is made, the single particle wavefunctions are solved for, the density is then recalculated from the K-S particles, and the total energy is recalculated with this new density. Once the total energy ceases to change with respect to successive trial densities, then the true electron density is considered found. In practical calculations, a convergence criteria is used to determine when a suitably accurate ground state density has been reached.

This representation is exact, but a precise form of the exchange-correlation functional $E^{X_C}$ is not known a priori, and may not in fact exist. Still, many useful approximations to the $E^{X_C}$ have been devised, the selection of which requires careful consideration for the system being studied and the properties being evaluated. The simplest approximation, the local density approximation (LDA), has been successfully applied for the study of metals, and assumes that the exchange-correlation energy density at a given point in a system is equivalent to the same energy density in a uniform electron gas with the same density, which can be calculated directly. A more advanced approach, called the generalized gradient approximation (GGA), extends LDA by incorporating the gradient of the charge density at a given position in the real system when calculating the $E^{X_C}$. The actual method of including the gradient has lead to a wide variety of GGA functionals, but two of the most commonly used are the Perdew-Wang (PW91)[56] and the Perdew-Burke-Ernzerhof (PBE) [57] functionals. The latter is used exclusively in this work, but results are generally equivalent between the two. These functionals tend to generally improve binding energies, bond lengths, and lattice constant descriptions over LDA, while being computationally efficient.

With the theory thus defined, a few additional aspects are needed with regard to actual numerical calculations. To calculate bulk properties of crystalline materials, Bloch’s theorem allows simplification of an infinite crystal to a representative 3D periodic cell. Next, the Kohn-Sham equations require the single particle wavefunctions $\psi_i$ to be expanded in terms of a suitable basis function, for which planewave basis sets are widely used for many condensed phase studies. An exceedingly high number of planewaves would
be needed to capture the rapid oscillations of the electronic wavefunction near the nuclei belonging to core electrons, thus an approximate effective potential is used to separate the "inert" core electrons from the valence electrons active in most interatomic interactions. This separation must be carefully considered, and for metals is typically accomplished by using pseudopotentials (PP) or the related projector augmented wave (PAW) potentials [58], which is a frozen core all electron method. For all calculations in this work, PAW potentials as implemented in VASP were used[59]. The single particle wavefunctions using a planewave basis set are expressed as

\[ \psi_j = \sum_{G \leq G_{\text{max}}} c^j_k e^{i(k+G \cdot r)} \]

where \( G_{\text{max}} \) is the maximum \( G \)-vector specified by the planewave energy cutoff, and \( k \) represents sampling points in the Brillouin zone. The accuracy of a calculation needs to be converged with respect to both of these quantities. To achieve an accuracy of < 1 meV/atom, a planewave energy cutoff of 400 eV was used for all calculations, and for the latter, a k-point mesh was chosen dependent on the system cell geometry such that the k-spacing was < 0.19 Å\(^{-1}\) along each reciprocal cell vector.

3.2. The Nudged Elastic Band Method

A powerful application of DFT is the search for minimum energy pathways (MEP) connecting two isolated configurational states of a system, which is useful for studying mechanisms and energetics related to a wide array of material phenomena such as defect migration, surface reactions, phase transformations, deformation processes, etc. One of the more robust methods to accomplish this is the nudged elastic band (NEB) method [60].

In this elastic band approaches, a chain of system images (or replicas) \([R_0, R_1, R_2, \ldots, R_N]\) is generated which represents a discrete path from the initial \((R_0)\) to final \((R_N)\) state. A reasonable starting guess in most cases is a linear interpolation of atom positions between these two endpoint states. The images are then relaxed with respect to an object
function using an optimization method towards the MEP. The function has a form typically as

\[ S(R_1, \ldots, R_N) = \sum_{i=1}^{N-1} F(R_i) + \sum_{i=1}^{N} \frac{k}{2} (R_i - R_{i-1})^2 \tag{12} \]

where the first term is the sum of forces on all atoms in an intermediate image, and the second is the sum of an artificial spring force with spring constant \( k \) separating the images, including the end points. This formulation mimics an elastic band, but suffers from several drawbacks; depending on the magnitude of the spring forces and interatomic forces near the transition state, either corner cutting (overestimation) or sagging (underestimation) of the MEP occur. This is addressed by using a nudging method. If the unit tangent at each image with respect to the path \( \hat{\tau}_i \) is known, the forces on each individual image should be the parallel component of the spring forces (separating the images), and the perpendicular component of the interatomic forces.

\[ F_i = -\nabla E(R_i)_{\perp} + F_i^s \cdot \hat{\tau}_{i,\|} \hat{\tau}_{i,\|} \tag{13} \]

Where \( \nabla E(R_i) \) is the gradient of the energy with respect to atomic positions at image \( i \), and \( F_i^s \) is the spring force acting on image \( i \). The perpendicular component of the gradient is found using

\[ \nabla E(R_i)_{\perp} = \nabla E(R_i) - \nabla E(R_i) \cdot \hat{\tau}_{i,\|} \hat{\tau}_{i,\|} \tag{14} \]

and the images are kept evenly spaced by evaluating the spring forces as

\[ F_i^{s\|} = k(|R_{i+1} - R_i| - (R_i - R_{i-1})|) \hat{\tau}_{i,\|} \tag{15} \]

A schematic of the forces on an image during the NEB optimization process is depicted in Fig. 3.1
Figure 3.1. A cartoon of the MEP search connecting an initial and final state using NEB is shown, adapted from Ref. [1]. The two components of \( F_i \) on each image are diagrammed in the inset, shown as \( F_i^\perp \) and \( F_i^\parallel \).

With the forces on each image thus defined, they can be minimized independently using different numerical methods, the efficiency of which depends on the nature of the MEP. One such method is using a velocity Verlet integration scheme, which describes the equations of motion for path "dynamics". The position and velocity of each image is defined respectively as

\[
R_i(t + \Delta t) = R_i(t) + \hat{R}_i(t) \Delta t + \frac{1}{2} \frac{F_i(t)}{m} \Delta t^2
\]

\[
\hat{R}_i(t + \Delta t) = \hat{R}_i(t) + \frac{1}{2} \frac{F_i(t + \Delta t) + F_i(t)}{m} \Delta t.
\]

Time and mass are analogous quantities, i.e. \( \Delta t \) controls the magnitude of displacement between iterations, and the mass \( m \) effectively scales the magnitude of the force. The optimal chain of states, and thus MEP, is found when a stationary solution of these equations is found. An extension of this approach, the quick-min method, is predominantly used in
this work, and trades off some efficiency for robustness without needing any system specific parameters. It modifies the velocity Verlet method by projecting the velocity in the direction of the image force and zeroing the velocity if it is antiparallel to the force, i.e.

\[
V_i = (V_i \cdot F_i) F_i
\]  
(18)

\[
V_i = 0 \text{ if } V_i \cdot F_i < 0,
\]  
(19)

similar to an inertial quenching process. A recent comparison of different methods for searching for MEPs can be found in Ref. [1]. For all NEB calculations performed in this work, a spring constant of -5.0 eV/Å was used. It is applied to study the \( \beta \rightarrow \omega \) transformation process in Chapter 4, vacancy migration barriers in Chapter 5, and the bulk and planar \( \omega \rightarrow \alpha \) transformation process in Chapter 6. In cases where the cell geometry changed between initial and final states, a linear interpolation was used of the cell vectors. While recent implementations of NEB can account for changes in cell geometry during the transformation [61], the version available at the time of this work (VTST v3.0c) was found in some instances to give erroneous forces on individual images and preventing the MEP from converging, and was thus avoided.

3.3. Visualization and Analysis Methods

Throughout this dissertation, system creation, visualization, and analysis of VASP output was performed with either VESTA [62, 63] or OVITO [64] software, shown in Fig. 3.2. VESTA was used primarily for charge density and coordination environment visualization, while OVITO was used for Voronoi analysis, atomic displacement analysis, and supercell creation. Two methods in particular, the differential charge density and Voronoi analysis, are explained in some detail here.

The charge density \( \rho(\mathbf{r}) \) produced after electronic minimization is a scalar field, defined on a fine grid at every point throughout the system. This data is found in the CHG file produced by VASP, and is outputted as \( \rho(\mathbf{r}) \ast V \), where \( V \) is the system volume. For a constant system volume, and constant number of grid points along each cell vector,
the charge density difference between two different systems can be evaluated at each grid point, and an isosurface can be interpolated between grid points with the same value and visualized within VESTA. This is a useful way to characterize the spatial extent of charge redistribution after substitution, as seen in Fig. 4.4. Alternate definitions of differential charge density have been used elsewhere, such as comparing the minimized charge density with the initial unminimized density, which corresponds to a non-interacting electronic state [65]. Qualitatively, the results indicate the same phenomena, though an additional benefit of the method used here is the identification of regions of charge increase and decrease relative to a reference all titanium state.

Voronoi tessellation is a method widely applicable to general problems of spatial partitioning, and characterizing properties of each partition such as its volume, centroid, number of faces, etc. Given a set of points, a voronoi tessellation will generate a cell associated with each point which partitions the region of space closer to that point than any other [66]. This is implemented in the Voro++ software utility [67], which was later incorporated as a library in OVITO versions > 2.4.1. The construction of a Voronoi cell is similar to the Wigner-Seitz cell, done by bisecting the distance between a given atom and its neighbors with a plane, and generating a cell from the convex hull generated from the intersection of all such planes. The cell is regenerated after each plane is added to
surface, and once new planes no longer intersect the surface, the search for neighbors stops, and the cell is defined. This can be done efficiently in parallel, calculating each atom’s voronoi cell individually. The voronoi cell is useful for calculating the volume and identifying structural differences at specific sites in a nonuniform system.
CHAPTER 4

THE EFFECT OF MO ADDITIONS ON THE β-TI LATTICE

4.1. Effect of Mo addition on the \( \beta \rightarrow \omega \) transformation

In this section, the effect of molybdenum addition on the \( \beta \rightarrow \omega \) transformation pathway is studied. As described in Chapter 2, this transformation is expected to occur by an ordered displacement wave facilitated by the softening of the \( L_2^3[111] \) phonon mode corresponding to the relative displacement of \( [111] \) chains of atoms relative to each other. This causes every two out of three \((111)\) planes to collapse into a \((0002)\) plane of \( \omega \), transforming a \( ABCABC \) stacking sequence to \( AB'AB' \) [9]. This can occur along any of the four independent \( \langle 111 \rangle \) directions. Thus, from a modeling perspective it is difficult to generate a supercell with an orientation and periodicity that would be commensurate with the potential displacements along all of these directions. Instead, a supercell was chosen which isolates only a single \( \langle 111 \rangle \) direction for displacement, and a deliberately simplified study of the effect of Mo concentration on the energetics of the \( \beta - \omega \) path is performed.

The BCC structure along the \( [111] \) direction and the \( \omega \) structure along the \( [0001] \) direction share a common trigonal symmetry, thus a trigonal, three atom unit cell representation can be derived of both structures. The lattice constants for the BCC cell after minimization are \( a = b = 4.600 \, \text{Å}, \) and \( c = 2.817 \, \text{Å}, \) and the same cell geometry is used for the \( \omega \) cell. The \( \vec{a} \) and \( \vec{b} \) lattice vectors are aligned along the \( [1 \bar{1} 0]_\beta \) and \( [01\bar{1}]_\beta \) directions respectively, and the \( \vec{c} \) lattice vector along the \( [111] \). The basis positions during the transformation are \((0,0,0), (\frac{1}{3},\frac{2}{3},\frac{1}{3} + z), \) and \((\frac{2}{3},\frac{1}{3},\frac{2}{3} - z), \) where \( 0 < z < \frac{1}{6}c. \) From this relaxed cell, a \( 2 \times 2 \times 2 \) supercell was constructed for a system with a total of 24 atoms. For the cases with Mo additions, two, three and four Mo atoms were initially randomly substituted into the minimized \( \beta \) and \( \omega \) Ti supercell to create 8.3, 12.5, and 16.6 at.% nominal concentrations. These substituted structures were once again minimized with respect to volume and ionic positions using a quasi-Newton method with an initial force threshold of 0.15 and then 0.02 eV/Å. This is done to preserve a metastable state after substitution.
that is as close to its native $\beta$ or $\omega$ structure as possible, and prevent immediate relaxation to the minimum energy structure. The selected endpoint structures for $\beta$ and $\omega$ for the pathway studies exhibited the least distortions as a result of Mo-Mo interactions across periodic boundaries.

The nudged elastic band (NEB) method, described in Chapter 3, was then used to determine the minimum energy pathway (MEP). Even in the absence of a dividing saddle-point, the NEB method can be useful to find the most probable path which connects any two points (i.e. two atomic configurations) on the potential energy surface. The benefit of this approach over linearly interpolating the pathway and calculating the corresponding energy of each intermediate structure is that atomic relaxations along the pathway of interest are also accommodated. This can reveal additional insights if any correlated mechanisms are occurring.

For these calculations, eleven intermediate images were used. In contrast to the pure Ti system, the substitution of Mo will break the lattice symmetry, and the atomic displacements will no longer be identical in each individual unit cell due to local Mo-induced effects. Thus, to provide a common coordinate for comparison between all of the compositions studied, the $z$ displacement is averaged over the two displacing atoms in all eight unit cells comprising the supercell, giving an average displacement for the entire transformation process. The reaction coordinate $0 < \chi < 1$ then represents the $0 < z < \frac{1}{6}c$ for a completed $\omega$ transformation. The resulting interpolated plots of the energies along the converged minimum energy pathway for each composition are shown in Fig. 4.1.

Between Pure Ti and 16.6 at% Mo, a progressive inversion in the energy for $\beta$ to transform to $\omega$ is observed, i.e. the omega transformation is increasingly suppressed. The energy of the lowest energy structure relative to $\beta$ ($\Delta E_{\text{min}-\beta}$) and the energy of the $\omega$ structure relative to $\beta$ ($\Delta E_{\omega-\beta}$) both exhibit a slight quadratic dependence with respect to composition, as shown in Fig. 4.2. The origin of this behavior is not understood, but may be related to the changing chemical potential of Mo in both the $\beta$ and $\omega$ phases with respect to composition. For the intermediate compositions, the partial $\beta/\omega$ nature of the lowest
energy structure along the pathway strongly depends on the concentration: concentrations of 8.3 at% and 12.5 at% have minima at a coordinate of 0.5 and 0.25 respectively. This is related to the heterogeneous collapse behavior, which is described next.

Fig. 4.3 compares the displacement behavior between the pure Ti and 8.3% Mo composition systems. While the pure Ti case demonstrates the classic $\beta$ to $\omega$ pathway with uniform displacement across all the unit cells, the 8.3% proceeds in stages. At the energy minima for this composition ($x = 0.5$), the unit cells without Mo appear fully collapsed, while the collapse is suppressed in unit cells containing Mo (shown in blue in the figure). This can be viewed as the Mo atom holding the adjacent $\langle 111 \rangle$ first nearest neighbor (1NN) Ti atoms in a BCC-like position, preventing the BC planes from collapsing to the B' plane in $\omega$. Fig. 4.4a and b show the relaxed initial $\beta$ structure from a [1\Bar{1}0]
Figure 4.2. Left: The energy of the lowest energy structure relative to the initial \( \beta \) phase with respect to Mo content (at.%). Right: The energy of the final \( \omega \) structure relative to the initial \( \beta \) phase. Both plots show a slight quadratic dependence.

Figure 4.3. The atomic positions at different stages of the transformation for the pure Ti system (top) and the 8.3% Mo system (bottom) are shown. \( \chi \) represents the reaction coordinate along the minimum energy pathway shown in ???.

and [111] view respectively, with the supercell boundary drawn in a dashed line, and the individual trigonal unit cells distinguished by fine dotted lines. Bonds are drawn to distinguish the 1NN atoms of Mo, all of which are Ti. Additional atoms are depicted outside the supercell as needed to clarify the coordination across periodic boundaries. The [111] atomic columns have been labeled as A, B, or C, to reflect the \( ABC \rightarrow AB' \) scheme for planar collapse and columnar displacement. Accordingly, the two Mo atoms both reside in C columns, and are coordinated by three A atoms, three B atoms, and two
Figure 4.4. First nearest neighbor coordination environment of Mo atoms in 8.3 at% Mo, and charge-density difference isosurfaces are shown. Mo and Ti atoms are shown in dark and light blue respectively, with bonds drawn from each Mo atom to its first nearest neighbor Ti atoms. (a) and (b): [110]_β and [111]_β views of supercell shown (⃗a and ⃗c, respectively), with individual [111] atomic columns labeled. B and C atoms are displaced during the β → ω collapse process. The [111] atomic columns which contain Mo-bonded Ti atoms will be hindered from transforming. (c) and (d): Isosurfaces representing the charge density difference between a pure Ti system and the derived Ti-8.3 at.% Mo substituted system superimposed over the lattice. The blue isosurface encloses regions of increased charge density, while the additional red isosurface shown in (d) encloses region of decreased charge density.

C atoms above and below. During the transformation, any of the columns containing these atoms are prevented from displacing in the [111] direction(s), leaving only the two C columns of Ti atoms mobile to accommodate the displacement.
A physical basis for this behavior can be qualitatively investigated by mapping the difference in valence charge density of the Ti-8.3 at.% Mo system with respect to a pure Ti system in the same atomic arrangement. This is accomplished by replacing Ti atoms at the Mo sites in the minimized alloyed $\beta$ structure, and then calculating the resulting charge density without ionic relaxation. Since the charge density is a scalar quantity calculated on a fine spatial grid, the difference between the two densities can readily be calculated, giving a spatial correlation to the charge modification. This is visualized using isosurfaces in Fig. 4.4c and d (with the same viewpoint as in a and b). In Fig. 4.4d, the blue isosurface corresponds to regions with an increase in charge density and red isosurface to regions of charge reduction. Mo, a group VI element, has two additional valence electrons relative to Ti. In addition to a substantial radial increase in charge density in the vicinity of the substituted site, there is also a distinct directionality along the $<111>$ directions.

A parallel can be drawn to a previous DFT study of single component Y, Zr, Nb, and Mo (the first four 4d transition metals) by Grad et al [68]. These elements follow an HCP $\rightarrow$ BCC stable structural trend, with Zr being allotropic and having a similar high temperature BCC phase as Ti. In their work, the $\beta$ and $\omega$ stability of these elements was studied, and features of the electronic structure and charge density were analyzed with respect to increasing BCC stability from Y $\rightarrow$ Mo. It was found that for the stable BCC elements, charge density is concentrated in the $\langle111\rangle$ bonding directions due to an increased filling of $d$-states, specifically from $d_{t-2g}$ character [68]. This effect becomes more pronounced from Zr $\rightarrow$ Nb $\rightarrow$ Mo, with Zr showing the weakest $<111>$ directionality. Furthermore, with this increased localization, the bonding becomes increasingly more directional due to reduction of charge screening, which has the effect of enhancing the restoring force with respect to relative displacements of $<111>$ atomic chains or $(111)$ atomic planes[69, 70, 71]. This has been described as partially covalent bonding character [5], and is directly related to the trend of increased stiffening of the $L_2^2(111)$ phonon mode from Zr $\rightarrow$ Nb $\rightarrow$ Mo [71]. Conversely, for Y, which is completely unstable in the BCC phase, the charge density is concentrated in the next nearest-neighbor direction, i.e. $<100>$. Thus, a clear trend is
observed between the stabilization of the BCC structure with a relative reduction of charge
density in the \(<100>\) directions and accumulation in the \(<111>\) directions.

Similar behavior marking BCC stabilization in the vicinity of Mo is observed from
the \(\Delta \rho\) isosurface for the Ti-8.3 at.%Mo system. Mo increases the charge density to its
1NN Ti atoms along the \(<111>\) directions, which likely signifies a similar increased oc-
cupation of \(d\)-states and strengthens these bonds. As a result, they will be hindered from
freely displacing towards an \(\omega\) structure. Furthermore, in Fig. 4.4a and b it is evident
that the two Mo atoms are on the same C plane, and share two common Ti 1NN atoms in
the \([1\bar{1}0]\) direction. These two Ti atoms are \(<100>\) 2NN neighbors, and the interstitial
region between them is in fact reduced in charge density. This may imply that as Ti atoms
become coordinated by additional Mo atoms, their electronic behavior becomes increas-
ingly similar to the stable BCC transition metals, causing increased resistance to \(\omega\)-like
displacements.

Surprisingly, the increase in charge density does not extend significantly beyond the
first NN Ti atoms of Mo. This indicates that non-Mo coordinated Ti atoms do not undergo
the same directional bond stiffening effects due to the increased \(d\)-electron concentration,
and hence remain unconstrained to displace towards the \(\omega\) phase.

This helps explain the observation of the inflection point observed for the 8.3 %
composition as seen in Fig. 4.1, corresponding to \(x=0.23\) in Fig. 4.3. Because of the con-
stricted nature of the lattice due to the arrangement of the Mo atoms, the displacing atoms
are observed to move in two \(\langle 111 \rangle\) directions simultaneously to accommodate transforma-
tion. This is visualized in Fig. 4.5a, where the larger dark blue atoms are Mo, the light
blue atoms are Ti, and the remaining white atoms are non-Mo neighboring Ti, which ac-
commodate all the motion during the transformation. A \((110)\) plane is shown, again with
the lattice expanded to better account for periodic effects. Fig. 4.5a shows the initial struc-
ture, with columns of atoms undergoing displacement highlighted. Fig. 4.5b shows the
structure after the concurrent displacement, at \(x=0.23\). The atom at the intersection point
has a net displacement along the \([110]\) direction, creating an intermediate site with what
Figure 4.5. An analysis of the $\beta \rightarrow \omega$ transformation in the Ti-8.3 at% Mo system, near the inflection point observed in the MEP at $\chi = 0.23$. Mo atoms are shown in dark blue, first NN Ti atoms in light blue, and the remaining Ti atoms in white. These "free" non-Mo bonded Ti are the only atoms which can shuffle to accommodate the transformation. Two $<111>$ columns are highlighted in red rectangles in (a). At $\chi = 0.23$, shown in (b), these two columns have both shifted slightly in their $<111>$ directions, leading to a net $<110>$ displacement at their intersection. This slight shift creates an intermediate, distorted HCP type local structure drawn in red in (c). The column is now free to continue displacing, and proceeds to the minima on the MEP at $\chi = 0.5$ corresponding to partially collapsed state (d).

appears to be a strained HCP ($\alpha$) structure symmetry, highlighted in ??c. In fact, this cooperative displacement behavior is like the $T_{12}^{1}$ (110) phonon which contributes to the BCC $\rightarrow$ HCP transformation, wherein atoms on alternating (110) planes moving in opposing $<1\bar{1}0>$ directions. The observation that two low energy, high amplitude modes become unstable at low temperatures can be expected to play a significant role in the evolution of the metastable structure, an idea revisited in this dissertation. Finally, Fig. 4.5d shows the partially collapsed structure at $x=0.5$ after the completed displacement along the primary [111] direction.
4.2. Complex Local Structural Distortions Induced by Mo Solute Atoms

The previous study was aimed at understanding the effect of Mo on a single [111] collapse direction. However, it should be expected that more complex interactions between the solute atoms would exist in more realistic randomized conditions. In this section, an alternate, less idealized dispersion within a larger system is studied to better understand the effects of Mo solute atoms. A new supercell geometry was chosen that would accommodate both \( \alpha \) and \( \omega \) transformations from the \( \beta \) parent phase as shown in Fig. 4.6. The supercell consists of 12x2x1 BCC unit cells, with an orientation described in the figure. Two (110) planes are shown, one darkened and the other lightened for contrast, which can potentially transform to the (0001) planes of the \( \alpha \) phase or the \( \{11\bar{2}0\} \) of \( \omega \). The [111] direction is again aligned with the [0001] direction of the \( \omega \) phase, as before.

![Figure 4.6](image)

**Figure 4.6.** The rotated 72-atom BCC Ti supercell, viewed along the [1\( \bar{1} \)0] direction with two (1\( \bar{1} \)0) planes is shown. The conventional BCC cell is marked in red for reference.

The substituted system before structural relaxation is shown in Fig. 4.7a. Three Mo atoms were substituted in each (1\( \bar{1} \)0) plane in the z-direction, with the distances between Mo atoms labeled. Across periodic boundaries, the Mo-Mo distance would be equivalent to the box length; it would be 7.98 Å in the y-direction and in the z-direction it would be 4.60 Å. Each (1\( \bar{1} \)0) plane has the same distribution pattern, but is shifted to maximize the distance between Mo atoms. Ionic positions and cell volume and shape were allowed to relax during energy minimization. The as-minimized structure was found to be identical
to that after eight and ten picoseconds of NVT ab-initio molecular dynamics at 800 K and subsequent minimization, suggesting this is a suitably accurate representation of the minima structure for the given alloy distribution.

The resulting relaxed atomic configuration is shown in Fig. 4.7b. Similar to the behavior studied in section 4.1, the Mo atoms in the minimized structure retain a BCC coordination environment in their immediate vicinity, as highlighted by the conventional BCC unit cell shown in the figure. This is consistent with the earlier inference that valence charge transfer between Mo and Ti causes the Ti-Mo bond to have a partial covalent character, making it significantly stiffer than the surrounding Ti-Ti bonds. This local enhanced stiffness causes preferential contraction of the Ti-Mo bonds, which begins to distort the non-Mo-coordinated Ti atoms away from their initial ideal BCC positions. All of these contractions occur in various ⟨111⟩ directions relative to the Mo atoms. These shifts initiate multiple local precursor transformations simultaneously, and the incomplete, competing
nature of these transformations create complex local structures during relaxation. A cursory glance at the Ti atoms surrounding the Mo-Ti BCC polyhedra in Fig. 4.7b shows significant rearrangement, without any discernable uniform crystal structure. To better understand the nature of these distortions and how they are being accommodated, the atomic coordination environments can be visualized at sites throughout the crystal. For reference, the polyhedra for the coordination environments of $\beta$, $\alpha$, and $\omega$ sites in pure Ti are depicted in Fig. 4.8, with respect to the resulting orientation after $\beta \rightarrow \alpha$ (Burgers mechanism) and $\beta \rightarrow \omega$ transformation. The relation between $\alpha$ and $\omega$ through the common $\beta$ parent phase is generally referred to as the Silcock OR [27], and is also observed experimentally at $\alpha/\omega$ interfaces. The $\omega \leftrightarrow \alpha$ transformation process is also closely related to this OR, and will be discussed in further detail in Chapter 6. The mutual OR between all three phases is

$$
\beta_{(011)} \parallel \alpha_{(0001)} \parallel \omega_{(11\overline{2}0)} \\
\beta_{[11\overline{1}]} \parallel \alpha_{[11\overline{2}0]} \parallel \omega_{[0001]}.
$$

Details of the crystallography of each structure can be found in Chapter 2; it is briefly reiterated here that the $\omega$ structure has two unique Wyckoff positions, $1a$ which is
Table 4.1. The coordination environment and corresponding atomic distances for Ti in the $\beta$, $\alpha$, and $\omega$ phases.

<table>
<thead>
<tr>
<th>Site</th>
<th>1NN</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>8</td>
<td>2.82</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>6</td>
<td>2.94</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.88</td>
</tr>
<tr>
<td>$\omega_{14}$</td>
<td>2</td>
<td>2.83</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>3.00</td>
</tr>
<tr>
<td>$\omega_{11}$</td>
<td>3</td>
<td>2.64</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.83</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3.00</td>
</tr>
</tbody>
</table>

fourteen coordinated (referred to as $\omega_{14}$), and $2d$ which is eleven coordinated (referred to as $\omega_{11}$). These two sites reside on alternate (0002) planes, and the difference between their coordination environments can be readily identified when viewed along the $[1\bar{1}20]_\omega$ as shown in Fig. 4.8. The $(1\bar{1}20)_\omega$ planes have ABAB stacking, and every $\omega_{14}$ site has six in-plane neighbors, and four out-of-plane neighbors above and below. For simplicity, this is referred to as a (4-6-4) coordination environment. The $\omega_{11}$ sites have five in-plane neighbors, and three out-of-plane neighbors above and below, or a (3-5-3) coordination environment. The analogous $\alpha$ coordination environment with respect to the [0001]$_\alpha$ direction is (3-6-3). The 1NN distances for each site in $\beta$, $\alpha$, and $omega$ Ti are given in Table 4.1.

The polyhedra at a specified site is constructed by searching for all nearest neighbor atoms within a specified distance, and generating a surface from their positions and the connecting edges. For the relaxed metastable system, the Mo-induced distortions break the symmetry and change the 1NN distances anisotropically, thus a site-dependent cut-off ranging from 2.9 - 3.2 Å is chosen for identifying the nearest matching coordination environment for either $\alpha$, $\beta$, or $\omega$. The resulting coordination environments are shown in Fig. 4.9, and colorized according to the particular structure observed. Surprisingly, $\alpha$,
ω, and β/ω (labeled as β′) like coordination are found for the Ti atoms within the alloyed structure. All the ω sites correspond to a single β → ω collapse direction, [11\(\bar{1}\)] as identified in Fig. 4.6. The behavior of Ti atoms with a Mo nearest neighbor (Ti\(_{NN,Mo}\)) is fundamentally different than those with only Ti nearest neighbors (Ti\(_{NN,Ti}\)). Ti\(_{NN,Mo}\) assume a mixed structural character, remaining BCC-like in the direction of the Mo atom, but accommodating the surrounding shuffling (Ti\(_{NN,Ti}\)) atoms which are not hindered by the directional stiffening effect of Mo substitution. Since both the α and ω phases are stable with respect to β in pure titanium at low temperatures, it may be expected that atoms would assume a structure derived from either of them with local strains induced by Mo. Both α-Ti and ω-Ti are energetically close, with ω-Ti being 7 meV/atom lower (though the energy to transform between the two is significantly higher, as will be discussed in Chapter 6). The presence and spatial distribution of Mo in the Ti lattice disrupts the transformation behavior from proceeding completely to one or the other. This is attributed to the disruption of the ordered β → ω displacement wave by Mo atoms, shortening of Mo-Ti bonds in all \(〈111〉\) directions, and cooperative local shifting of the titanium lattice. The various combination of effects depend on a given Ti-Mo distribution. Thus, it is useful to analyze and understand how Mo influences these possible transformations in this simplified structure. Later in Chapter 5, we will study the effect of the lattice distortions and α/ω/β structural coexistence on diffusion in this structure.

Primarily, three different local "correlated" behaviors were identified by contrasting the initial as-substituted metastable β structure with the minimized structure in Fig. 4.10. The unrelaxed local structural environment is shown on the left, and the minimized structure at the same sight is shown on the right, with arrows overlayed on the relevant atoms active in a particular displacive behavior to highlight its character. In cases where interactions between Mo atoms on multiple planes are involved, the upper plane is in red and the lower plane is in blue. Due to the periodicity of the structure, alternate planes exhibit the same behavior. Mo atoms are darkened relative to the Ti atoms, and bonds illustrating their nearest neighbor Ti atoms bonds are drawn to distinguish them from Ti\(_{NN,Ti}\) atoms.
The first scenario, shown in Fig. 4.10a, is the effect of two Mo atoms on intermediate Ti atoms in the same [111] atomic column. In this Mo-containing [111] atomic column, three Ti atoms separate the two Mo atoms. Prior to relaxation, the interatomic distance $d_{[111]} = d_{1NN} = 2.81 \text{ Å}$. After relaxation, the Ti atoms shift toward the Mo atoms, but the displacement is not evenly distributed among the three Ti atoms. The Mo-Ti bond length reduces to 2.59 Å (-7.8%), and the Ti-Ti bond length extends to 3.04 Å (+8.2%). The center Ti atom transforms to an $\omega_{14}$-like site, and the originally $\beta_{(111)}$ direction becomes $\omega_{(20\bar{2}3)}$, which in pure Ti has an interatomic distance of 3.00 Å. In the [11\bar{1}] direction, the corresponding Mo-containing atomic column does not contain any other Mo atoms. An alternate view of this atomic column is depicted in Fig. 4.10c, labelled as column IB. This Mo-Ti bond contracts to 2.49 Å (-11.4%). For reference, in pure Mo, $d_{1NN} = 2.75 \text{ Å}$, so the Mo-Ti bond lengths are considerably shorter than would be expected from a simple linear interpolation akin to Vegard’s law [72]. This is partially enabled by the charge transfer between Mo and Ti creating an asymmetric bonding (stiffness?) environment at the $\text{Ti}_{NN,\text{Mo}}$ atoms, which would preferentially displace these atoms towards Mo, but is also enabled by the coincidence of such displacements with the $\beta \rightarrow \omega$ pathway. The latter is likely to reduce the energy of the $\text{Ti}_{NN,\text{Ti}}$ atoms. In contrast, in the two out-of-plane $(11\bar{1})$ directions( [\bar{1}11] and [1\bar{1}1]), the Ti-Mo bonds slightly contract to 2.78 Å, within the range
Figure 4.10. A diagram of several atomistic mechanisms induced by Mo addition. Two (110) planes are shown, colored in blue and red, with Mo atoms darkened. (a) Mo atoms lying in same ⟨111⟩ column. Mo-Ti distances along this direction contract, but Ti-Ti bonds elongate. (b) Contractions along two ⟨111⟩ directions within the same (110) plane creates a net ⟨111⟩ displacement relative to the planes above and below. If a Mo atom is present on the next (110) plane, and exhibits the same contraction in the opposite direction, the net displacement mimics the shuffles of the $\beta \rightarrow \alpha$ process, and creates $\alpha$-like sites. (c) Mo atoms present in directly adjacent ⟨111⟩ atomic columns will induce contractions on the Ti atoms, and if Mo atoms are present on alternate (110) planes, and if the contractions are in opposite directions, then enhances the displacement pattern required for $\beta \rightarrow \omega$ transformation.
of Ti and Mo $d_{1NN}$ values, and no $\omega$-like displacements occur in these directions. This is restricted by the periodicity of the structure in the [1\bar{1}0] direction, which symmetrizes the out-of-plane forces on atoms in the (1\bar{1}0) plane from the adjacent ones. Increasing the length of the system in this direction while preserving the ABAB stacking of the substituted planes results in identical behavior.

The second scenario (Fig. 4.10b) illustrates the presence of $\alpha$-like distortions created by the combined effect of the [111] and [11\bar{1}] Mo-Ti bond contractions. The (1\bar{1}0) plane containing both of these contractions is shown. The resultant displacements of the two Ti atoms can be separated into orthogonal [110] components and anti-parallel [001]/[00\bar{1}] components. The [110] shift on both of the Ti atoms relative to the (1\bar{1}0) plane above and below is analogous to the $T_1[\xi\xi0]$ with [1\bar{1}0] polarization phonon mode in BCC metals[73]. This mode corresponds to alternate (110) planes displacing in opposite [1\bar{1}0] directions, which is the shuffle component of the $\beta \rightarrow \alpha$ transformation. Within this (1\bar{1}0) plane there will be four contracting Mo-Ti bonds, and thus Ti atoms shift in both the [110] direction and the [\bar{1}10] relative to the Mo atom. This displacement is only a precursor, however, the induced shift is not enough to completely form an alpha site adjacent to Mo. However, as shown in (Fig. 4.10b), if Mo atoms are placed favorably in alternate (110) planes, then the displacements of the Ti atoms on both planes will have an additive effect, creating a more idealized $\alpha$-like environment, as shown on the right in the figure. The blue atom surrounded by the dashed triangle has adapted a 12-coordinated $\alpha$-like environment, as well as the symmetrically equivalent red atom located on the neighboring (110) plane.

The anti-parallel [001]/[00\bar{1}] components of the bond contractions also facilitate this structural transition. These Ti atoms move towards each other in the [001] direction, contracting the distance from the initial $a = d_{2NN} = 3.25$ Å to 3.04 Å. This direction, originally 2NN [001]$_\beta$, becomes 1NN [1\bar{1}20]$_\alpha$, which in pure Ti is $d_{[1\bar{1}20]}=2.92$ Å. The in-plane angles between $\langle 111 \rangle$ directions and between $\langle 111 \rangle$ and $\langle 001 \rangle$ are originally 70.6° and 54.6° respectively, and after relaxation become 66.3° and 57.6°. The structure is
clearly still constrained from being ideal $\alpha$ due to the proximity to the Mo atoms. As will be seen in the next sections, this will play a role in the development of interfaces.

Lastly, Fig. 4.10c shows coupling between the $\omega$ type anti-parallel displacement and the Mo-Ti induced contraction. As mentioned previously, the $ABCABC$ stacking of planes in $\beta$ structure change to the $AB'AB'$ in $\omega$ during $\beta$ to $\omega$ transformation, with the A positions remaining invariant between the two. The $ABC$ planar stacking is seen along each [111] columns of atoms, and the same relations apply as in the planes; the A positions remain invariant, and the B and C columns displace in opposite directions to initiate the transformation. When Mo atoms are present on adjacent B and C columns, and are separated spatially by Ti atoms between them, the anti-parallel contraction of the Ti-Mo bonds on each [111] column would facilitate the formation of the $\omega$ phase. With this in mind, the as-substituted structure in Fig. 4.10c reveals new insights. As before, the chosen view portrays two (110) planes. The upper and lower plane atoms are depicted in red and blue respectively, and the Mo atoms are darkened relative to the Ti atom. The region of interest is marked by dashed lines, which would correspond to two columns of four BCC unit cells (labeled I and II) aligned according to the $\beta \rightarrow \omega$ path described in section 4.1. Using the convenient $ABC$ notation, we can consider the atoms along the dashed edges to be the invariant 'A' columns of atoms. A Mo atom lies in the 'B' column above the active region and in the 'C' column below, as marked by the dark spheres. After relaxation, column I has nearly completely shifted to $\omega$-type positions, though the extent of displacement is mitigated by the Ti atoms which are nearest neighbor to Mo (shown with bonds). However, the presence of the Mo atom in the adjacent column II interrupts the collapse pattern with respect to column I. The bottom two unit cells of column II remains commensurate with column I, but the contraction of the Mo-Ti bond above changes the displacement sequence and creates two incommensurate $\omega$ regions as shown in Fig. 4.11. Regions of continuous, commensurate collapse are shaded blue or red, and it is evident that the Mo atoms are "scattering" points disorganizing the $\omega$ formation process around it. Importantly, $\alpha$-type
**Figure 4.11.** Regions of mutually commensurate $\omega$ are shaded in blue and red. The Mo atoms disrupt the collapse pattern, causing discommensuration. Atoms separating the two regions are either $\alpha$-like if Ti (dashed triangles) or $\beta$-like of Mo. Sites are found at the boundary between the two regions. The two sites with HCP coordination are outlined by dashed triangles. This suggests that $\alpha$ and $\omega$ can co-exist due to the dispersion of Mo and the long-ranged interactions between the solute atoms. As will be seen later, the two lattices can accommodate each other well and co-exist with minimal energy penalty.
4.3. Interfaces between Mo-rich and Mo-lean regions

In this section, the structure and energetics of various interfaces between Mo-rich and and Mo-lean regions are studied. Recent experimental studies have shown that the formation of stable $\omega$ precipitates is preceded by the diffusion and partitioning of $\beta$-stabilizing elements, creating enriched and depleted regions. It is postulated that the degree of collapse is continuously varying with the increasing depletion of Mo within the $\omega$ phase, giving rise to a mixed-mode phase transformation [74, 4]. Sufficient annealing results in coarsening of these precipitates, with complete $\beta \rightarrow \omega$ collapse and nearly complete rejection of Mo.

We aim to study a simplified scenario of Mo partitioning in the [111] direction by preferentially substituting Mo in a concentrated region instead of over the entire crystal, using the same $\beta$-Ti supercell as used in section 4.2 (Fig. 4.6). Due to the periodic boundaries, these systems can be considered analogous to alternating semi-infinite Mo-enriched and pure Ti regions. After substitution, ionic positions, cell shape, and cell volume are allowed to relax with VASP with the same parameters as used previously.

Two different substituted configurations were created with local partitioned concentrations of 16.6 at% Mo and 33.3 at% Mo, as shown in Figs. 4.12 and 4.13. Both the initial and minimized states of the system are shown. After relaxation, the Mo-enriched region maintains a BCC-like structure, with the 33.3 at% system exhibiting fewer lattice distortions than the 16.6 at% one. The pure $\beta$-Ti region has transformed to the $\alpha$ phase in both configurations. This is an unexpected result, considering that omega Ti has a lower ground state energy at $T=0$ K, and indicates that interface structure and Mo distribution likely play a role in the preference of the $\alpha$ phase over the $\omega$. The effect of Mo at the interface between the $\beta$-stabilized and Ti regions is similar to what was demonstrated in Fig. 4.9b - two simultaneous $\langle 111 \rangle$ type contractions induce an additive [110] shift that creates $\alpha$ precursor sites. Because these displacements are no longer inhibited by other Mo atoms, this creates initiation points for the $\alpha$ transformation to begin in the pure Ti region.
Figure 4.12. Partially substituted titanium BCC lattice, corresponding to a local concentration of 16.6 at% Mo.

Figure 4.13. 8.3 at% Ti is substituted in one half of the supercell. This partially substituted titanium BCC lattice has an effective local concentration of 33.3 at% Mo. The dividing interface between the left half of the supercell with Mo atom and right half of supercell with pure Ti is shown by dashed red line.

The relative stability of the 16.6 and 33.3 at% Mo partitioned configurations can provide additional insight into the chemical driving force behind the phase separating behavior. We can estimate the formation enthalpy for each phase by performing random Mo
substitutions into an appropriate Ti-supercell as a function of concentration and by relaxing only the cell volume to maintain the parent lattice structure. A similar methodology was employed to study Ti-Nb and Ti-Mo systems, using smaller supercells [75]. This is performed for two random configurations at each concentration, and the averaged alloy formation energy per atom $E_{F,T=0K}$ is plotted for each phase. The formation enthalpy/atom for each phase $\sigma = \alpha, \omega, \text{or } \beta$ is defined as

\[
E^\sigma_F (\text{Ti}_x\text{Mo}_{1-x}) = E^\sigma_{\text{total}} / N - x\mu_{\text{HCP}}^{\text{Ti}} - (1 - x)\mu_{\text{BCC}}^{\text{Mo}},
\]

where $N$ is the total number of atoms in the system, $E^\sigma_{\text{total}}$ is the total calculated energy of the system, and $\mu_{\text{HCP}}^{\text{Ti}}, \mu_{\text{BCC}}^{\text{Mo}}$ is the reference chemical potential (or cohesive energy) for either HCP Ti or BCC Mo. These latter values were calculated using the same 24 atom cell and VASP parameters as the substituted configurations, giving $\mu_{\text{HCP}}^{\text{Ti}} = -7.891 \text{ eV/atom}$ and $\mu_{\text{BCC}}^{\text{Mo}} = -10.846 \text{ eV/atom}$. The resulting plot is shown in Fig. 4.14. As expected, Mo has limited solubility in the $\alpha$ and $\omega$ phases, and phase separation is favored. Furthermore, the solubility in the $\omega$ and $\alpha$ phases is nearly identical, indicating that there is no clear phase preference at dilute concentrations. The results match qualitatively with experimentally determined G-X plots, as shown in Fig. 4.15.

The interface structure reveals that $\beta$ and $\alpha$ phases share the Burgers OR and the interfacial habit plane is $(112)_\beta || (\bar{1}\bar{1}20_\alpha)$, shown in Fig. 4.16 for the 16.6 at% Mo system. The interfacial energy $\gamma_{\text{interfacial}}^{\beta+\alpha}$ for this system was found to be 99 mJ/m$^2$. This is calculated for the geometry shown as

\[
\gamma_{\text{interfacial}}^{\beta+\sigma} = \frac{E_{\text{tot}}^{\beta+\sigma}(N) - E_{\text{tot}}^{\beta}(N/2) - E_{\text{tot}}^{\sigma}(N/2)}{2A},
\]

where $E_{\text{tot}}^{\beta+\sigma}(N)$ is the total energy of an interface containing system with N atoms, $E_{\text{tot}}^{\beta}(N/2)$ is the total energy of the $\beta$ region of the system, $E_{\text{tot}}^{\sigma}(N/2)$ is the total energy of the Ti region in either the $\alpha$ or $\omega$ phase, and $A_{\text{interface}}$ is the approximate planar interfacial
Figure 4.14. Alloy formation energies for the \(\alpha\), \(\omega\), and \(\beta\) phases at \(T = 0\)K as a function of at\% Mo concentration. Energies were calculated for two different configurations for each concentration, and the averaged values were plotted.

Figure 4.15. Free energies of the \(\alpha\) and \(\beta\) phases at \(T = 673\) K calculated from ThermoCalc [2], adapted from [3]. Despite the temperature difference, the features of the plot match generally well to the DFT calculated curves in Fig. 4.14.

area. Since two equivalent interfaces are formed due to periodicity, the interfacial area is effectively doubled. \(E_{\text{tot}}^\beta(\frac{N}{2})\) can be calculated exactly, since an ordered Mo distribution is used, and \(E_{\text{total}}^\sigma(\frac{N}{2})\) is equivalent to \(\frac{N}{2}\mu^\text{Ti}_{\sigma}\).
Figure 4.16. The [111]_β/[0001]_ω interface structure between 16.6 at%Mo β and α-Ti is marked by solid red line. The (112)_β planes lie adjacent to (01\bar{1}0)_α planes at the interface. γ_{interfacial} = 99 mJ/m^2.

This is a relatively low energy, considering that the lowest prismatic stacking fault energy in Ti is 220 mJ/m^2. As mentioned previously, the same α-distortions observed in the 8.3 at% Mo system involving the coupled ⟨111⟩ contractions at the interface are observed here. These contractions enhance the coherency at the interface; according to the Burgers OR, ⟨112⟩_β and ⟨100⟩_β become equivalently ⟨1\bar{1}20⟩_α, and in pure Ti, these have atomic distances of \(d_{⟨112⟩}=2.81\,\text{Å}, \quad d_{⟨100⟩}=3.25\,\text{Å}, \quad \text{and} \quad d_{⟨1\bar{1}20⟩}=2.92\,\text{Å}.\) With alloying, \(d_{⟨112⟩}=2.83 - 2.94\,\text{Å}, \quad \text{and} \quad d_{⟨100⟩}=3.00 - 3.04\,\text{Å}\) at the interface, in better agreement with the α phase.

It is unexpected that the 16.6 at.% Mo partitioned system did not relax to the ω phase in the Mo-depleted region. To investigate this discrepancy, as well as ensure the β + α structure observed after relaxation is not a consequence of the force minimization method used, a new system was created by joining the Mo-enriched β phase with an ω Ti region and then relaxed. The resultant structure is depicted in Fig. 4.17. The interfacial energy of this newly crafted β-ω system is observed to be much higher at 208 mJ/m^2. The [112] averaged \(Δd_{B+C→B'}\) distance is plotted above each unit cell. This value is the summed displacement away from the ideal B and C β positions to the ω B' plane according
Figure 4.17. The interface structure between 16.6 at% Mo $\beta$ and $\omega$-Ti is marked by dashed lines in the bottom figure. The averaged collapse along the [111] direction of the supercell is plotted. $\gamma_{\text{interfacial}} = 208$ mJ/m$^2$.

to the $ABCABC \rightarrow AB'AB'$ transformation, and each displacement has a maximum range of $\frac{1}{6}d_{[111]}$. This plot confirms that Mo-enriched $\beta$ region is predominantly stabilized, though slight $\omega/\alpha$-like distortions are still present. The interface exhibits a transitional partial collapse over a distance of $\sim 2-4$ unit cells. This is in contrast to the sharp $\beta/\alpha$ interface with minimal mismatch.

The higher energy of this $[111]_{\beta}/[0001]_{\omega}$ interface relative to the previous $[112]_{\beta}/[10\bar{1}0]_{\alpha}$ one, despite being fully coherent, is likely related to the partial $\beta/\omega$ character of the Ti atoms. The Ti atoms along the same [111] atomic columns as Mo are displaced away from $\omega$ due to the Mo-Ti bond contraction, and this would be expected to raise the energy due to the substantial difference in the $\beta-\omega$ energy in Ti ($\Delta E_{\beta-\omega} = 114$ meV/atom). However, since this interface is aligned perpendicular to the $\beta \rightarrow \omega$ transformation path, at higher temperatures, the energy difference decreases with increasing vibrational entropic effects, and the energy of the interface will likely decrease accordingly. This is expected to lead to a wider, more diffuse interface with extended partial collapse as a function of temperature.
Figure 4.18. The [112]/[10\bar{1}0] interface between 16.6 at\% Mo \(\beta\) and \(\omega\)-Ti is marked by red dashed lines. The interfaces is coherent, and lacks any significant distortion induced by Mo-Ti bond contractions. \(\gamma_{\text{interfacial}} = 80\ \text{mJ/m}^2\).

In contrast, for an interface parallel to the collapsing direction, Mo-Ti contracted bonds minimally interfere with the Ti atoms in the adjacent \(\omega\) crystal, and as a result, the energy is drastically lowered. Using the same 16.6 at.\% Mo substitution distribution for the partitioned region, the [112]/[10\bar{1}0]_{\omega} interface was constructed in a similar manner and allowed to relax. The resulting system is shown in Fig. 4.18, and has an interfacial energy of 80 mJ/m\(^2\). It is clear that there is minimal lattice strain at this interface, in part due to the lack of \(\alpha\)-like distortions. This is due to the Mo atoms at the interface lying in the same [111] column separated by a single Ti atom, which prevents bond-contraction. These bond lengths are relatively unchanged, \(d_{[111],\text{Mo-Ti}} = 2.77 - 2.88\ \text{\AA}\), which matches well with \(d_{[0001],\omega}\).

There is a strong likelihood that the interfacial distribution of Mo atoms and their associated bond contractions play a role in how adjacent depleted regions transform. To investigate this further, we took the same 16.6 at.\% Mo configuration and created an alternate interface normal to the [11\bar{1}] direction. For simplicity, the previous [111] interface will be referred to as Variant I, and the present [11\bar{1}] interface will be referred to as Variant II. The added benefit of doing this is that the interfacial energy calculations become simpler because the energy of the reference 16.6 at\% Mo substituted region is already known.
Figure 4.19. Choice of two \langle 111 \rangle \) directions in a given \((1\bar{1}0)\) plane creates two different \langle 111 \rangle \) interfacial variants with differing Mo distribution patterns. For the same overall Mo composition, Variant I and II are shown red and green respectively.

The relation between the two variants is shown in Fig. 4.19. In Variant I, the Mo was regularly arranged at the interface at identical sites, as seen in the region highlighted in red. In Variant II, the distribution is more irregular, as shown in the region highlighted in green. The periodic repetition distance is also resultantly increased, allowing longer range effects to be captured. For the present calculations, 180 atom supercells will be used, maintaining the same systemwide 8.3 at.% Mo composition.

The relaxed structure used to calculate interfacial energy for Variant II is shown in Fig. 4.20. The pure Ti region does not relax to a single uniform \(\alpha\) or \(\omega\) structure, but rather an incommensurate \(\omega\) structure containing several commensurate \(\omega\) regions separated by various planar and linear defects. These regions have been colored individually to highlight transitions, and labelled as \(\omega_I\), \(\omega_{II}\), and \(\omega_{III}\). For clarity, the term "incommensurate" refers to irregularities in the \(\omega\) phase arising from transformation induced stacking defects,
solute additions, point defects, temperature, etc. Of these, discommensuration refers to regions of $\omega$ which are separated by narrow defects marking a change of phase of the $\beta \rightarrow \omega$ structural modulation [9]. Such defects are observed to occur here. The $\beta/\omega$ interface is fairly coherent with (112)$_\beta$ planes parallel to (10$\overline{1}$0)$_\omega$, and ledges form where (111)$_\beta$ planes meet (0001)$_\omega$. Comparing the interfacial Mo distribution in relation to the defected $\omega$ structure indicates that Mo always preferentially resides in a collapsing column, i.e. the $\beta$ columns which transition to $\omega_{11}$ [0001] atomic columns across the interface. This may explain the observed discommensuration within the $\omega$ phase as follows. The $\beta \rightarrow \omega$ collapse process initiates at the two separate interfaces by the contracting Ti-Mo bonds, but the displacement wave is phase-shifted along different $<111>$ columns. The resulting discommensuration defects, which lie on the prismatic $(10\overline{1}0)$ planes, surprisingly have HCP coordination environments. They are shown in Fig. 4.20 as overlapping shaded regions between $\omega_I-\omega_{II}$, and $\omega_{II}-\omega_{III}$ domains. The two columns of atoms lying on the marked border have 12-coordination, as shown by the dashed black line. These interfaces can be seen as akin to an intrinsic fault created by disordered displacive processes.

Fig. 4.21 schematically illustrates the atomic mechanism responsible for the $\alpha$-like displacive fault. When the displacement wave is disrupted in the middle as shown in the left figure, a single column displaces instead of the requisite two columns. The resultant faulted structure is shown in the right side figure. Again, the HCP-like sites lie on the boundary of the overlapping shaded region. This fault can be removed by either reverting to the $\beta$ phase or by transforming to the $\alpha$ phase as described later in detail in Chapter 6. In fact, these kind of HCP sites may serve as nucleation points for subsequent $\alpha$ formation. Another interesting possibility is that these faults, which create two layers of HCP atoms aligned along their prismatic planes, may enable slip in the $\omega$ phase. However, the planar extent of these faults are not known. In these systems shown, only two unique $(1\overline{1}0)$ planes are alternating periodically, assuming a semi-infinite interface and also semi-infinite faults. Given that these faults are generated by incommensurate collapse that may originate at the interface, any changes in geometry and Mo distribution would also likely
Figure 4.20. The relaxation at the Variant II interface creates a faulted $\omega$. Several $\omega$ regions corresponding to incommensurate collapse patterns are colored in red ($\omega_I$), blue ($\omega_{II}$), and yellow ($\omega_{III}$). The atoms lying on the boundaries of the overlapping colored regions have HCP-type structure and lie on the prismatic plane of $\omega$. The intersection of these incommensurate regions in the [0001]$_\omega$ direction creates a compact vacancy-like defect with minimal lattice distortion along the common $\omega_{11}$ column between the adjacent regions.

change the incommensuration, breaking the continuity of these structures. Hence, rather than planar, it may reduce to a linear fault. Further studies are needed to understand the likelihood, spatial extent, and behavior of such faults. We note that dislocations experimentally observed in $\omega$ from shock-loading may have some connection to the structures discusses here [14].
Figure 4.21. Schematic illustration of how disruption of collapse promotes the formation of HCP sites. In the left figure, atoms are colored according to which (110) plane they reside in, and columns are colored according to the shuffle direction. The unpaired shuffle is the cause of discommensuration. The resultant structure on the right has two out of phase $\omega$ regions, with HCP atoms lying on the overlapping region boundaries serving as a transitional structure.

Lastly, when two phase-shifted $\omega$ regions coincide along the [0001]$_\omega$ direction, another type of incommensuration defect is formed. These regions, and the six atoms adjacent to them, are highlighted in dashed red lines in Fig. 4.20. The defect site is surrounded by two each of $\omega_{11}$, $\omega_{14}$, and $\alpha$ atoms, however a single atom is missing with respect to each atom’s coordination environment. It thus appears to be a vacancy-like defect accommodated very compactly at the intersection of the two $\omega$ regions. The distance between $\omega_{11}$ sites across this defect is $\frac{3}{2}c$; if an $\omega_{11}$ atom jumps towards the defect by $\frac{1}{2}c$ (which is shown in Chapter 5 to be the preferred migration mechanism in $\omega$-Ti), it switches over to the (0001) plane of the other $\omega$ region, and the incommensurate defect migrates by $-\frac{1}{2}c$. Thus, it functions similar to a vacancy, or potentially a line defect, considering the periodicity of the present system. A diagram of this potential mechanism is depicted in Fig. 4.22. A similar structure may have been predicted by Kuan and Sass [76, 77]. This may have implications for enhancing diffusion at low temperatures, due to such incommensurate "vacancies" being generated from $\beta \rightarrow \omega$ transformation instead of ordinary quenching.
The incommensurate vacancy-like defect, found at the intersection of two displacively out-of-phase omega regions, can migrate by exchanging with neighboring $\omega_{11}$ atom, circled in a dotted black line. This atom switches to the other $\omega$ variant after jumping by $\frac{1}{2}c$.

The formation energy of such a defect and its mobility is not addressed here, but would be an interesting subject for future work.

The interfacial energy of this Variant II structure is difficult to calculate, since the incommensurate defects present in the $\omega$ Ti region introduce additional energy penalties. However, using the same $\beta + \omega$ interface creation method as done for Variant I can provide some idea as to the relative energy contribution of interfacial Mo-Ti interactions or bulk $\omega$-Ti defects to the system energy (specific to these size scales). The new joined $\beta + \omega$ interface is depicted in Fig. 4.23. This structure has a higher total system energy relative to the incommensurate Variant II structure ($\Delta E = 0.61$ eV), and given the same energy for the $\beta$ region, and the higher energy of the defective $\omega$ Ti relative to ideal $\omega$, the energy of the interface is thus more dominant. In comparison to Variant I, the Mo atoms no longer reside at equivalent positions in the [111] direction, thus the position of the $\beta - \omega$ transition fluctuates by one or two unit cells as shown by the dashed red line. However, these fluctuations are balanced across the interface, and the volume fraction of $\omega - Ti$ and Mo-stabilized $\beta$-Ti are still equal as in Variant I.
Accordingly, the interfacial energy for this system is calculated to be 315 mJ/m\(^2\). The large increase relative to Variant I is surprising; structurally, both variants possess similar transitional partial \(\beta/\omega\) collapsed regions across the interface, over the same 2-4 unit distance, and no other distortions are readily apparent. Instead, the reason for the increased energy is likely related to the position of certain Mo atoms in \(\beta\) [111] atomic columns which transition towards \(\omega_14\) [0001] sites across the interface. In Fig. 4.23, the Mo atoms near the \(\beta-\omega\) interface have been highlighted according to which type of site they are aligned with in the \(\omega\) region, colored green for \(\omega_{11}\), and colored red for \(\omega_{14}\). Two Mo atoms are identified at each interface which correspond to the latter. In \(\omega\)-Ti, a single substituted Mo atom was found to have a strong site preference for \(\omega_{11}\), with the relative energy \(\Delta E_{\omega_{14} - \omega_{11}}^{Mo} = 0.33\) eV. Further details of these calculations can be found in Chapter 5. By adjusting for this energy difference when calculating the interfacial energy according to

\[
\gamma_{\text{interfacial}}^{\beta+\omega} = \frac{E_{\text{tot}}^{\beta+\omega}(N) - E_{\text{tot}}^{\beta}(\frac{N}{2}) - E_{\text{tot}}^{\omega}(\frac{N}{2}) - M \cdot E_{\omega_{14} - \omega_{11}}^{Mo}}{2A},
\]

where \(M\) is the number of Mo atoms at \(\omega_{14}\) sites at the interface, the energy of the interface can be estimated if instead all Mo atoms were along \(\omega_{11}\) columns, as in the Variant I [111]\(_{\beta}\)/[0001]\(_{\omega}\) interface. The resulting modified value is calculated to be 217 mJ/m\(^2\), which is in good agreement with the energy calculated for the Variant I, indicating that Mo site selectivity plays a role in \(\beta-\omega\) interface energetics. This \(\omega_{11}\) site preference was also observed in the original Variant II interface, and dictated how the \(\beta\)-Ti region transformed to \(\omega\) by inducing defects.

The ratio of the lowest energy Variant I [111]\(_{\beta}\)/[0001]\(_{\omega}\) and [112]\(_{\beta}\)/[10\(\bar{1}\)0]\(_{\omega}\) interfacial energies is \(\sim 2.6:1\), which agrees well with the ratio of the [0001]/[10\(\bar{1}\)0] axes of ellipsoidal \(\omega\) precipitates in the Ti-Mo system [78, 33, 4]. Furthermore, the lower energy [112]\(_{\beta}\)/[10\(\bar{1}\)0] is observed to be planar, while the [0001]/[10\(\bar{1}\)0] is more diffuse and
marked by ledges, as seen from HRTEM imaging of the $\beta/\omega$ interface reproduced from [4] in Fig. 4.24.

In all the 16.6 at% Mo partitioned systems studied thus far, the width of the pure Ti region between interfaces had a width of 1.5 nm, indicating that such structural complexities begin developing at exceedingly small scales. And as seen in section 4.2, even within the 8.3 at.% system with evenly distributed Mo, there are precursor $\alpha$ or $\omega$ like structures present within Mo-free regions 0.6 nm in size. In addition to the Mo-enriched regions dictating the structure of the Mo-depleted region, the pre-existing lattice distortions around Mo in the quenched state may dictate how $\omega$ nuclei initiate and evolve. To better understand diffusion and growth mechanism of such nuclei at low temperatures, vacancy behavior in the metastable state needs to be understood, which is the subject of the next chapter.
FIGURE 4.23. The Variant II $\beta + \omega$ interface created by joining the relaxed 16.6 at.% Mo $\beta$ structure with an ideal $\omega$ Ti structure. The Mo atoms are colored in dark blue, Ti atoms in light blue. Mo atoms present in [111] columns which transition to $\omega_{11}$ Ti atomic columns are highlighted in green, and those transitioning to $\omega_{14}$ Ti atomic columns are highlighted in red. These latter Mo atoms raise the energy of the interface because of Mo’s relative insolubility at $\omega_{14}$ sites. The $\beta - \omega$ transition position along the interface is marked with a dashed red line.
Figure 4.24. HRTEM image along $<011>\beta$ zone axis of a $\beta$ matrix/$\omega$ precipitate interface, demonstrating the planar nature of the [112]$_\beta$/[10$\bar{1}0$]$_\omega$ interface, and the more diffuse nature of the [111]$_\beta$/[0001]$_\omega$ interface, in good agreement with the corresponding calculated interfacial energies (80 mJ/m$^2$ and 208 mJ/m$^2$ respectively. Reproduced from [4].
CHAPTER 5

VACANCY PROPERTIES IN PURE Ti AND METASTABLE Ti-MO

The energetics of vacancy formation and migration are expected to dictate the initiation of diffusional-displacive type transformations such as $\beta \rightarrow \omega$. Upon quenching metastable $\beta$ titanium, the formation of nanoscale athermal $\omega$ phase is preceded by compositional partitioning which would entail diffusion with minimal thermal activation. However, little is known about how the vacancy behavior changes in the alloyed state and how it changes with composition. As shown in the previous chapter, an 8.3 at% Mo substitution can induce various local coordination environments depending on the interaction of the Mo-induced distortions, with titanium atoms rearranging to nearly $\omega$-like or $\alpha$-like sites. This same prototypical system is now used to examine how the vacancy formation energy may vary at such sites, as well as how barriers for vacancy migration along different paths and exchanging with different species will be affected.

5.1. Vacancy formation in pure Ti and near Mo solute atom

The vacancy formation energy $E_{V}^{f}$ in both the $\omega$ and $\alpha$ phases is initially calculated to provide reference values for subsequent analysis in the alloyed system, using the definition

$$E_{V}^{f} = E_{tot}(N - 1) - (E_{tot}(N) - \mu^{Ti}),$$

where $E_{tot}(N - 1)$ is the total energy of a system of $N$ atoms with a vacancy, $E_{tot}(N)$ is the energy of the reference system with $N$ atoms, and $\mu^{Ti}$ is the reference energy of a single Ti atom in the appropriate structure. For pure Ti structures, $(E_{tot}(N) - \mu^{Ti})$ is equivalent to $(N - 1) \cdot \mu^{Ti}$. These were computed using 120-atom and 96-atom supercells for $\omega$ and $\alpha$ respectively, and the volume was held fixed during vacancy structural relaxation.

The $\omega$ phase has markedly different formation energies for its two distinct $\omega_{11}$ and $\omega_{14}$ lattice sites, with $E_{V,\omega_{11}}^{f} = 1.52$ eV and $E_{V,\omega_{14}}^{f} = 2.92$ eV. The latter has nearly twice
the formation energy of the former. This is in good agreement with prior DFT calculations with similar methods and a 108-atom supercell\cite{79}. There is a discrepancy with more recent calculations ($E_{V,\omega_{11}}^f = 2.59$, $E_{V,\omega_{14}}^f = 4.21$ eV) also using a similar approach as used here\cite{80}, however their reference per-atom energies may be insufficiently accurate, and their planewave cutoff energy (300 eV vs 400 eV used in this work) may not be sufficient to reduce the error in larger systems containing the defect. Systematic errors can be minimized by using equivalent supercells with and without the defect, and using the same K-point mesh and energy cutoff between both systems, as done here. The relative formation energy between the $\omega_{11}$ and $\omega_{14}$ sites, however, are in good agreement with their results. This site-specific formation energy indicates that vacancies undoubtedly prefer residing at $\omega_{11}$ sites, and will predominantly stay confined to these sites during migration. This will be discussed in further detail in section 5.3.

Additionally, $E_{V}^f$ in the vicinity of a single substituted Mo atom was also calculated, in order to understand vacancy-solute interactions. Mo was substituted at both the $\omega_{11}$ and $\omega_{14}$ positions in the 120 atom supercell, and a clear preference for the $\omega_{11}$ site is observed, with a relative energy 0.337 eV lower than the $\omega_{14}$ site. The more compact volume of the $\omega_{11}$ site (3.9% smaller compared to $\omega_{14}$, using Voronoi analysis) as well as its lower coordination likely contribute to the increased relative stability of Mo. The vacancy formation energy was then calculated at several nearest neighbor sites relative to the Mo atom at either $\omega_{11}$ or $\omega_{14}$ positions. These Mo-vacancy pairs have been labeled in Table 5.1, with the position of each component and their mutual orientation specified as well. For the energetically favorable Mo$_{\omega_{11}}$ case, no distinct preference is observed for an adjacent vacancy at either the [0001] or [11\bar{2}0] NN $\omega_{11}$ site (pair I and II), but both of these sites have a lower formation energy compared to pure Ti, with a $\Delta E_{V,\omega_{11}}^f$ of -0.17 and -0.20 respectively. For the nearest $\omega_{14}$ site (pair III), $\Delta E_{V,\omega_{14}}^f$ is calculated to be -0.09 eV. Thus, at sufficiently dilute Mo concentrations, vacancies would be expected to prefer sites adjacent to Mo$_{\omega_{11}}$. 

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<td>[11\bar{2}0]</td>
<td>1.32</td>
<td>-0.20</td>
</tr>
<tr>
<td>III</td>
<td>$\omega_{11}$</td>
<td>$\omega_{14}$</td>
<td>[20\bar{2}3]</td>
<td>2.83</td>
<td>-0.09</td>
</tr>
<tr>
<td>IV</td>
<td>$\omega_{14}$</td>
<td>$\omega_{11}$</td>
<td>[20\bar{2}3]</td>
<td>1.09 (1.43)</td>
<td>-0.43 (-0.09)</td>
</tr>
<tr>
<td>V</td>
<td>$\omega_{14}$</td>
<td>$\omega_{14}$</td>
<td>[0001]</td>
<td>2.93 (3.27)</td>
<td>0.01 (0.35)</td>
</tr>
</tbody>
</table>

Table 5.1. Vacancy formation energies in the vicinity of a single Mo solute atom in $\omega$-Ti for different Mo-vacancy site pairings. The site of both the Mo atom and the vacancy is given, as well as the pair orientation, the vacancy formation energy $E_f^V$, and the relative value with respect to pure Ti $\Delta E_{f}^{V,Ti}$. For pairs IV and V, the formation energy relative to the Mo$_{\omega_{11}}$ reference system is given in parenthesis for comparison.

When Mo is substituted at the $\omega_{14}$ site and the vacancy resides at the [0001] NN $\omega_{14}$ site (pair V), $\Delta E_{f}^{V,\omega_{14}}$ is 0.01, while at the [20\bar{2}3] NN $\omega_{11}$ site (pair IV), $\Delta E_{f}^{V,\omega_{11}}$ is a substantially lower -0.43 eV, indicating the strongest Mo-vacancy interaction. The choice of reference system energy is important when considering the significance of the vacancy formation energy; if the energy of the Ti$_{119}$Mo$_1$ system with Mo$_{\omega_{11}}$ is used as reference for calculating $E_f^V$ for pairs IV and V, the energy for the Mo$_{\omega_{14}}$-vacancy pair with a $V_{\omega_{14}}$ or $V_{\omega_{11}}$ site is 3.27 eV or 1.43 eV respectively. This can be interpreted to mean that in terms of all possible Mo-vacancy pair configurations for the system studied (i.e. dilute limit of Mo in Ti), pair II is the lowest in energy, and pair V is the highest.

Despite the Mo$_{\omega_{11}}$ site preference, there may be some fraction of Mo residing at $\omega_{14}$ sites due to the quenched nature of the alloy; thus, in a sufficiently dilute system with a mixture of both Mo$_{\omega_{11}}$ and Mo$_{\omega_{14}}$ sites, vacancies would be more strongly bound near Mo$_{\omega_{14}}$ as in pair IV. However, given the large penalty for vacancies to exchange with $\omega_{14}$ sites, it is probable that Mo$_{\omega_{14}}$ will remain trapped at those sites. This will be discussed in greater detail in section 5.3, when the energy barriers for vacancy migration are calculated for exchange with either a Ti or Mo atom in $\omega$-Ti.
In α-Ti, $E_{V}^{f}$ is calculated to be 2.01 eV for the 96 atom supercell used, which is within the range of several prior DFT calculations [79, 81, 82, 83, 84]. It is interesting to note, though no physical basis is established for it, that the vacancy formation energy in α-Ti and the weighted average value for ω-Ti (1.99 eV, considering two ω_{11} and one ω_{14} site), are nearly equivalent within the error of the calculation. This may be due to the small energy difference between the two structures ($\Delta \mu_{\omega-\alpha}^{Ti} = 0.007$ eV), yet it is an unexpected correlation, and likely closely related to the nature of the electronic structure in α and ω. Previous DFT calculations of the density of states for titanium for both structures show very similar characteristics but how the character of the total and site-projected DOS is modified by a vacancy remains to be seen, and would be of interest for future DFT investigations.

A similar ω–α interrelation is observed for the Mo substitutional (or solute) energy in both structures, which can be defined as

\begin{equation}
E_{Ti}^{1Mo} = E_{tot}((N - 1)Ti + 1Mo) - (E_{tot}(N) - \mu^{Ti}) - \mu^{Mo},
\end{equation}

where $E_{tot}((N - 1)Ti + 1Mo)$ is the energy of a system with Mo substituted at a Ti site, and $\mu^{Mo}$ is the reference energy of a single Mo atom in the BCC structure. In ω Ti, $E_{Ti,\omega_{11}}^{1Mo} = 0.248$ eV and $E_{Ti,\omega_{14}}^{1Mo} = 0.586$ eV, and in α Ti, $E_{Ti,\alpha}^{1Mo} = 0.415$ eV. The average of both ω sites is 0.417 eV, equivalent to the α value. This is also likely why the enthalpy of formation curves calculated in Fig. 4.14 for randomized substitutions in α and ω are nearly identical. If instead Mo atoms selectively occupied ω_{11} sites exclusively, the formation enthalpy might be expected to be lower than α at lower concentrations.

Mo-vacancy interactions in α are not quite as significant as in ω, but still indicate a similar site preference adjacent to Mo. Vacancies were created at two basal and nonbasal 1NN sites relative to the substituted Mo atom. For the basal sites, $E_{V}^{f} = 1.92$ and 1.98 eV ($\Delta E_{V,Ti}^{f} = -0.09$ and -0.03 eV), and for the nonbasal sites, $E_{V}^{f} = 1.90$ and 1.96 eV ($\Delta E_{V,Ti}^{f} = -0.11$ and -0.05 eV).
Calculations for $E_{V,\beta}^f$ are excluded; since $\beta$ is structurally unstable phase at T=0 K, the relaxation of Ti atoms around the vacancy causes multiple $\langle 111 \rangle$ displacements which induce $\omega$-like distortions, making the $E_{V}^f$ negative relative to the BCC phase. This is related to the same softening of the $L_2^2[111]$ phonon mode involved in the $\beta \rightarrow \omega$ transformation, since $\nu^2 < 0$ at T=0 K. For the unrelaxed vacancy, however, $E_{V,\beta}^f$ was calculated using a 54 atom supercell to be 2.12 eV, which is within the range of previous DFT calculations (2.03 eV [81] - 2.20 eV[85]). The calculated value is surprisingly close to the relaxed $E_{V,\alpha}^f$ value, and coincides nearly exactly with the unrelaxed $E_{V,\alpha}^f$ value, calculated to be 2.12 eV. As with the previous $\omega$-$\alpha$ similarity, there is likely an electronic basis to this relation, though it is not investigated in further detail in this work.

5.2. Vacancy formation in Ti-8.3 at.% Mo

To study vacancy formation energy in the 8.3 at.% Mo system, a new 96-atom supercell using the same Mo substitutional distribution as in section 4.2 is constructed, shown in Fig. 5.1a (the $x$-dimension is truncated according to supercell symmetry for sake of clarity), with the relaxed cell dimensions and angles given in Table 5.2. The $x$ and $z$ directions correspond approximately to the $[111]$ and $[11\bar{2}]$ directions from the original BCC unrelaxed structure, though are no longer orthogonal due to lattice distortions, while the $y$ direction is the $[1\bar{1}0]$. The equivalent approximate $\omega$ and $alpha$ directions are given in Table 5.2 as well. The distribution of Mo in a single $(1\bar{1}0)$ plane is shown in Fig. 5.1b. Each $(1\bar{1}0)$ plane has the same Mo distribution pattern, but every alternate plane is translated by $(0.25)x$ and $(0.5)z$. As a result, the titanium atoms contained in each plane adopt the same local structural relaxation, but with the same aforementioned shift relative to its adjacent plane.

The spatial distribution of the coordination environments for each atom is visualized more readily by performing an in-plane Voronoi tessellation (see Chapter 3 for method details), which generates a unique polygon for each geometrically distinct site as shown in Fig. 5.1b. The corresponding region for each site is shaded in light, medium, or dark gray,
corresponding to $\omega_{11}$, $\alpha$, or $\omega_{14}$ respectively. Visually differentiating the $\omega_{14}$ and $\alpha$ sites is difficult without the adjacent (110) planes, as they both appear hexagonal (or nearly so in the $\omega$ case); the $\omega_{14}$ will be coordinated out of plane by four atoms, and the $\alpha$ by three. The regions corresponding to Mo atoms are white, as they have a BCC-like environment. For a comparison, the in-plane Voronoi tessellation for a single $(1\bar{1}0)_{\omega}$, $(110)_{\beta}$, and $(0001)_{\alpha}$ plane in pure Ti is shown in Fig. 5.2, with the same shading scheme. All of these structures have an ABAB planar stacking sequence in the depicted $[1\bar{1}0]_{\beta}/[1\bar{2}0]_{\omega}/[0001]_{\alpha}$ direction.

As described in Chapter 4, Fig. 4.11, the distribution of Mo prevents a globally self-commensurate collapse towards $\omega$ throughout the entire structure, and instead two separately commensurate regions are observed which are separated by $\alpha$ sites. An alternate representation of this behavior can be seen in a rotated, expanded version of the single plane tessellated diagram in 5.1b, redrawn in Fig. 5.3. Regions of incompletely $\omega$-like atoms can be clearly observed in comparison with the reference pure Ti $\omega$ in Fig. 5.2, highlighted in red and blue corresponding to each self-commensurate region. If these atoms completed transformation, the $\omega_{11}$ sites within each highlighted region would become co-planar after displacing by $\frac{1}{6}d_{(222)}$ to the marked positions. Using a similar method as in section 4.1, the extent of displacement in both of the commensurate regions can be calculated with respect to the non-$\langle 111 \rangle_{\beta}$ shuffling atoms, resulting in an average displacement of $\chi \approx 0.47$. Given the distorted nature of the lattice, this can be considered in good agreement to the $\chi \approx 0.5$ at the minimum energy for the same composition from section 4.1.

Using this 96 atom supercell, the vacancy formation energy at each titanium site is then calculated with respect to the reference $\mu_{Ti}^{a}$ value and the defect-free initial system using Equation 23. All calculations used a gamma-centered k-point mesh of $3 \times 2 \times 4$ and a planewave cutoff of 400 eV. The choice between $\alpha$ and $\omega$ as the reference state for $\mu_{Ti}^{a}$ is negligible, as their energy difference is $< 10$ meV, and the error due to supercell size effects is estimated to be greater. Due to the internal symmetry of the supercell, six distinct
Figure 5.1. (a) The supercell used for the 8.3 at% Mo metastable system, shown here halved in the x-direction to better illustrate the periodicity of the Mo distribution. The lengths and angles are given in Table 5.2. (b) A single (110) plane is depicted, with each site shaded according to its approximate coordination environment: Mo (β) in white, ω11 in light gray, α in medium gray, and ω14 in dark gray.

<table>
<thead>
<tr>
<th>Cell Vector</th>
<th>Length (Å)</th>
<th>β_{[hkl]}</th>
<th>ω_{[hkl]}</th>
<th>α_{[hkl]}</th>
<th>Cell Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>11.258</td>
<td>[112]</td>
<td>[3034]</td>
<td>[1100]</td>
<td>α = 90.00</td>
</tr>
<tr>
<td>y</td>
<td>15.832</td>
<td>[110]</td>
<td>[1210]</td>
<td>[0001]</td>
<td>β = 92.83</td>
</tr>
<tr>
<td>z</td>
<td>9.144</td>
<td>[111]</td>
<td>[2023]</td>
<td>[1120]</td>
<td>γ = 90.00</td>
</tr>
</tbody>
</table>

Table 5.2. Cell dimensions, approximate corresponding directions for the β, ω, and α local structure observed after relaxation, and cell angles for the 96-atom supercell for the Ti-8.3 at.% Mo system.

Figure 5.2. The in-plane Voronoi tessellation for the (1120)_{ω}, (110)_{β}, and (0001)_{α} planes, with the sites corresponding to each coordination environment shaded as white (β), light gray (ω_{11}), medium gray (α), or dark gray (ω_{14}).
Figure 5.3. A rotated and expanded view of Fig. 5.1b, highlighting the self-commensurate regions within a single \((1\bar{1}0)_B/(10\bar{1})_\beta\) plane (outlined in dashed red and blue lines), and the \(\alpha\) sites which accommodate the transition. The ideal \(\omega\) positions are marked with colored line segments, indicating that the titanium atoms are in a partially collapsed \(\omega\) state.

Ti sites are present, which approximate the various coordination environments in pure Ti. Of these six distinct sites, three can be characterized as \(\omega_{11}\), two as \(\omega_{14}\), and one as \(\alpha\). Two distinguish between similarly coordinated sites with different \(E^f_V\) values, a letter designation \((\omega_{11a,b,c} \text{ and } \omega_{14a,b})\) is used. To understand the distribution of these sites and the correlation of their value to the local structure, the diagram of the metastable system from Fig. 4.11 is reproduced in Fig. 5.4a. The six different \(E^f_V\) values are marked in Fig. 5.4b, distinguished by both their magnitude (color) and initial coordination environment of the site (shape).

The result is surprising; in the minimized metastable alloy, the shuffles amongst the titanium atoms can create a highly varied local structure, with vacancy formation energies that are dictated by the coordination environment they most closely adapt. In Table 5.3, the \(E^f_V\) values at the various sites are compared with their corresponding reference value in pure Ti, and the two values are found to be in good agreement. The variations in energy at each type of site may be related to Mo-vacancy interactions, prevention of atomic
Figure 5.4. A map of the sites with distinct vacancy formation energies in the Ti-8.3 at% Mo system. Left: Fig. 4.11 reproduced here highlights the \( \omega \)-like regions and the \( \alpha \)-like transitional regions which separate the \( \omega \) regions. Right: Vacancies were created at each of the Ti sites, and six distinct formation energies were found. These energies were correlated to the structure they were closest to, and are marked with □, △, or □ symbols for \( \omega_{11} \), \( \alpha \), or \( \omega_{14} \) respectively. A rainbow color scale, with blue being the lowest and red being the highest, contrasts the relative \( E_f \) for each site, ranging from 1.39 eV to 3.25 eV.

<table>
<thead>
<tr>
<th>Site</th>
<th>( E_f ) (eV)</th>
<th>( E_{f,ref} ) (eV)</th>
<th>( \Delta E_f ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega_{11a} )</td>
<td>1.39</td>
<td>1.52</td>
<td>-0.13</td>
</tr>
<tr>
<td>( \omega_{11b} )</td>
<td>1.55</td>
<td></td>
<td>0.03</td>
</tr>
<tr>
<td>( \omega_{11c} )</td>
<td>1.72</td>
<td></td>
<td>0.20</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>2.12</td>
<td>2.01</td>
<td>0.11</td>
</tr>
<tr>
<td>( \omega_{14a} )</td>
<td>2.67</td>
<td>2.92</td>
<td>-0.25</td>
</tr>
<tr>
<td>( \omega_{14b} )</td>
<td>3.25</td>
<td></td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 5.3. Vacancy formation energies at different sites throughout the Ti-8.3 at% system, both in absolute energy and relative energy compared to \( E_f \) in the pure titanium reference structure.
relaxation, or the change in coordination type of a given Ti site’s nearest neighbors. Since
the beta, alpha, and omega coordination environments are interconnected in a spatially complex
manner, atoms which lie at the transition between two (or more) structures have a partial
structural character of both, which may alter the $E_V^{f}$. Such effects are now discussed.

For the omega$_{11}$ site, the range in energies spans 1.39 – 1.72 eV, with relative values of
$-0.18 – +0.15$ eV compared to $E_{V,\omega_{11}}^{f}$. The omega$_{11a}$ site has a formation energy in line with
the pair I configuration shown in table 5.1, and has a similar atomic environment. The
omega$_{11a}$ site is a [111]$_{\beta}$/[0001]$_{\omega}$ nearest neighbor of Mo, which coincides with the $\beta \rightarrow \omega$
collapse direction (see Fig. 4.10c for details), and has partial $\beta/\omega$ like structure. The
change in the structure after the creation of the vacancy is highlighted in Fig. 5.5a, with
arrows signifying the direction and relative magnitude of displacement after relaxation.
The creation of the vacancy in a NN site of Mo causes the Mo atom to undergo a large
shift towards it, and in doing so leaves its beta position towards the omega$_{11}$ position at $(\frac{1}{2}c)$ unit
cell (omega cell boundary drawn in a dashed red line for reference). This has two effects: it
enhances the collapse of the other Ti atoms on either side along the same atomic column
it was previously hindering, and it attracts the next closest Ti atom towards it. However,
this latter displacement is not expected to raise the energy, because it coincides with the
$\langle 11\bar{2}0 \rangle$ relaxations associated with a V$_{\omega_{11}}$ in pure Ti.

The omega$_{11b}$ site is only coordinated by Ti atoms (as would naturally be the case in pure
Ti), and is the least distorted of the omega$_{11}$ sites, and is thus closest to the reference $E_{V,\omega_{11}}^{f}$
value. The omega$_{11c}$ site is neighboring a Mo atom like in the previous omega$_{11a}$, but now lying
in the [111]$_{\beta}$/[1120]$_{\omega}$ direction, and no longer parallel to the existing partially collapsed
omega direction. The creation of this vacancy has a complex effect; similar to omega$_{11a}$, Mo shifts
significantly towards the vacancy, and in the process attracts the next nearest Ti atom
within it's (110) plane. However, in this instance it is displacing this Ti atom away from
the omega position and towards a more beta-like one. This is depicted in Fig. 5.5b. Interestingly,
the displacement of the Mo atom in the [111] direction towards the vacancy appears to
favor the creation of an alternately oriented omega cell, as highlighted in green. In both the
Figure 5.5. The atomic displacements after the creation of vacancies at $\omega_{11a}$, $\omega_{11c}$, and $\omega_{14a}$ sites. The $\omega$ regions are highlighted in dashed lines, and the approximate location of the vacancy is marked with a red square. The Mo atoms are in dark blue, and the Ti atoms in light blue.

In the $\omega_{11a}$ and $\omega_{11c}$ cases, the Mo atom shifts from its initial BCC-like site and assumes an $\omega_{11}$ position, with the vacancy lying in an adjacent [0001] site. This is analogous to the energetically favorable Mo$_{\omega_{11}}$-V$_{\omega_{11}}$ pair configuration seen for the single Mo solute system described in section 5.1.

The $\alpha$ site, like the $\omega_{11b}$ site, is completely coordinated by Ti atoms, and has a $E_V^f$ of 2.12 eV, 0.11 eV greater than in pure Ti but in reasonably good agreement. The additional energy penalty may be related to either the incomplete nature of the $\beta \rightarrow \alpha$ transformation at the site, or the hindrance in atomic relaxation of its nearest neighbor Ti atoms which are bonded to Mo atoms, preventing their displacement. This is supported by the observation that for an unrelaxed vacancy in pure $\alpha$-Ti, $E_V^f = 2.13$ eV, nearly the same as observed for the "relaxed" $\alpha$ site in the present system.

The $\omega_{14}$ site displays two different vacancy formation energies, both with rather large deviations from the pure Ti values. The lower energy site ($E_{V,\omega_{14a}}^f = 2.67$ eV) is completely coordinated by Ti, but since these neighboring Ti atoms are in partially displaced states (w.r.t. $\beta \rightarrow \omega$), its energy may be expected to be lower than the ideal $\omega_{14}$ value.
Additionally, two of the six in-plane nearest neighbors to the $\omega_{14a}$ are $\alpha$ sites, which appear to alter the relaxation behavior, as shown in Fig. 5.5c. The $\alpha$ coordination environment is drawn in green for reference. In pure $\omega$ Ti, the $V_{\omega_{14}}$ exhibits very little structural relaxation of its local bonds (∼1-2%), but in the present case the $\omega_{11c}$ atoms adjacent to the site relax significantly (∼16%) towards the vacancy. The $\omega_{11c}$ atoms lie in the transitional region between the two commensurate $\omega$ regions, and likely have a partial $\omega/\alpha$ character.

The higher energy site, on the other hand ($E_{V,\omega_{14b}}^f = 3.25$ eV) exhibits very little atomic relaxation (∼1-3%) similar to the ideal $\omega_{14}$ site. It is coordinated by two Mo atoms, and the increase in energy can likely be attributed to the interaction between the vacancy and both of the Mo atoms. In section 5.3, the change in the adjacent vacancy energies after Mo migrates to either the $\omega_{11a}$ or $\omega_{11c}$ site is examined, which eliminates the double Mo-coordinated site, and $E_{V}^f$ is found to be reduced closer to $E_{V,\omega_{14}}^f$ in pure Ti.

To understand the spread and distribution of $E_{V}^f$ values amongst all Ti sites in the alloy, the $E_{V}^f$ for each type of site was plotted (by increasing value) against the cumulative fraction of Ti sites in the alloy. For instance, pure $\omega$-Ti has two $E_{V}^f$ values, $E_{V,\omega_{11}}^f = 1.52$ eV and $E_{V,\omega_{14}}^f = 2.92$ eV, with two thirds of sites having the former value and one third the latter. This distribution is shown in Fig. 5.6 by the red dashed line. For $\alpha$-Ti, a single value of $E_{V,\alpha}^f = 2.01$ eV reflects all Ti sites. The 8.3 at.% Mo case for the previous $E_{V}^f$ calculations is shown in blue. It is clear the trend is strongly influenced by the distribution in the pure $\omega$ phase, but instead of a sharp division between the low and high energy sites, there is a smearing of the values induced by partial character of several of the sites. The presence of the $\alpha$ site lowers the energy of the neighboring $\omega_{14a}$ site, and raises the energy of the neighboring $\omega_{11b}$ site relative to the ideal $\omega$ values. As the system gets increasingly randomized and the variety of partially $\alpha/\beta/\omega$-like sites increases, these discretized $E_{V}^f$ values will increasingly smear out.

For comparison, the same distribution was also determined for increased Mo content to characterize how the $E_{V}^f$ distribution and range is affected. $E_{V}^f$ was calculated for the symmetrically distinct Ti sites present in idealized 16.6 at% and 33.3 at% Mo systems,
Figure 5.6. Distribution of vacancy formation energies for 8.3, 16.6, and 33.3 at% Mo concentrations. The increasing β stability with additional Mo content removes the low energy ω_{11} sites, and thus hinders further diffusion at lower temperatures.

Using the same Mo site substitution for each concentration as depicted in the partitioned systems in Figs. 4.12 and 4.13. Both of these structures are derived from the same 8.3 at.% Mo system studied above by the substitution of additional Mo atoms. The resulting 16.6 at% Mo system has three symmetrically distinct Ti sites, while the 33.3 at.% Mo system has only one, thus a second configuration was created with two unique sites and included in the distribution. The resulting $E_f^{\text{V}}$ distributions for 16.6 and 33.3 at% Mo are shown in Fig. 5.6 by black and green curves respectively.

Comparing the 16.6 at.% with the 8.3 at% site, it is clear that the number of low energy sites (i.e. ω_{11}-like) has decreased, and that higher energy sites are beginning to dominate. No values in the α range are observed, and the energy range has decreased to 1.64 eV for the low energy sites and 2.40-2.47 eV for the high energy ones. This is generally related to the stiffening of the lattice due to additional Mo-Ti bonds, which has several consequences. First is that "mobile" Ti atoms (i.e. Ti atoms not neighboring Mo) are increasingly removed, which hinders local ω structures from emerging and causes Ti...
atoms to retain a more $\beta$-like state. Thus the creation of sites like $\omega_{11a,b}$ in the Ti-8.3 at.% system would be diminished since their presence depends on unhindered Ti atoms relaxing towards the vacancy. Furthermore, the creation of a vacancy near a Mo atom is observed to shift the Mo atom towards the vacancy and displace the Ti atoms around it to create a Mo$_{\omega_{11}}$-V$_{\omega_{11}}$ pair configuration, which is why low energy sites are still observed. However, this displacement is enabled by the softer Ti-Ti bonds along [111] atomic chains, and thus the increase of Mo will inhibit this relaxation from occurring at a higher fraction of sites. It is interesting to note that the average over all $E^f_V$ values within the system for both the 8.3% and 16.6 at.% Mo compositions is the same, $E^f_{V,\text{avg}} = 2.11$ eV, which is close to $E^f_{V,\alpha}$, as well the unrelaxed $E^f_{V,\beta}$ value, further indicating the close relationship between all three Ti allotropes. Further investigation into the atomic relaxation around each type of vacancy may shed some additional light on the values observed here, which is left for future work.

Increasing Mo content further from 16.6 to 33.3 at.% changes the distribution significantly. For the two configurations studied, all of the lower energy sites have been eliminated, and $E^f_V$ has increased to 2.76-2.89 eV. While it appears that this value is very close to the $E^f_{V,\omega_{14}}$ in pure Ti, the structure is nearly ideal BCC, with no evident $\omega$-like displacements. It may instead be converging towards the $E^f_V$ in BCC Mo, which is calculated to be 2.90 eV using a 54-atom supercell. This is likely related to both the increase in $d$-electrons from Mo alloying, as well as the restriction of atomic relaxation. $\omega$ or $\alpha$-like displacements of Ti atoms are now largely prohibited due to coordination by multiple Mo atoms, which resultantly also inhibits atomic relaxation around the vacancy. Previous studies using DFT and tight-binding $d$-band models have shown that unrelaxed vacancy formation energy characteristically increases with increasing $d$-electron concentration between group IV and VI, drastically between group IV and V, and to a lesser degree between V and VI [86, 87, 5]. However, structural relaxation plays a significant role in lowering the group V formation energy compared to group VI. For instance, comparing V and Mo, the unrelaxed $E^f_V$ is 2.85 eV and 3.00 eV respectively, but the relaxed $E^f_V$ is 2.44 and and
2.90 eV. The addition of Mo increases the average $d$-electrons to 2.66/atom, which is less than group V, but also prevents structural relaxation due to the stiffened, directional Ti-Mo bonds, thus raising $E_{V}^{f}$. The choice of chemical potential in calculating $E_{V}^{f}$, taken as $\mu_{\alpha}^{Ti}$ here, may need to be considered when interpreting the results. Likewise, the narrow 2.76-2.89 eV range observed reflects the uniformity in Ti sites and their Mo coordination; in a more randomized Mo distribution, variation in Mo coordination likely changes the local $d$-electron concentration, and some lower energy sites may be created. Without local relaxation to an $\omega$ structure, the lower bound is likely 2.12 eV, the unrelaxed $E_{V,\beta}^{f}$ value.

On the basis of these distributions, it is clear that as Mo content is increased, the number of low energy $\omega_{11}$ sites systematically decreases, and the energy of these sites will also increase. This slows diffusion in a variety of ways. Firstly, the remaining low energy sites will become increasingly isolated, removing continuous diffusion paths. Secondly, in the case of nanoscale athermal $\omega$ precipitation, vacancies will partition preferentially to Mo dilute $\omega$ areas, meaning vacancy migration will become increasingly unidirectional and will be self-limiting as a function of temperature. With aging at higher temperatures, remaining vacancies on the $\beta$ side of the interface can activate, and likewise some fraction of vacancies on the $\omega$ side can migrate back over to the $\beta$ regions. This is likely at least in part why athermal $\omega$ is limited in size to tens of nanometers, as diffusion is effectively halted due to both Mo-pile up and accordingly vacancy deactivation at the $\beta - \omega$ interface. Lastly, this data suggests that the same minute compositional fluctuations that initiate a spinodal decomposition from $\beta \rightarrow \beta + \omega$ [4, 88], simultaneously initiates a concurrent vacancy partitioning, which facilitates the rapid nucleation process upon quenching.

5.3. Vacancy migration barriers in alpha and omega titanium

Based on the results of the previous section, it is clear that the vacancy formation energies within the metastable alloyed structure are very heterogeneous, and are correlated to the different coordination environments present in either $\alpha$– or $\omega$– Ti. The evolution of this structure will be highly dependent on the kinetics for vacancy diffusion, and
first principles methods provide a robust way to investigate the pathways and associated atomic structures. First, an overview of migration barriers is given for $\alpha$ and $\omega$ titanium, to provide a basis for comparison against the alloyed state.

Self-diffusion in the HCP phase has previously been investigated in depth with DFT [81, 82, 83] using similar methodologies as employed in this work, and thus was excluded from the present calculations. A summary of the formation energies and migration barrier energies from these studies is provided in Table 5.4.

There is a clear preference of basal over nonbasal vacancy self-diffusion, with the migration barrier on average 12 meV lower for the former. Furthermore, Sheng et al. showed that the basal diffusion pathway has anomalous characteristics compared to other non-group IV HCP materials, with a symmetric double saddlepoint in the minimum energy pathway and a midpoint 16 meV lower than the peak value. By looking at the atomic

<table>
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<th></th>
<th>DFT (eV)</th>
<th>Expt. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_f^V$</td>
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<td>$1.2^{d} 1.27^{c}$</td>
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<td></td>
<td>$2.10^{c}$</td>
<td>$1.55^{f}$</td>
</tr>
<tr>
<td>$E_{V,\parallel}^m$</td>
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<td>$0.52^{c}$</td>
</tr>
<tr>
<td>$E_{V,\parallel}^a$</td>
<td>$2.63^{a} 2.39^{b}$</td>
<td>$2.0^{f} 3.14^{h}$</td>
</tr>
<tr>
<td>$E_{V,\perp}^a$</td>
<td>$2.52^{b} 2.65^{c}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4. Vacancy formation, migration, and activation energies from different DFT studies and experiments for HCP Ti. $E_{V,\parallel}^m$ or $E_{V,\perp}^m$ refers to migration parallel or perpendicular to the HCP basal plane.
motion of the migrating atom and the displacements on the surrounding lattice, it was observed that the diffusing atom follows a path similar to the HCP→BCC Burgers mechanism, with the midpoint having a distorted BCC-like structure. The presence of this midpoint was attributed to the high temperature BCC stability, as similar behavior was also previously reported in Zr [83], but not observed in Mg or Zn. Experimental activation energies have a large spread, as they are significantly influenced by sample purity; in single crystal 99.9% pure $\alpha$-Ti, an activation enthalpy of 2.0 eV was found [71], whereas in 99.99% pure Ti, an activation enthalpy of 3.14 was found [92]. Likewise, in polycrystal $\alpha$-Ti, activation enthalpies of 1.27, 1.75, and 2.39 were observed for 99.9%, 99.97%, and 99.99% levels of purity [93, 94, 95]. The DFT calculated values are on average 2.53-2.58 eV for both basal and nonbasal diffusion, within the single crystal experimental range, but underestimating the values calculated from the high purity titanium. More clarity from experiment is needed for a better understanding of reasons of discrepancy with theoretical calculations.

For the omega phase, no theoretical or experimental evaluations of the vacancy migration energies have previously been performed. The inaccessibility of the $\omega$ phase in high purity titanium (due to precedence of $\beta \rightarrow \alpha$ transformation) as well as its low temperature regime make experimental characterization exceedingly difficult. However, it has been suggested that the $\omega$ phase may play a central role in the self-diffusion process in the high temperature BCC phase of group IV metals near the $\beta/\alpha$ transus temperature [96, 97, 98, 99, 100]. Additionally, since the $\omega$ phase is observed upon quenching in alloys, a high concentration of vacancies may be expected to be quenched in as well, and characterizing the energies of the potential vacancy jumps provide valuable insight into how they behave. Only monovacancies are considered here, but recently theoretical calculations have been performed showing possible vacancy ordering in the $\omega$ phase [80].

Several pathways are generated, corresponding to the different possible nearest neighbor vacancy jumps between $\omega_{11}$ and $\omega_{14}$ sites. The calculations are performed for pure $\omega$-Ti as well as for a vacancy exchange with a single substituted Mo atom. Diagrams of each jump pathway and its corresponding migration barrier along the minimum
Pathway | $E^m_V$ (eV) | $E^m_{V,1Mo}$ (eV) | $Q^a_V$ (eV) | $Q^a_{V,1Mo}$ (eV)  
---|---|---|---|---
$\omega_{11} \xrightarrow{[11\bar{2}0]} V_{\omega_{11}}$ | 0.30 | 0.27 | 1.82 | 1.65 
$\omega_{11} \xrightarrow{[0001]} V_{\omega_{11}}$ | 0.18 | 0.30 | 1.70 | 1.59 
$\omega_{11} \xrightarrow{[20\bar{2}3]} V_{\omega_{14}}$ | 0.45 | 0.61 | 3.37 | 3.11, 3.43 
$\omega_{14} \xrightarrow{[0001]} V_{\omega_{14}}$ | 0.98 | 0.91 | 3.90 | 3.84 

**Table 5.5.** Vacancy formation energies at different sites throughout the Ti-8.3at% system, both in absolute energy and relative energy compared to $E^f_V$ in the pure titanium reference structure.

energy pathway are shown in Fig. 5.7. The paths considered are $\omega_{11} \xrightarrow{[11\bar{2}0]} \omega_{11}$ and $\omega_{11} \xrightarrow{[0001]} \omega_{11}$ corresponding to jumps between $\omega_{11}$ sites either perpendicular or parallel to the $c$-axis, $\omega_{11} \xrightarrow{[20\bar{2}3]} \omega_{14}$ for jumps between $\omega_{11}$ and $\omega_{14}$ sites, and $\omega_{14} \xrightarrow{[0001]} \omega_{14}$ for jumps between $\omega_{14}$ sites parallel to the $c$-axis. A summary of the calculated migration energies, and the effective activation energies ($Q^a_V = E^f_V + E^m_V$) is given in Table 5.5. For the Mo-vacancy exchange in the [2023] direction, the change in chemical potential for Mo between the $\omega_{11}$ and $\omega_{14}$ sites will give different activation energies, so an average of the two values is given in the table.

Several important observations can be made on the basis of this data, starting with pure Ti. It is apparent that the $\omega_{11}$ sites dominate the diffusion process in pure $\omega$-Ti, with
Figure 5.7. Diagram of vacancy diffusion pathways and corresponding energies.
the lowest migration barrier found for [0001] jumps. The migration barrier between \( \omega_{11} \) in \( \langle 11\bar{2}0 \rangle \) directions is calculated to be 30 meV, however this diffusional mode has additional potential jump sites (three vs two for [0001]). A detailed analysis of the diffusion pre-factor needs to be made to better characterize the true anisotropy of diffusivity, which is left for future studies. The [0001] jump is found to have an unexpected stable midpoint, which is created when the diffusing atom displaces by \( \frac{1}{2}c \) and becomes co-planar with the three \( \omega_{14} \) atoms (shown in Fig.5.8). This forms a trigonal arrangement similar to the original \( \omega_{11} \) site, which is likely why it has such a stable energy. Additionally, the two \( \omega_{14} \) sites in the adjacent \( \langle 11\bar{2}0 \rangle \) become 13-coordinated, in a 3-6-4 pattern (see Fig.??). This type of site is formed during the \( \omega \rightarrow \alpha \) transformation according to the Silcock pathway, and is also the same local coordination environment found at prismatic stacking faults in \( \alpha \)-Ti, and can be considered a low energy structure. The details of the Silcock pathway will be discussed in greater detail in Chapter 6. Recent DFT and experimental investigations in the Ti-Mo system have shown evidence of vacancy ordering, which may mediate the \( \omega \rightarrow \alpha \) transformation process. If another vacancy is created on the other side of the 13-coordinated site, it will directly become a 3-6-3, or \( \alpha \) site. As shown in the previous section, it is likely that vacancies will preferentially partition to the \( \omega \) phase, as they have a much lower formation energy there compared to the Mo-enriched matrix, so it is possible that vacancies may form ordered regions which facilitate nucleation and growth of \( \alpha \).
Figure 5.8. Atomic positions corresponding to the endpoints and midpoint along the MEP described in 5.7b during $\omega_{11} \rightarrow \omega_{11}$ vacancy diffusion. Dark and light blue atoms are $\omega_{14}$ and $\omega_{11}$ sites respectively. The atom swapping with the vacancy is highlighted in red, and the site of the vacancy is marked with a red square.

The calculated migration barriers confirm that $\omega_{14}$ sites are effectively inoperative for low temperature diffusion, however the calculated MEPs have several interesting characteristics. The migration barrier for the vacancy to migrate to the $\omega_{11}$ site is calculated to be 0.44 eV, which is very similar to the basal vacancy migration barrier in $\alpha$-Ti (see Table 5.4). Recalling that the $(11\bar{2}0)_\omega$ plane is related to the $(0001)_\alpha$ plane through the mutual $\alpha/\beta/\omega$ OR (Fig. 4.8), and that the $\omega_{14}$ site is quasi-six-fold coordinated within this plane (two $\omega_{14}$ and four $\omega_{11}$ neighbors), the $\omega_{14} \rightarrow \omega_{11}$ jump can be considered analogous to the basal $\langle 1\bar{1}20 \rangle$ jump in HCP. The barrier to the nearest neighbor $\omega_{14}$ site, however, is much higher, $E^m_V=0.98$ eV. This curve shows an unusual flatness at its peak, which occurs when the diffusing atom displaces by $\frac{1}{2}c$ and passes through the ring of six $\omega_{11}$ sites. The $\omega_{11}$ atoms are minimally displaced, expanding by $\sim2$-$3\%$ relative to the center. The migrating atom at this midpoint is solely coordinated by these six surrounding atoms. This bares some similarity to the diffusion process in an ideal BCC structure; for a $\frac{1}{2}[111]$ exchange with a NN vacancy, the migrating atom passes through the two (111) planes, and at the midpoint also has a coordination of six, although in the BCC case these are non-coplanar. For comparison, the migration barrier for a vacancy in Mo was calculated
using a 54-atom supercell (4x4x4 k-point mesh, 400 eV plane wave cutoff) and overlayed with the $\omega_{14}^{[0001]} \rightarrow \omega_{14}$ barrier in $\omega$-Ti. Both curves are shown to have similar magnitudes and characteristic flatness, although Mo possesses a double saddle point pathway, with the peaks at $\chi = \frac{1}{3}$ and $\chi = \frac{2}{3}$ corresponding to the migrating atom passing through one of the (111) planes. Further investigation into the behavior of the local density of states during migration may provide further insights into the electronic basis of this phenomena. However, it is interesting to note that while both the $\omega_{11}^{[0001]} \rightarrow \omega_{11}$ and $\omega_{14}^{[0001]} \rightarrow \omega_{14}$ are analogous to $\frac{1}{2}[111]$ jumps in the BCC phase, they have drastically different characteristics. The possible implications of this in BCC diffusion will be discussed shortly.

**Figure 5.9.** Comparison of the minimum energy pathway for $\omega_{14}^{[0001]} \rightarrow \omega_{14}$ vacancy migration in $\omega$-Ti and for $\frac{1}{2}[111]$ migration in Mo. The Mo pathway has a flat double saddlepoint shape, with each peak corresponding to the migrating atom passing through a (110) plane, whereas the Ti pathway has a flat single barrier.

For the single Mo solute-vacancy exchange (MEP shown in red in ??) the $\omega_{11}^{[0001]} \rightarrow \omega_{11}$ stable midpoint is no longer observed, and the barrier for [1120] and [0001] migration become nearly equivalent, 0.27 eV and 0.30 eV respectively. While the activation energy $Q^a_V$ is still lower for a Mo$_{\omega_{11}}$-$V_{\omega_{11}}$ jump than a Ti$_{\omega_{11}}$-$V_{\omega_{11}}$ one, the jump distance is also longer, which undoubtedly affects the prefactor. For present discussions, such effects are
ignored. The activation energies for such jumps are close enough that vacancies would not be expected to be strongly bound near $\omega_{11}$ sites, which is important for transport of the vacancy. The nearly equivalent [11\bar{2}0] and [0001] Mo$_{\omega_{11}}$-V$_{\omega_{11}}$ migration energy may indicate that, once sufficiently dilute, Mo does not diffuse selectively in either direction, which may reflect the radial growth of the ellipsoidal precipitate after isothermal annealing. For the pathways involving $\omega_{14}$ sites, the migration barriers are not significantly altered relative to Ti, indicating that $\omega_{11}$ vacancies will never exchange with atoms at $\omega_{14}$ sites regardless of the chemical species present there. This is likely why some residual Mo is expected remain in the $\omega$ structure, despite isothermal aging; when Mo is quenched in from a randomized BCC configuration, the atoms generally do not have a distinct $\omega_{11}$ or $\omega_{14}$ character, but as Mo diffuses out and the $\omega$ structure becomes increasingly refined, the residual Mo atoms will be either at $\omega_{11}$ or $\omega_{14}$, and the Mo$_{\omega_{11}}$ atoms will be highly favored for further diffusion. It might be possible that during this selective diffusive process, when two Mo atoms are sufficiently close to each other that their mutual lattice distortions locally destabilize the $\omega$ structure (with the assistance of thermal $\beta$ stabilization), a Ti atom can replace the Mo atom at the $\omega_{14}$ site, and the Mo atom can be "freed" to diffuse to the interface. Eventually, however, only Mo$_{\omega_{14}}$ sites will be left.

The unexpectedly low migration barrier for the $\omega_{11} \xrightarrow{[0001]} V, \omega_{11}$ vacancy jump, and its stable midpoint, may provide new insights into the anomalously fast self-diffusion of the group IV metals. While all BCC metals exhibit some degree of curvature in their self-diffusivity Arhennius plots ($\ln D$ vs $\frac{1}{T}$), the effect is much more pronounced for Ti, Zr, and Hf, as shown in Fig. 5.10. Sanchez and Defontaine originally proposed a phenomenological model that the diffusional jump process in the [111] direction created $\omega$ embryo structures. The concentration of these embryos was a function of the temperature and the $\beta \rightarrow \omega$ transus temperature. In the BCC structure, atoms diffusing in the [111] direction pass through two (111) planes until reaching the vacancy site. When passing through these planes, the diffusing atom becomes coplanar with three nearest neighbors in a trigonal arrangement with a separation of 2.64 Å, which is identical to the $\omega_{11}$ sites in

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Figure 5.10. Arrhenius plots of self diffusion in BCC transition metals, with FCC metals shown in the shaded region. The group IV elements (Ti, Zr, and Hf) exhibit significantly higher diffusivity and strong curvature with decreasing temperature. Reproduced from [5].

ω. In their work, they suggested due to the low temperature stability of the ω phase, this barrier would be drastically reduced compared to non-polymorphic BCC transition metals [96, 98]. Later, Köhler and Herzig found that while the presence of ω embryos was possible, it would be governed by the softening of the phonon mode responsible for the β → ω transformation, L_{2/3}[111]. For all BCC metals this mode is characteristically soft, but follows a groupwise trend from (Cr, Mo, W) → (V, Nb, Ta) → (Ti, Zr, Hf) of increased phonon softening as well as decreasing temperature dependence. A strong correlation was established between the effective activation energy for monovacancy diffusion and the square of the frequency ratio $\nu_2/\nu_0$, as shown in Fig. 5.11.

5.4. Vacancy migration barriers in the metastable Ti-8.3 at% Mo system
Figure 5.11. Left: A strong correlation is found between the normalized activation energy for self diffusion and the normalized frequency of the $L_{2/3}[111]$ phonon mode, $\nu_{2/3}$. Right: The change in the phonon dispersion for the 4d transition BCC metals Zr, Nb, and Mo show an increasing frequency moving from group IV to VI.
\[ \omega_{11a} \rightarrow V, \omega_{11b} \]

\[ \omega_{11a} \rightarrow V, \omega_{11b} \]

\[ \omega_{14b} \rightarrow V, \alpha \]

**Figure 5.12.** Diagram of Ti-vacancy migration jumps and corresponding minimum energy pathways.
\( \beta_{\text{Mo}} \rightarrow V, \omega_{11a} \)

\( \omega_{11a}^{[11\bar{2}0]} \rightarrow V, \omega_{11b} \)

\( \beta_{\text{Mo}} \rightarrow V, \omega_{14b} \)

\( \omega_{14b} \rightarrow V, \alpha \)

**Figure 5.13.** Diagram of Mo-vacancy migration jumps and corresponding minimum energy pathways.
In this chapter, the Silcock pathway is revisited using nudged elastic band calculations coupled with DFT, and re-examined as the basis of a heterogeneous transformation pathway between $\omega$ and $\alpha$, and the components of the atomistic mechanisms are described in detail. Finally, the effect of the presence of Mo on this transformation is calculated.

6.1. The Silcock Pathway Revisited

We begin by evaluating the homogeneous transformation pathways. Using the Variant II OR and the displacements described in Silcock's paper, we simplify the transformation as follows. In the original description, the displacement of 12 (10-10) planes is described, but the pattern is actually identical between the first set and second set of six planes if the latter is uniformly displaced by $\frac{1}{2}c_\omega$. This can be accomplished by shearing a 6-atom cell in the [0001] direction by $\frac{1}{2}c_\omega$ normal to the [1010] axis, so that in periodic terms each successive set of 6 (1010) planes will be displaced by $\frac{1}{2}c_\omega$. This would mean that after every 12 (10-10) planes, the net displacement of the lattice will be $c_\omega$. If instead, no net displacement is assumed and there is no macroscopic cell shear, then all rearrangements are expected to be internal within a 12-atom cell.

These two configurations and their corresponding $\omega$ and $\alpha$ endpoints are depicted in Fig. 6.1. Nudged elastic band (NEB) calculations were then performed after linearly interpolating atomic positions between these two points in order to obtain the minimum energy pathway (MEP). The energy per atom along each pathway is depicted in Fig. 6.2. The barrier determined for the 12-atom cell corresponds well with previous NEB calculations using DFT [38, 37]. The 12-atom system possesses multiple intermediate barriers during the transformation, corresponding to a complex sequence of planar displacements. Since different regions of the 12 atom cell are transforming at each barrier on the MEP, the transformation cannot be considered homogeneous. Thus the energetics of the two pathways cannot be directly compared, but as an estimate, a more useful value would be
Figure 6.1. The 6- and 12-atom unit cells used as endpoints for nudged elastic band calculations. Dark and light atoms are used to distinguish alternate planes; both $\omega$ and $\alpha$ have AB stacking in this direction.

The sum of the successive barriers for the 12-atom case, which gives an energy/atom of 90 eV/atom, compared with a barrier of 64 eV/atom for the 6-atom case.

Interestingly, though different unit cells were used in the calculations here, the barrier energy for the 6-atom calculation is identical to the one calculated for TAO-2 in the work by Trinkle et al. In that work, 6-atom unit cells corresponding to a common subgroup along that pathway were used, but the authors comment that the TAO-2 pathway can also be constructed from the Variant II OR as done here, and in all likeliness the
pathway is indeed the same. While that work describes the TAO-2 to be a new pathway, the displacements correspond well with the pattern proposed originally by Silcock, which is only directly evident if the Variant II-derived cells are used. Thus, throughout this chapter this mechanism shall be referred to as a Silcock-type.

A closer examination of the structure at the saddlepoint indicates that half of the unit cell is transforming through a distorted BCC structure, while the other half is transforming directly to HCP. The energetics are also remarkably similar; $\Delta E_{\omega \rightarrow \beta} = 116$ meV/atom and $\Delta E_{\omega \rightarrow \alpha} = 7$ meV/atom, and $\frac{1}{2}(\Delta E_{\omega \rightarrow \beta} + \Delta E_{\omega \rightarrow \alpha}) = 62$ meV/atom, which is very close to the calculated barrier of 65 meV/atom. At the saddlepoint, the atoms which were originally at the $\omega_{11}$ sites reverse the $\omega_{[0001]}$ displacement of the $\beta \rightarrow \omega$ transformation, and the structure is found to be BCC-like with $d_{N,N}$ of $2.82 \pm 0.04 \text{ Å}$, as depicted in Fig. 6.3.
Figure 6.3. The BCC-like structure is highlighted at the saddlepoint of the \( \omega \rightarrow \alpha \) transformation process, with \( d_{NN} = 2.82 \pm 0.04 \) Å.

Using this same mechanism, we can also look at the transformation process as a step-wise process, starting from the \( \omega \) phase and transforming multiple layers in a sequential manner to the \( \alpha \) phase. A larger 24-atom supercell is now used, and the barriers for transformation of successive sets of 6 [10\overline{1}0]$_\omega$ from \( \omega \rightarrow \alpha \) was calculated. As this is now being considered as a planar, heterogeneous transformation, the planar energy barrier is a more useful quantity to calculate rather than a per-atom value. The first transformation step will expectedly be the highest, as there will be an additional energy penalty associated with the creation of two \( \alpha/\omega \) interfaces, as well as a strain energy associated with the restriction of the necessary volumetric dilations required for the ideal HCP structure. This is in part due to rigid box boundary conditions which must minimize stress globally on the system by expanding or contracting each dimension of the box. The energy barriers of the first three transformation steps are shown in Fig. 6.4.

As can be seen, the barrier continues to decrease as the \( \alpha \) phase grows. With subsequent steps, the barrier now becomes associated with migrating a single interface, and will be driven in part by the growing strain mismatch between the \( \alpha \) and \( \omega \) phases. As the \( \alpha \) phase grows relative to the \( \omega \), the volumetric strain of \( \alpha \) in the [1\overline{1}20] and [0001] directions (i.e., the directions transverse to the [1\overline{1}00] growth direction) is increasingly relieved. This effect is also observed in the reduction of the energy of the structure at the final endpoint with each successive transformation step.
As mentioned before, each transformation step displaces the lattice by $\frac{1}{2}c_\omega$; successive steps can either increase this displacement, or reverse direction and cancel it out. For the case shown here, each step proceeds in alternating directions, and the barrier is expected to be independent of this choice. This is important because the matrix does not necessarily need to deform extensively to accommodate the strains induced by this glide-assisted transformation.

By examining the transformation as a planar, heterogenous process, it was found that the relative energetic contribution of the individual atomistic mechanisms (the atomic shuffle and glide) can be calculated separately. Here, the cell shear component from the homogeneous transformation translates to a glide component due to the fact that the transformation causes the aforementioned $\frac{1}{2}c_\omega$ displacement of the lattice relative to the untransformed region. The resulting individual barriers for the shuffle mechanism and the glide mechanism are depicted in Fig. 6.5.

As can be seen, the shuffle component, corresponding to the intermediate BCC structure, strongly dominates the total transformation barrier, with an energy of 482 mJ/m$^2$ compared to the 162 mJ/m$^2$ of the glide component. This may indicate that this

**Figure 6.4.** The planar energy barriers for successive transformation steps during the $\omega \rightarrow \alpha$ transformation process.
component of the transformation is very strongly thermally activated; as $\omega$ becomes increasingly unstable with respect to $\beta$, the shuffle component can proceed increasingly easier as the restoring forces get softer, allowing this transformation to proceed more readily. A similar process is believed to occur in the transformation from $\alpha \rightarrow \beta$, following the Burgers mechanism of shear displacements along $\{10\bar{1}0\}$ prismatic planes. The $c_{66}$ elastic constant is the modulus responsible for $\{10\bar{1}0\}\langle 11\bar{2}0 \rangle$ shear, and reduces significantly as the temperature approaches the $\beta$ transus, as shown in Fig. 6.6 [6]. Similar data is not available for the $\omega$ phase due to experimental difficulties, except for a recent study using inverse Voigt-Reuss-Hill approximations on polycrystalline $\omega$ Ti which found that $c_{44}$, the analogous modulus for the aforementioned $\{10\bar{1}0\}\langle 0001 \rangle$ shear occurring during $\omega \rightarrow \alpha$ transformation, was higher at room temperature than values determined by DFT [101]. Detailed vibrational studies of true single crystalline $\omega$ phase Ti have yet to be undertaken, and would be a valuable insight for better understanding anisotropic anharmonic effects on martensitic transformations.

Recently, first-principles methods were used to calculate the free energy of the $\alpha$, $\beta$, and $\omega$ phases of titanium, and it was found that while the $\omega$ phase had lower enthalpy
than $\alpha$ phase at all temperatures, it also had lower entropy at all temperatures [24]. A plot depicting the calculated free energies of the $\omega$ and $\beta$ phases relative to the $\alpha$ phase is reproduced in Fig. 6.7. The diagram suggests that there is an increasingly strong driving force for $\omega$ to transform to $\alpha$ in pure Ti once the temperature exceeds 200 K. However, experimentally, $\omega$ precipitates are observed to begin transforming around 675 K [102], which is much closer to when $\omega$ becomes metastable with respect to $\beta$, calculated as 780 K for pure Ti. This is further evidence that the transformation process is highly thermally dependant.
FIGURE 6.8. Potential coordination environments after changes to the out of plane coordination for $\omega_{14}$ (Top) and $\omega_{11}$ (Bottom). $Z$ represents total coordination, and the planar coordination below, within, and above is labelled to demonstrate the local stacking pattern. $Z=14$ (4-6-4) and $Z=11$ (3-5-3) represent the ideal case for both sites.

Next, the structural changes are more closely examined after each step of the transformation. The change in coordination environment before and after the initial atomic shuffle is depicted in Fig. 6.9, corresponding to the reaction coordinate $\chi = 1$ in Fig. 6.5. To simplify the view of the structure, a single (1120) plane of $\omega$ is shown. The atoms are colored to distinguish their coordination. It is useful to recall the in- and out- of plane coordination environments associated with the different sites, and the potential new environments induced by various structural changes, depicted in Fig. 6.8.

The $\omega_{11}$ sites have 3-5-3 coordination, and $\omega_{14}$ sites have 4-6-4 coordination. The in-plane neighboring bonds are drawn in to better differentiate the five- and six-coordinated sites. The shuffle of a single $\omega_{11}$ site by $\frac{1}{2}c_\omega$ causes the adjacent rows of atoms to switch
Figure 6.9. Change in local coordination after the shuffle component of the Silcock-type $\omega \rightarrow \alpha$ transformation process. Atoms are colored according to their coordination environment, with $\omega_{11}$ atoms in dark blue, $\omega_{12}/\alpha$ in light blue, $\omega_{13}$ in green, and $\omega_{14}$ atoms in yellow. The red arrows mark the row of $\omega_{11}$ atoms displaced by $\frac{1}{2}[0001]$. The dashed magenta line marks where the glide step occurs.

It can be readily seen that if the upper section of the crystal containing the $\omega_{13}$ layer displaces by another $\frac{1}{2}c_\omega$, 4 layers with in-plane coordination of 6 will be created, of which one shall remain $\omega_{14}$. This is in fact what occurs in the next step involving glide, which converts the 3-5-3 layer to a 3-6-3, and the 4-5-4 to 3-6-3. The net effect is the creation of 6 3-6-3 HCP sites, 3 on each (1120)$_\omega$ plane, which have now become (0001)$_\alpha$ planes. The final structure is depicted in Fig. 6.10.

Note, the sum of these two barriers individually exceeds the barrier calculated as a single process (516 mJ/m$^2$), and this is likely because the two processes are complementary. The $\omega \rightarrow \beta$ reversion requires the reversal of the ABC$\rightarrow$AB' $\beta_{(111)} \rightarrow \omega_{(0001)}$ planar collapse described previously. However, all the B and C atoms also correspond to individual {112} planes in $\beta$ titanium; the process of reverting from B'→BC causes a relative motion of {112} planes in opposite <111> directions that would also potentially facilitate
Figure 6.10. Final structure after completion of a single shuffle and glide Silcock mechanism, which creates six rows of α sites. Same color scheme as shown in ?? is used here.

Glide in an analogous manner as the \{112\}\langle111\rangle slip-system in BCC. Furthermore, the glide cannot precede the shuffle; either they are simultaneous, or the shuffle must occur first.

The glissile components of certain martensitic transformations have been termed transformation dislocations, and more generally transformation disconnections to address their dislocation and step like character [103, 104, 105]. The most straightforward example can be found in HCP ↔ FCC type transformations, which is mitigated by Shockley-type partial dislocations. A similar phenomena is also seen in certain BCC ↔ HCP derived transformations, such as the recent Ti-Nb class of shape memory alloys [7], where the transformation strain was found to be primarily accommodated by transformation disconnections within an α”/β interface. α” is an orthorhombic metastable martensite similar to α, but without the complete cell shear component required for ideal Burgers BCC → HCP transformation. The shape memory effect is a reversible martensitic transformation from α”/β → α”/α”.
Figure 6.11. HRTEM images of $\alpha''/\beta$ interface structure in Ti-22Nb, showing the glissile transformation disconnections which facilitate the shape memory effect. Reproduced from [7].

The interface between $\alpha''/\beta$ as imaged in that work is reproduced in Fig. 6.11, with the interfacial transformation disconnections appearing as ledges. Under stress induced martensitic transformation, these disconnections move in a conservative and glissile manner on the terrace plane $(2\overline{1}1)_\beta/(110)_{\alpha''}$ in a manner similar to the $\{112\}$$\langle111\rangle_{BCC}$ slip-system and the $\{10\overline{1}0\}$$\langle11\overline{2}0\rangle_{HCP}$ prismatic slip system. Interestingly, there are athermal $\omega$ particles, which suppress the martensitic transformation by impeding motion of the interface. At higher temperatures, it may be expected that the $\omega$ particles would also transform in much the same way given the favorable mutual orientation between $\alpha''/\omega/\beta$, except irreversibly.

6.2. The effect of Mo on the $\omega \rightarrow \alpha$ pathway

In this section, the effect of Mo in the transformation plane is explored. This is relevant for several reasons, as partitioning of beta-stabilizing elements is highly dependant on the thermal history of the material. For instance, isothermal aging of athermal $\omega$ causes further Mo depletion from the $\omega$ phase while also significantly growing the pre-existing
particles. In the Ti-9Mo system, aging at 475°C (748 K) for 0.5 hours developed 30-50nm sized precipitates with a residual Mo concentration of 4 at%, while after 48 hours the average size grew to 80nm with a residual concentration of 2 at% [4]. The concentration of Mo, or any beta-stabilizer, will likely play a role in kinetics of \( \omega \to \alpha \) transformations. It may also give some insights on the relative role of the \( \beta \) matrix, \( \beta/\omega \) interfaces, and the \( \omega \) precipitate in the development of \( \alpha + \beta \) microstructures. Recent HRTEM investigations of low-cost beta (LCB) titanium with low misfit (Ti-6.8Mo-4.5Fe-1.5Al) demonstrated the existence of platelets of \( \alpha \) within ellipsoidal \( \omega \), and subsequent growth controlled by interface mobility [42]. While the Silcock OR was directly imaged across a perfectly planar \( \alpha/\omega \) interface, the authors only refer to a displacive transformation without any clear indication of the atomistic mechanism. They do mention that there are two kinetic regimes for \( \alpha \) growth, the first involving consumption of \( \omega \) phase, and the the second involving subsequent diffusion assisted growth, which supports a previous study on Ti-Mo alloys [34]. It is quite possible that the reason for \( \alpha \) nucleation inside the \( \omega \) rather than from the \( \beta/\omega \) interface has to do with solute effects, and the low temperature at which the isothermal \( \omega \) is being annealed.

To understand what effect Mo has on the transformation pathway, we take a similar system as the pure \( \omega \to \alpha \) case and substitute Mo specifically at the transforming layers. Recalling the description of the shuffle/glide mechanism in the previous section, six (1010)\( \omega \) planes are transforming with each transformational step, three of which go through an intermediate BCC structure. Mo was substituted in these layers to give a nominal local concentration of 8.3% and 12.5%, and the minimum energy pathway was recalculated. For the 8.3% case, the resulting energy barriers for both the shuffle and shear component is shown in Fig. 6.12, with the atomic structures corresponding to specific points of interest on the curve given in Fig. 6.14. The system used has two unit cells in the [11\( \bar{2} \)0] direction, the front cell contains Mo, the back cell does not.

At point a), the energy initially decreases, because the Mo atom shifts away from an \( \omega \) position and locally stabilizes the \( \beta \) environment, while the Mo-free cell remains as
Figure 6.12. Modification of the $\omega \rightarrow \alpha$ transformation energetics in the presence of a planar concentration of 8.3 at% Mo.

$\omega$ This is very similar to the partial collapse behavior studied in Chapter 4 for the 8.3 at.% Mo case, where the most stable structure along the path had a mix of $\beta$ and $\omega$ coordination environments. At point b), the barrier structure, the Mo-free cells have also shifted to a BCC like position. The energy, relative to the lowest point, is accordingly nearly half of what it was for pure Ti, calculated to be 224 mJ/m$^2$ compared to 480 mJ/m$^2$. This is strong evidence that this barrier diminishes with $\beta$ stabilization, either due to thermal or solute effects. At point c), it is clear that the Mo-containing cell still remains as $\beta$, and the Mo-free cell has proceeded to the midpoint structure, which generates $\omega_{13}$ sites. The energy of this structure is also greatly reduced, being nearly identical to the initial purely $\omega$ energy. At point d) however, the glide component does shift the Mo containing cells to the $\alpha$ position. The barrier between point c) and d) is slightly raised, from 162 mJ/m$^2$ in pure Ti to 187 mJ/m$^2$, but not substantially. This indicates that the $\beta$ stabilization primarily affects only the shuffle part of transformation, not the glide. The energy of the final structure, relative to the initial, is practically identical, however the reverse barrier to transfer back to the midpoint, is also reduced, indicating partial $\beta$ stabilization with respect to $\alpha$. 

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Figure 6.13. The corresponding atomistic structures for selected points on the calculated MEP shown in Fig. 6.12 for Ti with a planar 8.3 at.% Mo concentration. The system has two unit cells in the [1120] direction.

Increasing the concentration further to 12.5% Mo completely removes the barrier for the shuffle component, but also destabilizes the glide component, and it can be assumed this region would locally remain $\beta$. While it is unexpected for such concentrations of Mo to be found in the $\omega$ phase, residual Mo or any $\beta$ stabilizer for that matter could greatly reduce the barrier for initiating the $\omega \rightarrow \alpha$ transformation.
Figure 6.14. Further increasing Mo content to 12 at.% completely stabilizes the $\beta$ phase for the shuffle component of the transformation, and but the structure after the glide component is unstable, and will likely revert back to $\beta$ in-plane.
CHAPTER 7

SUMMARY AND FUTURE WORK

In this work, several aspects of metastable $\beta$ titanium alloys and their evolution upon quenching were studied using first-principles based modeling methods. The Ti-Mo system was chosen as a representative model of this class of materials, and phenomena such as the effect of Mo on the energetics of $\beta \rightarrow \omega$ transformation, local structural distortions, vacancy behavior, interfaces, and the $\omega \rightarrow \alpha$ transformation were addressed.

The minimum energy pathway was calculated for the $\beta \rightarrow \omega$ transformation as a function of Mo composition, and an inversion in the energy difference was observed between pure Ti and 16.6 at.% Mo, with intermediate compositions possessing a stable structure exhibiting nonhomogeneous transformation behavior. For these compositions, the degree of partial transformation was directly correlated to the Mo content. This was correlated to the modification of bonding between Ti and Mo atoms, which directionally enhances charge density in the $<111>$ directions and consequently stiffens against the displacements necessary for $\omega$ transformation. However, Ti atoms uncoordinated by Mo remain relatively mobile, and can proceed to locally displace towards $\omega$ positions. When an alternate system geometry was chosen which allows for global transformation of either $\beta \rightarrow \omega$ or $\beta \rightarrow \alpha$, a minimized Ti-8.3 at.% Mo system was found to have Ti atoms with both $\alpha$ and $\omega$ coordination environments. The creation of this mixture of sites is attributed to both the disruption of uniform $\beta \rightarrow \omega$ transformation by the Mo atoms, as well as overlap of Ti-Mo bond contractions which facilitate displacements to either of the two relatively stable structures in Mo-free regions.

Several interfaces between Mo-stabilized $\beta$ and $\omega$- or $\alpha$- Ti were studied, spe. It was observed that the distribution of Mo at the interface strongly dictates the resulting structure of Mo depleted regions even over widths of approximately 1.5 nm in size. The structure of a defected omega region was characterized, and planar defects with $\alpha$-like coordination environments were identified, giving evidence that even in pure Ti regions, the
two structures can co-exist, and these defects may act as sites where $\omega \rightarrow \alpha$ transformation may initiate.

Vacancy formation energies were characterized in the $\omega$ phase in both pure Ti and near a single Mo solute atom, as well as the metastable 8.3 at.% Mo system. The $\omega$ structure has two distinct sites which are either 11- or 14- coordinated ($\omega_{11}$ or $\omega_{14}$), and it is found that both Mo and vacancies prefer to reside at the $\omega_{11}$ site. Increasing the concentration of Mo systematically eliminates low energy $\omega_{11}$ sites due to enhanced $\beta$ stabilization, which is expected to inhibit further diffusion as Mo partitioning occurs. In the 8.3 at.% Mo metastable system which contains a mixture of $\alpha$ and $\omega$ coordination environments, the vacancy formation energies are found to match well with the corresponding reference value.

Lastly, the Silcock pathway for $\omega \rightarrow \alpha$ transformation was revisited, which although has previously been shown to not be the lowest energy transformation path, produces the most commonly observed $\omega/\alpha$ mutual orientation relationship. Present analysis indicated that the transformation likely proceeds in a planar fashion, and has a thermally activated component and a glide component, with the former requiring a partial local transformation to an intermediate BCC-like state. This is supported by the observation that the presence of Mo lowers or eliminates the thermally active component of the barrier, while minimally affecting the glide component. This supports experimental observations of transformation from elliptical $\omega$ precipitates to lathe and needle-like $\alpha$ which implies large shear deformations during transformation.

Over the course of completing this work, several interesting questions arose which were beyond the present scope, but would be interesting to expand upon in future investigations.

(1) In Chapter 6, the Silcock mechanism was predicted to proceed in a planar manner with a shuffle and glide component, analogous to the BCC$\leftrightarrow$HCP mechanism in certain materials. What is the nature of this transformation dislocation (or disconnection), and what is Peierls stress required for it’s motion? How does it
interact with coherency strains? If the $\omega$ phase becomes sufficiently unstable at high temperature, does the growth of $\alpha$ becomes auto-catalytic? This would be challenging to address with DFT methods, but would be relatively straightforward using the MEAM interatomic potential, which has been proven to correctly predict the energy difference between the two phases and the elastic constants of each.

(2) In Chapter 5, it was observed that the $\omega_{11}$ vacancy migrational midpoint creates a coordination environment similar to that observed in the intermediate stage of the Silcock mechanism (13-coordinated site). It was also observed in recent work that vacancies have an ordering tendency in the $\omega$ phase [80]. It would be of interest to see how the presence of vacancies changes the barrier for the Silcock and TAO-1 mechanism, whether it impedes or accelerates it, or changes the process altogether. Typically, vacancies cause drag on the motion of dislocations, does this hold true for transformation dislocations? Also, how is the vacancy accommodated after phase transformation?

(3) In $\beta + \omega$ microstructures, the choice of stabilizing element can create low-misfit precipitates (i.e. elliptical) or high-misfit (i.e. cuboidal). Using a similar methodology as used in Chapter 4, it would be straightforward to understand the chemistry of different stabilizing elements at the interface, how it changes the interfacial energy, and how that correlates to the $\omega$ morphology. Furthermore, the bulk modulus or elastic modulii can also be characterized for the $\beta$ phase stabilized by different elements, allowing a better understanding of whether elastic compatibility or interfacial chemistry dominates.

(4) Likewise, the distortion of the titanium $\beta$ lattice by Mo atoms is strongly related to the degree of charge transfer and atomic size, how does substituting with different elements change the resulting structure, if at all? How does it change the vacancy formation energy in the alloyed state?
(5) In Chapter 5, it was observed that the vacancy formation energy in \( \omega \) and \( \alpha \) were closely related, as well as the Mo substitutional energy. What is the electronic basis for these correlations? How is the density of states modified by the creation of a vacancy?

(6) How does the addition of \( \alpha \)-stabilizers such as aluminum affect \( \omega \) formation, vacancy formation, and vacancy migration? It was observed that the solubility of Mo was nearly identical in \( \alpha \) or \( \omega \), does that hold true for \( \alpha \) stabilizers as well?

(7) Can first principles methods be used to explain the observance of substrate effect on \( \alpha \) or \( \omega \) phase selection in sputter deposited zirconium? Can a suitable substrate be found for the deposition of titanium? This may be a functional way to characterize the \( \omega \) phase's mechanical and transformation properties, especially if co-deposition with stabilizing elements is possible.

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