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Thermodynamic modeling of interstitials in titanium alloys

A dissertation submitted in partial satisfaction
of the requirements for the degree

Doctor of Philosophy
in
Materials

by

Naga Sri Harsha Gunda

Committee in charge:

Professor Anton Van der Ven, Chair
Professor Carlos G. Levi
Professor Tresa Pollock
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December 2019

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December 2019

Thermodynamic modeling of interstitials in titanium alloys

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Naga Sri Harsha Gunda

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Curriculum Vitæ

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Publications

2019	N. S. Harsha Gunda and Anton Van der Ven, <i>Oxygen induced chemical short range ordering in Ti-Al based alloys</i> , Manuscript in preparation
2018	N. S. Harsha Gunda and Anton Van der Ven, <i>First-principles insights on phase stability of titanium interstitial alloys</i> , <i>Physical Review Materials</i> 2 (2018), 083602
2018	N. S. Harsha Gunda, Brian Puchala, and Anton Van der Ven. <i>Resolving phase stability in the Ti-O binary with first-principles statistical mechanics methods</i> , <i>Physical Review Materials</i> 2 (2018), 033604
2017	Gregory H. Teichert, N.S. Harsha Gunda, Shiva Rudraraju, Anirudh Raju Natarajan, Brian Puchala, Krishna Garikipati, and Anton Van der Ven, <i>A comparison of Redlich-Kister polynomial and cubic spline representations of the chemical potential in phase field computations</i> , <i>Computational Materials Science</i> 128 (2017) 127

Presentations and Posters

2019	N. S. Harsha Gunda and Anton Van der Ven, <i>Effect of interstitials on the phase stability of Titanium rich alloys using first-principles statistical methods</i> , Gordon Research Conference 2019, Southern New Hampshire University, Manchester, NH
2018	N. S. Harsha Gunda and Anton Van der Ven, <i>Thermodynamic analysis of substitutional and interstitial Ti alloys</i> , TMS 2018, Phoenix, AZ
2017	N. S. Harsha Gunda and Anton Van der Ven, <i>Cluster expansion statistical models to resolve the thermochemistry of Ti alloys</i> , TMS 2017, San Diego, CA

Abstract

Thermodynamic modeling of interstitials in titanium alloys

by

Naga Sri Harsha Gunda

Titanium is recognized as the metal for the 21st century. Its alloys are relevant in diverse fields from aerospace to bio-medical applications. Interstitial elements such as oxygen, nitrogen and carbon can dissolve in a bulk Ti matrix to form solid solutions. Especially oxygen can dissolve up to 33 at % in hcp-Ti. The solute atmosphere created by interstitial elements is crucial for various strengthening mechanics in structural materials. Hence, from materials design perspective, it becomes important to investigate the extent to which titanium alloys can dissolve interstitial elements at finite temperatures. Upon dissolution into titanium alloys, these interstitials form many ordered and disordered compounds. The crystal structures of these compounds are poorly characterized in the literature. Furthermore, interactions between interstitial and substitutional alloying elements in bulk Ti remain poorly understood. This dissertation uses first-principles methods along with coarse grained cluster expansion models to predict accurate phase stability in titanium alloys with interstitial solutes.

The binary Ti- X ($X = \text{C, N, O}$) interstitial systems consist of a multitude of stable and metastable oxides that are used in wide ranging applications. In this dissertation, the stable ordered interstitial compounds were investigated using first-principles methods at 0 K. A systematic search was performed to discover ground state structures as a function of interstitial concentration by considering interstitial-vacancy and/or titanium-vacancy orderings over parent crystal structures such as hcp-Ti, ω -Ti and rocksalt crystals. This

dissertation presents the newly discovered ground states while reinforcing observations from previous experimental and computational studies. The phase stability at finite temperature was explored using cluster expansion Hamiltonians and Monte Carlo simulations. The calculations predict a high oxygen solubility in hcp-Ti and the stability of suboxide and vacancy ordered rocksalt phases that undergo order-disorder transitions upon heating in the Ti-O system. In the carbide and the nitride systems, the ordered rocksalts transformed to a disordered rocksalt phase that can tolerate high vacancy concentrations at intermediate to high temperatures. Trends in phase stability, rooted in electronic structure, are revealed upon comparing the calculated Ti-X phase diagrams. Predicted stable and metastable phase diagrams are qualitatively consistent with experimental observations. Some subtle but important discrepancies are revealed between the first-principles based phase stability predictions and the current understanding of phase stability in this system.

In the final part of this dissertation, a phase stability analysis of substitutional titanium alloys that simultaneously contain interstitial species was explored. In particular, the focus was on the effect of substitutional Al in Ti-Al alloys on the solubility of oxygen. There is a strong tendency for short range ordering in alpha-Ti, whereby Al and O atoms avoid being nearest neighbors. This changes phase stability in the Ti-Al binary as a function of the oxygen chemical potential. Pseudo-binary phase diagrams drawn at different degrees of oxygen solubility show a significant change in order/disorder temperature and compositional variance of phases in the binary. The insights from this dissertation can shed light on similar interactions between interstitial solutes and metal atoms observed in other alloy systems. The thermodynamic models developed in this dissertation are part of a crucial first step in building multiscale models to predict oxidation microstructure in titanium alloys.

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Chapter 1

Introduction

Structural materials consist mainly of metallic alloys where the atoms are arranged as face centered cubic (fcc), body centered cubic (bcc) or hexagonal close packed (hcp) crystal systems. The metal sublattice is formed by the arrangement of atoms on the close packed planes in the crystal. Point defects on the metal sublattice substitute some of the metal atoms with vacancies or other types of atoms. A significant amount of research in the area of structural materials concerns the ordering of these point defects, especially substitutional defects in transition metals. In addition to substituting on the host lattice, atoms can also reside between the metal lattice planes, these types of point defects are called interstitials. Interstitial impurities generally introduce atoms from s and p blocks of the periodic table such as hydrogen, boron, carbon, nitrogen and oxygen into the crystal[1].

The presence of interstitial elements has a significant effect on the mechanical properties of the materials. For example, austenitic steel dissolves a substantial amount of interstitial carbon[2], which results in solid solution strengthening[3], dynamic strain aging[4] and yield point phenomena[5] in the material. While nitrogen improves the

strength of steel[6], interstitial elements like hydrogen embrittle it[7], Recent work in the area of high entropy alloys suggests that dissolved oxygen in the TiZrHfNb alloy forms ordered oxide complexes that improve the strength and ductility in the material [8]. In general, interstitial elements are prevalent and crucial in materials for structural applications.

This dissertation details the thermodynamic modeling of interstitial alloys and provides insights on the interaction between the interstitial elements and the metal atoms. The motivation for investigating titanium interstitial alloys will be presented in this chapter. Using the example of oxidation in bulk titanium, the need to resolve the thermodynamics of titanium interstitial alloys will be presented. The chapter concludes with an outline of the results presented in this dissertation.

1.1 Motivation

1.1.1 Interstitials in titanium

Titanium is a refractory transition metal which is in the hcp crystal structure at room temperature and the bcc crystal structure at high temperatures[9]. It is used in weight sensitive applications as it has a very high strength to weight ratio[10]. Table 1.1 suggests that significant quantities of interstitial elements can dissolve in hcp-Ti. Interstitial oxygen causes a dramatic solute strengthening effect in titanium[11]. Oxygen atoms pin dislocations in hcp-Ti and make the dislocations immobile thereby reducing ductility in the material[12]. Interstitial elements are also known to induce discontinuous yielding in titanium leading to a dynamic strain aging effect at high temperatures[13][14]. Dislocations pile up around a solute atmosphere before they can break free causing the flow curve to be jerky with peaks and plateaus making the material less reliable for

	H	B	C	N	O
Maximum solubility in hcp-Ti (in at. %)	7%	<1%	2%	23%	33%

Table 1.1: Maximum solubility of interstitial elements in hcp-Ti[18, 22, 19, 16, 17]

structural applications[15].

Phase diagrams from experiments on titanium interstitial systems are available in literature. Interstitials such as nitrogen and oxygen stabilize hcp titanium[16, 17]. Carbon is a mild stabilizer of hcp-Ti but hydrogen destabilizes the formation of hcp-Ti[18, 19]. Interstitial atoms also affect the phase stability of ordered compounds. Anatase and rutile are well known polymorphs of ordered titanium dioxide. Rutile form of the oxide is most commonly found in nature as it is more stable than other polymorphs at room temperature, but the addition of carbon stabilizes the formation of the less stable anatase form of titanium dioxide[20]. Interstitial elements in titanium diffuse at a faster rate than vacancies or other substitutional defects[21]. Therefore, impurities from the surface can readily dissolve into the bulk affecting the phase stability and mechanical properties of the alloy.

1.1.2 Thermodynamics of titanium oxidation

Although titanium and its alloys have been investigated since the early 20th century [23], several basic questions about its thermodynamic properties have yet to be settled. The following example of oxidation in bulk titanium demonstrates the need to understand the thermodynamics of this system. An experimental binary phase diagram of the Ti-O system shows the various oxides that can form upon oxidation of bulk titanium[17]. Figure 1.1a) shows a schematic of a cross section of a sample of pure titanium upon annealing in an oxygen environment at high temperatures under equilibrium conditions.

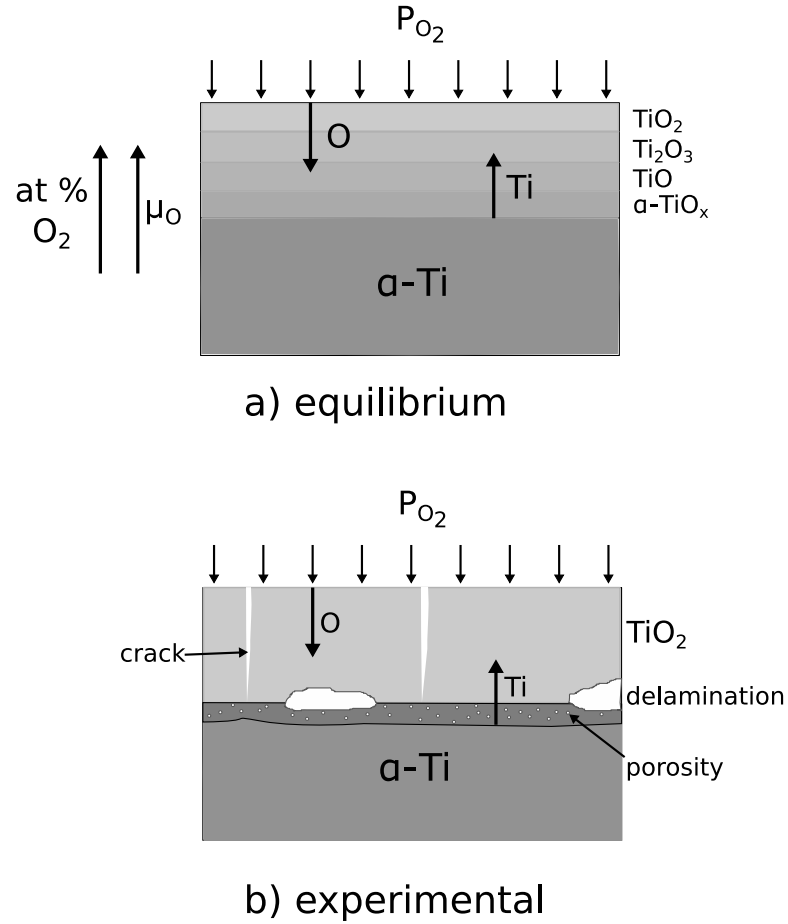


Figure 1.1: Oxidation microstructure observed a) at equilibrium and b) in experiments

In this idealized scenario, oxides with higher oxygen concentration form at the surface, with lower oxides and suboxides appearing deeper in the sample where there is reduced access to oxygen in the environment. Figure 1.1b) shows a schematic of a cross section expected in an actual experiment. Instead of having several layers of oxides, there is a thick layer of the dioxide phase with a smaller inner layer of oxide. Experiments also show voids, cracks and porosity in the oxide layers leading to a delamination at the interface between the oxide and the bulk[24, 25, 26, 27].

Experimental techniques have limitations when characterizing oxygen in titanium, but they can be supplemented with simulations to obtain a thorough understanding of the

underlying phenomenon. Computational methods using a combination of first-principles and statistical mechanics methods can be employed to model the thermodynamics of oxidation. Similar methods have previously been used to model the Zr-O system[28]. Free energy at finite temperature for stable and metastable phases in the system can be derived in order to determine the oxidation sequence after annealing the sample. Additionally, the relative strain between different oxide phases which cause the formation of cracks and voids in the sample can be estimated. The cracks provide access to oxygen for regions far from the surface of the sample thereby changing the oxidation sequence when compared to equilibrium. Modeling the phase stability of the system with vacancies and other point defects can be used to analyze the formation of porosity across the cross section. Kinetic Monte Carlo simulations can provide insights on the diffusion of titanium and oxygen through various oxides and help predict the growth of the oxide layers at different annealing conditions.

An integrated computational materials engineering (ICME) approach for materials design couples simulations of various length scales with experimental validation. In the current study, the thermodynamic properties of the system, such as the free energy, are derived using first-principles simulations that operate at the atomic scale. Continuum meso scale methods, such as phase field simulations, and macro scale methods, such as finite element methods, can be built on the thermodynamic information obtained from simulations at atomic scale. This multiscale model can provide the microstructural evolution and the mechanical response of the bulk sample for a complete analysis of the system.

1.2 Outline

In this dissertation, the focus is on building thermodynamic models for various titanium interstitial systems and analyze the interactions between titanium and interstitial elements such as carbon, nitrogen and oxygen. These interstitials stabilize hcp-Ti and also have significant solid solubility in titanium. In the first part of the dissertation, chapters 3 and 4 use density functional theory (DFT) simulations to determine the stable and metastable orderings of interstitial elements on various crystal systems at zero Kelvin. Chapter 3 illustrates the sensitivity analysis of various DFT methods in predicting the relative stability of oxide compounds. Chapter 5 describes the bonding between the interstitial elements and titanium and explores the electronic structure of the stable interstitial compounds. The zero Kelvin analysis suggests that carbon stabilizes fcc crystal based ordered compounds, whereas oxygen stabilizes hcp crystal based phases. The chapter links the unique pattern in electronic structure to the stability of phases based on the fcc and the hcp crystal systems. Chapters 5 and 6 build finite temperature thermodynamic models for the binary interstitial systems using cluster expansion and Monte Carlo methods. These chapters provide a comparison of the calculated finite temperature phase diagrams to experimental observations and propose vibrational and kinetic contributions that can improve the models. In the next part of the dissertation, ternary systems containing both substitution and interstitial elements in titanium are analyzed. Chapter 7 provides the calculated ternary phase diagrams of the Ti-Al-O system at zero Kelvin and at finite temperatures. The chapter also describes the new ternary stable phase discovered in the system and the influence of oxygen on the binary Ti-Al phase diagrams. Oxygen was observed to introduce chemical short range ordering in the disordered solid solution and increase the relative stability of disordered phases in the system.

Chapter 2

Theory and Computational methods

A combination of first-principles and statistical mechanics methods was used to derive the finite temperature thermodynamics of the titanium interstitial systems. Figure 2.1 shows the workflow employed to understand the underlying physics in the system. Similar workflow was used to build thermodynamic models for Mg[29, 30, 31], Zr[28] and Ni[32, 33] based alloy systems in the literature. Density functional theory(DFT) as implemented in the Vienna ab initio simulation package(VASP) along with the cluster expansion package being developed in Van der Ven group, a clusters approach to statistical mechanics(CASM)[34, 35, 28, 36] was used to draw the finite temperature phase diagrams presented in the coming chapters.

The present chapter outlines the methods and techniques used to study titanium interstitial systems. Section 2.1 broadly describes the adopted workflow with the various techniques employed in the current study. Further sections expand on the theory behind different parts of the workflow. Section 2.2 describes density functional theory(DFT) and its implementation in VASP package. Section 2.3 examines the theory behind cluster expansions and the tools explored to fit a predictive coarse grained model. Section

2.4.1 analyzes the statistical averaging done in the current study using methods such as grand canonical Monte Carlo. Finally section 2.4.2 discusses the ways to interpret the data from Monte Carlo to draw phase diagrams and understand finite temperature thermodynamics.

2.1 Workflow

The process starts with setting up a project by providing the input to the CASM code which consists of the crystal systems of interest in the system and the degrees of freedom on the various sublattices present in the crystal. As an example in the Ti-C binary system, observations from the literature and previous computational work done in similar systems suggested that hexagonal close packed(hcp) and face centered cubic(fcc) crystal systems are important. In these crystals, Ti occupies the metal sublattice with close packed triangular lattice planes and while the vacancies on this sublattice are found to be energetically unstable. Both C and vacancies were allowed to occupy the interstitial sublattice. This forms the input for exploring the thermodynamics of the system.

CASM calculates the factor group which represents the symmetry of the primitive structure of the input crystal structure. Next step is the enumeration of configurations using CASM to obtain various ordering of vacancies and atoms in the system. The symmetry operations in the factor group are used to enumerate only the symmetrically unique configurations. Since the primitive structure cannot accommodate all the orderings, we have to enumerate supercells of higher volume than the primitive crystal while ordering atoms on the various sublattices in the crystal. We find the energy of these configurations using DFT implemented in the VASP package.

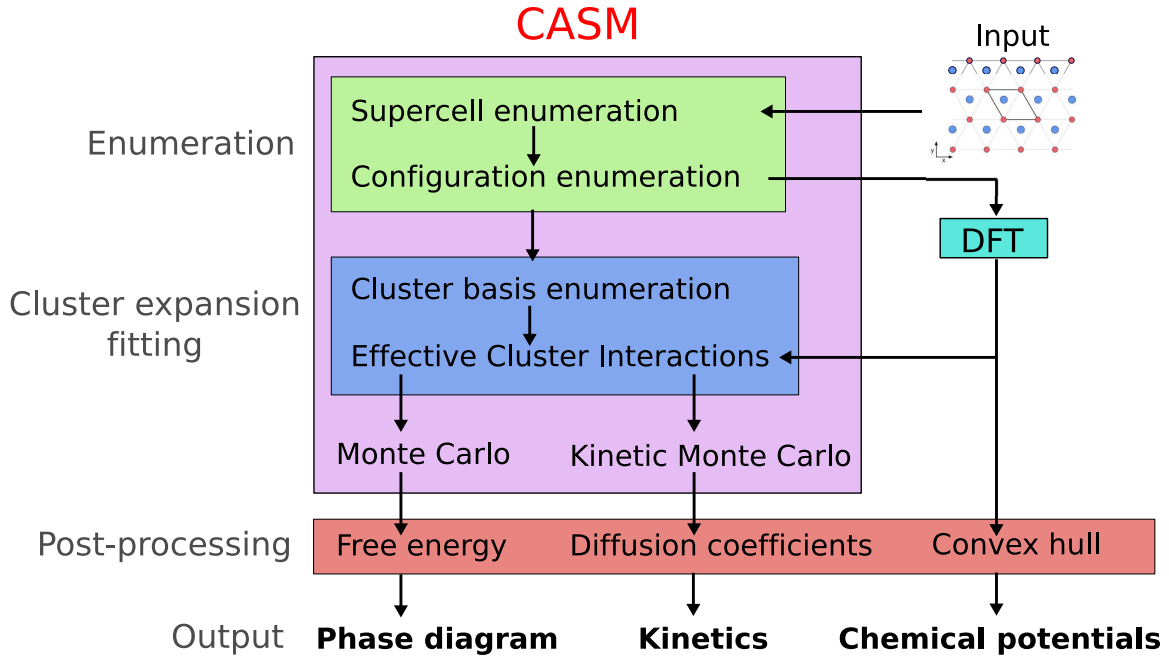


Figure 2.1: Workflow diagram to obtain high temperature thermodynamics and kinetics of a system.

Density functional theory calculations are done at 0 K and the energies of the configurations are obtained after allowing the ions within the structure to relax to their lowest energy positions. Section 2.2 explains the theory behind obtaining the energy of the configurations from first-principles DFT methods. A convex hull of these energies across varying composition determines the stable ground state orderings. Chapters 3 and 4 utilizes the convex hull to determine the ground state ordering of interstitial atoms in Ti.

A cluster expansion model should be constructed to coarse grain the DFT energies and determine the finite temperature phase stability of the system. The model parametrizes the energy of a configuration using clusters of sites enumerated in the system. CASM implements algorithms using python's scikit-learn package[37] to determine the important clusters in the system and provide weights to the clusters which are referred as effective

cluster interactions (ECIs) [38]. Section 2.3 discusses the various methods used in the current study to fit a cluster expansion model. The cluster expansion models reduce the computational cost to determine the energy of a configuration and were used to carry out statistical sampling of a system at finite temperatures using Monte Carlo simulations.

We can get statistical averages of the various thermodynamic properties across temperature and composition space using grand canonical Monte Carlo simulations. At high temperatures, configurational entropy of the system has a significant contribution to the free energy. A series of Monte Carlo simulations across the temperature and chemical potential space using CASM was used to determine the free energy of the system at varying alloying compositions. Section 2.4.1 describes the theory behind the statistical methods to obtain the free energy of the system. We can minimize the free energy to draw phase diagrams as described in Section 2.4.2. This is broadly the workflow that was adopted in the current study and specific chapters discuss the results and challenges in applying the workflow to obtain finite temperature thermodynamics.

2.2 First-principles calculations

Quantum mechanics theory established in the first half of the 20th century can be used to determine the energy of a many electron system. This is a first-principles, or *ab initio*, calculation meaning we start from established theory and do not add any empirical models or parameter fitting to augment the result.

2.2.1 Many electron Hamiltonian

The ground state energy of a many electron system can be obtained using Schrödinger equation[39] expressed as

$$H\Psi = E\Psi \quad (2.1)$$

where H is many body Hamiltonian and Ψ is the wave function which represents the current state of the system. The eigenvalues, E are the solution to the equation and provides the energy of the system. Both the Hamiltonian (H) and the wave function (Ψ) depend on the positions of the nuclei and electrons in the system. For a system with N electrons at positions r_i and M nuclei at position R_i , $H(R_1, R_2, \dots, R_M, r_1, r_2, \dots, r_N)$ represents the complete many body Hamiltonian for the system. We need to divide the Hamiltonian into the kinetic (T) and the potential (V) contributions to analyze the solutions for the equation. Considering the vast difference in mass between the nuclei and the electrons in the system, we can use the Born-Oppenheimer approximation [39] to consider nuclei as point-like particles and simplify the Hamilton (H) as follows

$$H(\vec{r}, \vec{R}) = T(r_i) + V_{ee}(r_i, r_j) + V_{nn}(R_i, R_j) + V_{en}(r_i, R_j) \quad (2.2)$$

The kinetic factor(T) depends only on the positions of electrons as the nuclei are considered to be at "rest". The electrons with charge e and a nuclei with charge $Z_i e$ interact via the Coulomb potential which can be used to determine the electron-electron potential(V_{ee}), the nuclei-nuclei potential(V_{nn}) and the electron-nuclear potential(V_{en}). The Hamiltonian with all the individual kinetic and potential contributions is expressed

as

$$H(\vec{r}, \vec{R}, Z) = - \sum_i^N \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i,j(i \neq j)}^{N,N} \frac{1}{2} \frac{e^2}{|r_i - r_j|} + \sum_{i,j(i \neq j)}^{M,M} \frac{1}{2} \frac{Z_i Z_j e^2}{|R_i - R_j|} + \sum_{i,j}^{N,M} \frac{1}{2} \frac{Z_j e^2}{|r_i - R_j|} \quad (2.3)$$

Solutions for simple Hamiltonians such as particle in a box or single electron systems are possible, but a generalized approach to solve a N electron Hamiltonian and derive an anti-symmetric wave function Ψ is very difficult. There are other approaches available in the literature to simplify the Hamiltonian. In the Hartree approximation [40], the electrons are considered independent simplifying the N particle wave function as shown in eq 2.4. This method does not capture the cohesion of molecules in solids and the solution does not provide an anti-symmetric form of the wave function. In the Hartree-Fock approximation [40], the anti-symmetry is explicitly taken into account by writing the wave function using Slater determinants as shown in eq 2.5. This approximation is known to work well for small molecules but fails for bulk metals and solids as it neglects correlation between electrons due to Coulomb interaction. There are some beyond Hartree-Fock methods such as configuration interactions(CI)[41] and coupled cluster(CC)[42] methods which are computationally expensive to implement.

$$\Psi^H = \psi_1(r_1)\psi_2(r_2) \dots \psi_N(r_N) \quad (2.4)$$

$$\Psi^{HF} = \left\| \begin{array}{cccc} \psi_1(r_1) & \psi_1(r_2) & \dots & \psi_1(r_N) \\ \psi_2(r_1) & \psi_2(r_2) & \dots & \psi_2(r_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \dots & \psi_N(r_N) \end{array} \right\| \quad (2.5)$$

2.2.2 Density functional theory

Reconstructing the many electron Hamiltonian by replacing the wave function Ψ in eq 2.1 with electron density $\rho(r)$ as the fundamental variable is known to work. This is referred as the density functional theory(DFT) and was proposed by Hohenberg, Kohn and Sham [43, 44]. In this dissertation, DFT implemented in VASP package[45, 46, 47, 48] was used to solve the Hamiltonian. The electron density $\rho(r)$ in terms of the wave function Ψ is expressed as

$$\rho(r) = \int |\Psi(r_1, r_2, \dots, r_N)|^2 dr_1 dr_2 \dots dr_N \quad (2.6)$$

The Rayleigh-Ritz variational principle[49] suggests that a observable such as the ground state energy of a many electron system can be determined by minimizing the expectation value of a Hamiltonian as shown in 2.7. The electron density $\rho(r)$ which minimizes the expectation value will provide the ground state energy E_0 .

$$E_0 = \min E[\rho] = \min \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2.7)$$

The energy functional $E[\rho]$ can be separated into electron contributions($F[\rho]$) and external contributions as shown in eq 2.8. The potential V_{ext} comprises of all the factors external to electron-electron interaction. This includes the electron-nuclei interactions along with other external potentials that affect the electron density in the system.

$$E[\rho] = F[\rho] + \int \rho(r) V_{ext} dr \quad (2.8)$$

The functional $F[\rho]$ can be further decomposed as shown in eq 2.9. $T_S[\rho]$ is the kinetic energy of the electrons whereas E_H is the Hartree energy equivalent to the Coulomb

energy of non-interactions electrons. E_{XC} is the remaining part that takes care of energy contribution from exchange and correlation between the electrons.

$$F[\rho] = T_S[\rho] + E_H[\rho] + E_{XC}[\rho] \quad (2.9)$$

The Kohn-Sham equation obtained by reworking the basic many body Hamiltonian equation is as follows

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{eff} \right) \phi_i = \epsilon_i \phi_i \quad (2.10)$$

$$V_{eff} = V^H + V^{XC} + V_{ext} \quad (2.11)$$

where $\rho(r) = \sum_i^N |\phi_i|^2$ and ϵ_i is the energy of the Kohn-Sham orbital.

The potential V^{XC} is the functional derivative of the exchange correlation energy E_{XC} . These are the unknowns which require further approximation to solve the Kohn-Sham equations. Various approximations are available for the exchange correlation term which have to be chosen carefully for each system of interest. In this dissertation, generalized gradient approximation(GGA) is used where the exchange correlation energy $E_{XC}[\rho]$ depends on a function ϵ^{XC} whose variables are the local electron density at a point $\rho(r)$ and the gradient of the density at the point $\nabla\rho(r)$ as shown in eq 2.13. Parametrization of the GGA exchange correlation functional as proposed by Perdew, Burke and Ernzerhof(PBE) [50, 51] was used in the current study.

$$V_{XC} = \frac{\delta E_{XC}[\rho]}{\delta \rho(r)} \quad (2.12)$$

$$E_{XC} = \int \rho(r) \epsilon^{XC}(\rho(r), \nabla\rho(r)) dr \quad (2.13)$$

Further simplification of the electron-electron interaction is possible by coarse graining the contributions from core electrons. This way only the interaction between valence electrons needs to be handled explicitly to determine the ground state energy in the system, reducing the computational cost. This is usually a good approximation as bonding and cohesion in the system is mainly determined by the overlap of valence electrons. Even though core electrons do not participate in bonding, they create a shielding effect on the valence electrons. The Coulomb repulsion from the core electrons and Pauli repulsion when the valence electrons have the same angular momentum as the core electrons reduce the combined attraction the valence electrons experience from the nuclei. The effective potentials that reproduce the combined influence of core electrons and nuclei are termed as pseudopotentials. The potentials implemented in VASP package using the Projector Augmented Wave (PAW) method are used in this dissertation. There are different options for pseudopotentials in VASP depending on the size of the core radius. In this dissertation, VASP recommended potentials were used. The Ti potential considers $3s$, $3p$, $3d$ and $4s$ electrons as valence whereas the interstitial elements consider the $2s$ and $2p$ electrons as valence.

Convergence of the various parameters used in VASP is crucial to reproduce accurate physics of the systems. One of the parameters is the energy cutoff (E_{cut}) which determines the size of the basis set used in the calculations. The electron density in VASP is expressed as a sum of planar waves as seen in eq 2.14. All the plane waves (G) whose energy is below the E_{cut} are used in calculations. Another parameter which is crucial is the grid of the k -space or reciprocal space points at which the wavefunctions are calculated. The plane wave basis used in VASP are easier to handle in reciprocal space as they can be represented by a single point rather than a function that extends to infinity. The number of points in the reciprocal space dictate the accuracy of the calculations. These parameters change

for the different crystal systems and the chemical species of interest and the values used in this dissertation are provided in the individual chapters.

$$\rho(r) = \sum_G \rho_G e^{iGr} \quad (2.14)$$

2.3 Cluster expansion method

Cluster expansion models act as a bridge between first-principles calculations and statistical averaging by Monte Carlo. In section 2.4.1, it will be evident that to calculate thermodynamic averages using Monte Carlo sampling, we need to determine the energy of a large number of configurations. DFT calculations are computationally expensive and scales poorly with the number of atoms in the simulation cell. Cluster expansions can evaluate the energy of large configurations in microseconds. In a system with N lattice sites where each site can be occupied with two types of species, there are a total of 2^N possible configurations (≈ 1 million configurations for a system with 20 sites). Evaluating the energy of this many configurations is tractable with a cluster expansion. Cluster expansion models proposed by Sanchez[52] and De Fontaine[53] were successfully used to coarse grain the first-principles energies in a wide variety of alloy systems[54].

The cluster expansion model can be considered as a generalized Ising model[55] that maps the energy a configuration to the interaction between atoms in small clusters. The model assumes that atoms are in their ideal positions, so systems with minimal relaxation of the atoms are preferred for this method. The 0 K analysis using cluster expansion models are used to determine the true ground states in the system. At high temperatures they can be used in Monte Carlo simulations to determine the energy of configurations and achieve accurate statistical sampling of the configuration space in the system.

2.3.1 Clusters and basis functions

We can define any configuration in the system by using occupation variables on the lattice sites. For example in the fcc Ti-C binary system, the metal sublattice is fixed as it does not allow any vacancies, but the interstitial sites can be occupied by either vacancies or carbon atoms. Occupational variable(σ_i) for an interstitial site i can be defined such that it is equal to 0 when vacancy is present at the site and 1 when a carbon occupies the site. The metal sublattice does not need occupational variables as it does not have any degrees of freedom. Any configuration in the binary system can be defined using the vector $\vec{\sigma} = [\sigma_1, \sigma_2, \dots, \sigma_n]$ which is a collection of the occupation variables of the n interstitial sites in the system.

Occupation variables contain local information of species at the sites, but the energy of system is dependent on the repulsive and attractive interactions between the atoms. To capture the interactions, we can use basis functions of site clusters which are polynomials of the occupation variables in the cluster. Clusters are usually groups of 2(pairs), 3(triplets) or 4(quadruplets) sites in the crystal. Figure 2.2 shows few examples of the pair, triplet and quadruplet clusters on a 2d triangular lattice plane. The basis function(ϕ_α) for a cluster α is formed by multiplying all the occupation variables in the cluster as shown below

$$\phi_\alpha = \prod_{i \in \alpha} \sigma_i \quad (2.15)$$

The cluster basis functions form a complete orthonormal basis set over the configuration space. Any scalar such as the energy of the system can be expressed in terms of the basis sets as

$$E(\vec{\sigma}) = \sum_{\alpha} V_{\alpha} \phi_{\alpha}(\vec{\sigma}) \quad (2.16)$$

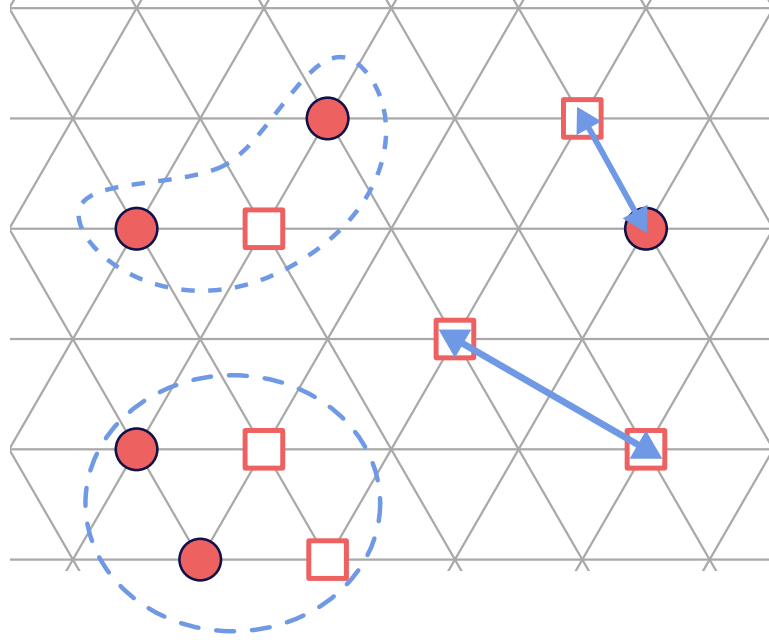


Figure 2.2: Examples of pair, triplet and quadruplet clusters used in making the cluster basis functions.

where $V_\alpha = \langle E | \phi_\alpha \rangle$ is the effective cluster interaction (ECI) of the cluster α . It can be understood as a weight that determines the contribution of the interactions in the cluster, to the energy of the system.

The number of clusters scale exponentially with the size of the system, but in practice we enumerate clusters that are within a certain predefined radius. This is a reasonable simplification because the correlation terms in the first-principles calculations approach zero after a certain distance. This limits the interaction distance between chemical species in the system. Also the clusters should be grouped according to the symmetry of the crystal. The factor group of the system contains symmetry operations that map the system onto itself. Application of these symmetry operators should not change the energy of the system, hence all the clusters that map onto each other by these symmetry operators must have same ECI(V_α). The set of the symmetry equivalent clusters is called an orbit referred as Ω_α , where the cluster α represents all the other clusters in the orbit. Con-

ventionally, we define “correlations” as the average values of the cluster basis functions in the orbit normalized by the multiplicity of the orbit(m_α) and the number of primitive cells in the configuration(N_p) as shown below

$$\langle \phi_\alpha(\vec{\sigma}) \rangle = \frac{\sum_{\beta \in \Omega_\alpha} \phi_\beta(\vec{\sigma})}{m_\alpha N_p} \quad (2.17)$$

We can rework the expression in eq 2.16 to describe the energy normalized by the number of primitive cells($\overline{E}(\vec{\sigma})$) the as follows

$$\overline{E}(\vec{\sigma}) = \frac{E(\vec{\sigma})}{N_p} = \sum_{\alpha} V_{\alpha} m_{\alpha} \langle \phi_{\alpha}(\vec{\sigma}) \rangle \quad (2.18)$$

2.3.2 Determining the effective cluster interactions(ECIs)

We can construct the cluster expansion models by parametrizing the first-principles energies. The CASM code can enumerate clusters as well as configurations in the project using the degrees of freedom in the system and provide the average correlations of cluster orbits for the configurations. Fitting the model will be solving the linear equation in eq 2.19.

$$\overline{E}_{DFT} = \overline{\phi} \overline{V} \quad (2.19)$$

where $\overline{E}_{DFT}$ is a column vector of the DFT energies. $\overline{\phi}$ is the correlation matrix where rows are configurations and columns are the average correlations of cluster orbits. Finally $\overline{V}$ is the column vector of the ECI’s which needs to be resolved.

The solution for the cluster expansion fitting is expected to be sparse in nature which means that many of the entries in the ECI vector $\overline{V}$ are expected to be zero. The aim is to find a sparse $\overline{V}$ by selecting only the important clusters in the system and calculate the values of ECI for the selected clusters by minimizing the root mean squared(rms)

error between the DFT and the predicted energies of the configurations as shown below

$$\min_V \sqrt{\sum_i \left(\bar{E}_{DFT}(\vec{\sigma}_i) - \sum_{\alpha} V_{\alpha} m_{\alpha} \langle \phi_{\alpha}(\vec{\sigma}_i) \rangle \right)^2} \quad (2.20)$$

Selecting the correct clusters is crucial for deriving a predictive cluster expansion fit. Typically for a binary system, we determine ECIs using DFT energies of around 200 to 400 configurations. During Monte Carlo simulations the cluster expansion fit needs to predict energies of thousands of configurations, which have not been calculated in DFT, hence it is important to discover a fit with good predictive power. Machine learning methods such as genetic algorithms[56] can be used to search through various choices for selecting a group of clusters[38]. We can get a good predictive fit by selecting the group of clusters that minimize the cross-validation score. A cross-validation score is the rms error between DFT and cluster expansion predicted energies of the configurations that were left out while selecting clusters. Typically around 10% of the configurations can be left out of the input for genetic algorithms and a “good” fit should be able to predict the energies of these configurations to a reasonable accuracy[57]. This ensures the prediction quality for the selected cluster expansion fit.

It is important for the cluster expansion fit to predict accurate energies for ground states of the system. This becomes crucial during Monte Carlo simulations as ground states are sampled more often than other states. Hence while calculating the prediction error, a weighted average is typically used. Each configuration is weighted according to its distance from the convex hull(ΔE) as $A \exp(-\Delta E/k_B T)$ [28]. Values for A and temperature T in the expression determine how skewed the weights are towards the configurations close to the convex hull.

In practice, cluster expansion fitting is an iterative process. Initially the DFT energies of the configurations with smaller supercell sizes are used to generate the fit. As the convex hull from these configurations is not guaranteed to contain the true ground states for the system, the fit is used to predict energies of configurations of larger supercells and then predict ground states in this expanded set of configurations. The DFT energies of the predicted ground state configurations are calculated and the cluster expansion model will be refit including the newly calculated energies in the input. These iterations in model fitting are performed until a cluster expansion fit is found that can predict accurate energies of the ground states and do not predict any new ground states configurations in the larger supercells. In a system where configurations from more than one crystal system are stable, this iterative process has to be used to derive an individual fit for each crystal system modeled using configurations enumerated on that crystal.

2.4 Thermodynamic averaging of the system

Cluster expansion models can be used to extract the macroscopic properties of the system using statistical sampling. If a system is under equilibrium, the thermodynamic properties such as free energy, entropy and heat capacity can be calculated by performing an ensemble average of the microstates of the system[58]. Any state that a system can achieve is considered a microstate of the system. As the temperature rises, the system keeps fluctuating between the different microstates of the system. The probability(P) that a system is at a certain microstate(σ) can be defined as

$$P = \frac{1}{Z} \exp(-\Omega(\sigma)/k_B T) \quad (2.21)$$

where k_B is the Boltzmann constant, T is the temperature, Z is the partition function and Ω is the potential of the microstate(σ) in a certain ensemble.

The Partition function(Z) for an ensemble is defined as

$$Z = \sum_{\sigma} \exp(-\Omega(\sigma)/k_B T) \quad (2.22)$$

The independent parameters that a system is allowed to experience decides the type of ensemble to be used. The choice of the ensemble determines the appropriate potential (Ω) to be used in calculating the probability of a microstate. In a canonical ensemble where the number of atoms, volume and temperature are the independent variables, the potential Ω is equal to the energy(E) of a microstate.

The average of any thermodynamic property that depends on the microstates can be measured by taking a weighted average of the property over all microstates. The probability of a microstate acts as the weight of the microstate in the average. For example average energy(E) of the system can be defined as in eq 2.23. We can use Monte Carlo methods to perform the summation and free energy integration techniques can be used to determine the finite temperature free energy of the system using the thermodynamic averages.

$$E = \sum_{\sigma} E(\sigma) P(\sigma) \quad (2.23)$$

2.4.1 Grand canonical Monte Carlo

In order to get finite temperature free energy and thereby the phase diagrams we need to work in the grand canonical ensemble. In this ensemble the independent parameters are temperature, volume and the chemical potential of the species(μ). The potential

$\Omega(\sigma)$ for the ensemble is defined as

$$\Omega(\sigma) = E(\sigma) - \sum_i \mu_i N_i \quad (2.24)$$

As the number of microstates is large, it is impossible to calculate averages by taking a summation over all the microstates in the system as suggested in eq 2.23. Also many microstates have a very low probability making their contributions to the average negligible. Monte Carlo methods are a way to sample the microstates according their probability. By averaging over all the samples during a Monte Carlo simulation we can get thermodynamic average very close to the ensemble averages of the system. There are many Monte Carlo methods to sample the states, in this dissertation Markov chain Monte Carlo (MCMC) sampler was used. The sampler provides a way to switch between microstates A and B using the transition probability, $P_{A \rightarrow B}$.

For example if the simulation starts at the microstate A and is trying to switch to microstate B. Then the change is the potential(Ω) is

$$\Delta\Omega_{A \rightarrow B} = \Omega(\sigma_A) - \Omega(\sigma_B) \quad (2.25)$$

If the switch from A to B lowers the potential, the switch is always favored

$$if \quad \Delta\Omega_{A \rightarrow B} < 0 \quad then \quad P_{A \rightarrow B} = 1 \quad (2.26)$$

But if the switch from A to B increases the potential, then the switch is accepted by a probability that depends on the change in potential.

$$if \quad \Delta\Omega_{A \rightarrow B} > 0 \quad then \quad P_{A \rightarrow B} = exp(-\Delta\Omega_{A \rightarrow B}/k_B T) \quad (2.27)$$

In practice, this probability is enforced using random number generators. A random value between 0 and 1 is generated using uniform distribution. If the exponential value in eq 2.27 is greater than the random value then the switch is accepted. We can perform these switches between different states repeatedly and collect the trajectory of the thermodynamic values while sampling. The average of the values in the trajectory provides the thermodynamic average of the property in the system. It is important to make sure that the system has equilibrated before starting to collect samples and also the thermodynamic values should be converged before we stop the simulations. There are methods described in the literature to make sure accurate values of the thermodynamic properties are obtained[59].

2.4.2 Free energy Integration

We can calculate Gibbs free energy(G) using the thermodynamic averages from a grand canonical Monte Carlo simulation. The Gibbs free energy is defined as

$$G = U - TS + PV \quad (2.28)$$

where U is the internal energy which is equal to the energy(E) of system. The PV term can be neglected as DFT simulations are performed at zero pressure. But entropy(S) is not something that can be directly obtained from Monte Carlo simulations.

We can use integration techniques[59, 60] to calculate the grand canonical potential ϕ defined as follows

$$\phi = G - \sum_i \mu_i N_i = U - TS + PV - \sum_i \mu_i N_i \quad (2.29)$$

$$d\phi = -SdT - \sum_i N_i d\mu_i \quad (2.30)$$

Using the definition of ϕ we can derive the following equation where $\beta = 1/k_B T$

$$d(\beta\phi) = (U - \sum_i \mu_i N_i) d\beta - \beta \sum_i N_i d\mu_i \quad (2.31)$$

As mentioned earlier, in a grand canonical ensemble the independent variables are temperature (T) and chemical potential of the species (μ_i). We can run Monte Carlo simulations on pathways where one of the variables is kept constant while increase the other changed in incremental steps. In the case of a constant temperature pathway, we can substitute $dT = d\beta = 0$ in eq 2.31 and integrate both sides of the equation from an initial state I to final state F to derive

$$\int_I^F d(\beta\phi) = - \int_I^F \beta \sum_i N_i d\mu_i \quad (2.32)$$

$$\phi_F = - \int_I^F \sum_i N_i d\mu_i + \phi_I \quad (2.33)$$

We can obtain the average values of N_i along the path and calculate the integrand in eq 2.33 using numerical integration techniques. If we start from a initial state I with extreme values of chemical potential of the species (μ_i), we can neglect the configurational entropy (S) in the system to get the value of ϕ_I and determine the free energy at the final state ϕ_F of the system. Similar derivation can be done for the pathways where the chemical potential of the species (μ_i) are constant.

By performing the integration along several constant temperature pathways we can get the Gibbs free energy of the system over the (T, μ_i) space. We can utilize the common tangent construction method to derive the phase boundaries of the stable phases in the system and draw the temperature-composition phase diagrams. In this dissertation, chapters 5 and 6 use this method to derive binary Ti-X ($X = \text{C}, \text{N}, \text{O}$) phase diagrams whereas chapter 7 presents the ternary Ti-Al-O phase diagram.

Chapter 3

Low temperature ordering in titanium oxides

3.1 Introduction

Titanium is a highly reactive element and forms a rich variety of compounds and solid solutions with elements such as oxygen [61, 17], nitrogen [62], carbon [19] and boron [22].

The Ti-O binary in particular consists of a wide variety of stable and metastable oxides and suboxides [61]. These include the rutile, anatase, brookite and bronze-B polymorphs of TiO_2 , the family of TiO_{2n-1} Magnéli phases, corundum Ti_2O_3 , a vacancy containing rocksalt form of TiO and hcp based TiO_x suboxides. The list of suboxides was recently expanded after the synthesis of a new polymorph of TiO having an ω -Ti sublattice with oxygen filling a subset of its interstitial sites [63].

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The oxides of Ti are used in many wide-ranging applications. The various polymorphs of TiO_2 , for example, are actively studied as electrodes for Li and Na-ion batteries and for photocatalytic applications[64, 60, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75]. Many of the oxides in the Ti-O binary form as part of a multi-layer oxide scale as Ti and its alloys are exposed to oxygen rich environments. Each oxide polymorph has very distinct properties. The metastable anatase form of TiO_2 , for example, is a more favorable coating of Ti alloys for biomedical applications than the stable rutile form[76, 77]. In photocatalysis applications, the presence of both anatase and rutile are desired to realize optimal properties [78, 79]. The formation of a particular oxide polymorph on the surface of an oxidized Ti alloy seems to be very dependent on the sequence of suboxides formed during the initial stages of oxidation and methods to select favorable TiO_2 crystal structures during oxidation are actively sought [20, 80, 81].

In spite of the apparent complexity of the Ti-O binary there is a remarkable commonality among the stable and metastable Ti oxides and suboxides. Most of the oxides and suboxides can be viewed as Ti-vacancy and/or oxygen-vacancy orderings over four common parent crystal structures. For example, rutile TiO_2 , the Magnéli TiO_{2n-1} phases and corundum Ti_2O_3 can all be described as different Ti-vacancy orderings over the octahedral interstitial sites of an hcp oxygen sublattice. The anatase TiO_2 and rocksalt TiO phases, in contrast, both share the same fcc oxygen sublattice, differing primarily in the number and arrangement of Ti cations filling octahedral interstitial sites. At Ti rich compositions, oxygen dissolves into hcp Ti, partially filling its octahedral sites. At intermediate temperatures the dissolved oxygen in hcp Ti is disordered while at low temperature it orders to form the hcp based Ti_6O , Ti_3O and Ti_2O suboxides. The fourth class of oxides consists of an ω -Ti sublattice with oxygen occupying pyramidally coordinated interstitial sites. Early studies reported a Ti_3O_2 stoichiometry as having an ω -Ti

sublattice [82], while the recent study of Amano et al. [63] demonstrated an ability to synthesize TiO having such a crystal structure.

In this chapter, we report on the first-principles study to determine the ordering of atoms in the stable and metastable Ti-O binary phases at zero kelvin. Section 3.3 describes a systematic search for the lowest energy oxygen-vacancy and/or titanium-vacancy orderings within four parent crystal structures: (i) hcp Ti, (ii) ω -Ti, (iii) rocksalt TiO and (iv) hcp oxygen. Section 3.4 compares the predicted Ti-O phases to experimental observations and reveals several discrepancies. These discrepancies are further investigated by exploring the sensitivity of predicted relative stabilities of oxides using a range of approximations to DFT and extensions such as DFT+U and HSE.

3.2 Methodology

First-principles electronic structure methods were used to predict phase stability in the Ti-O binary at zero kelvin. All first-principles calculations were performed with the VASP package [45, 46, 47, 48]. The enumeration of different oxygen-vacancy and titanium-vacancy orderings over various parent crystal structures was performed with the CASM software package [34, 35, 28, 36]. CASM was also used to construct and parameterize cluster expansion Hamiltonians and to perform finite temperature Monte Carlo simulations.

The majority of first-principles electronic structure calculations were performed within the generalized gradient approximation to density functional theory using the Perdew, Bruke and Ernzerhof (DFT-PBE) parameterization[50, 51]. Bench mark calculations were also performed with other approximations and extensions to DFT. These included the local density approximation (LDA) as parameterized by Perdew and Zunger [83]

and other GGA approximations such as those by Perdew and Wang (PW91)[84, 85], Perdew, Ruzsinszky, Burke *et. al.* revised for solids (PBEsol)[86] and the latest potential developed by Sun, Ruzsinszky and Perdew (SCAN)[87]. We also used DFT-PBE+U following the approach prescribed by Dudarev *et. al.*[88] and the hybrid DFT-Hartree Fock approach by Paier *et. al.* (HSE)[89] as implemented in VASP.

Interactions between core and valence electrons were accounted for with the projector augmented wave (PAW) pseudopotential method [90, 91]. The PAW potentials treat the 3s, 3p, 3d and 4s orbitals of Ti (Ti sv) and the 2s and 2p orbitals of O as valence states. A plane wave energy cutoff of 550 eV was used. A k-point convergence analysis was performed for the primitive cells of each distinct parent crystal structure and the k-point grids were scaled to ensure the same or higher k-point density in reciprocal space for all structures that are supercells of the primitive cells. The following Γ -centered k-point grids were found to converge the energy to within 2 meV/atom: (i) a $14 \times 14 \times 8$ k-point grid for the suboxides having an hcp Ti sublattice; (ii) a $13 \times 8 \times 8$ k-point grid for suboxides and oxides having an ω -Ti sublattice; (iii) a $15 \times 15 \times 15$ k-point grid for the rocksalt based oxides and (iv) a $15 \times 15 \times 6$ k-point grid for rutile, which was used to assess k-point convergence for the oxides having an hcp O sublattice. All the structures were first relaxed with respect to both their lattice vectors and their internal coordinates to achieve a force convergence of 0.02 eV /Å and an energy convergence of 10^{-6} eV. A final static run was performed at the relaxed volume. Partial occupancy during relaxation runs was treated with the method of Methfessel-Paxton (order 2) and the tetrahedron method with Blochl corrections was used for the static runs.

Most PBE calculations were performed non-spin polarized. Magnetism in titanium oxides is not common and is only expected to occur in the presence of Ti^{3+} ions. This Ti

valence may occur in the composition interval between Ti_2O_3 and TiO_2 . We performed spin-polarized calculations on all structures residing on the convex hull and found that all ferromagnetically initialized states relaxed to a non magnetic state without any local moments. There is some experimental evidence in the literature for the existence of magnetism in the corundum Ti_2O_3 compound[92, 93] and the Magnéli phases[94, 95]. These phases all share a common hcp O sublattice with Ti ordering over a subset of octahedral sites. Therefore, all PBE calculations for the structures obtained by decorating the octahedral sites of hcp O with Ti were performed spin polarized. All other benchmark calculations (LDA, PW91, PBEsol, SCAN, HSE and DFT+U) were performed spin polarized.

3.3 Ground state analysis

We systematically enumerated different Ti-vacancy and/or oxygen-vacancy orderings within four classes of parent crystal structures: (i) hcp Ti with oxygen filling octahedral sites, (ii) rocksalt TiO allowing for Ti-vacancy and oxygen-vacancy orderings over the fcc Ti and fcc O sublattices, (iii) ω -Ti with oxygen filling a subset of the pyramidal interstitial sites, and (iv) hcp O with Ti filling octahedral interstitial sites.

As measures of concentration, we use x to denote the ratio of the number of oxygen, N_{O} , to the number of titanium, N_{Ti} , (i.e. $x = N_{\text{O}}/N_{\text{Ti}}$) and y to denote the atom fraction ($y = N_{\text{O}}/(N_{\text{Ti}} + N_{\text{O}})$). To distinguish the different parent crystal structures, we adopt the following naming scheme. Since hcp Ti is conventionally labelled α , we will refer to any of the suboxides having an hcp Ti sublattice as $\alpha\text{-TiO}_x$. Similarly for the oxides and suboxides that have an ω -Ti sublattice we use $\omega\text{-TiO}_x$. The high temperature disordered form of rocksalt is named γ in the literature [61, 17]. We will, therefore, refer to rocksalt

derived phases using γ and add a prime to distinguish a vacancy ordered rocksalt phase from the disordered solid solution (e.g. γ' -TiO for the ordered phase versus γ -TiO for the disordered phase).

Below we describe the lowest energy orderings in each parent crystal structure. Formation energies are all expressed relative to the same reference states, taken to be hcp-Ti and anatase-TiO₂. The formation energies, $E_f(y)$ for each suboxide Ti_{1-y}O_y, can be expressed as

$$E_f(y) = E(y) - (1 - 3y/2)E[\text{Ti}] - (3y/2)E[\text{TiO}_2] \quad (3.1)$$

where $E(y)$ is the total energy per atom and $E[\text{Ti}]$ and $E[\text{TiO}_2]$ are the energies per atom of hcp-Ti and anatase TiO₂ respectively.

3.3.1 Hcp based TiO_x suboxides

Hcp Ti consists of an ABAB stacking of triangular close-packed planes. Dissolved oxygen in hcp Ti occupies octahedral sites [96]. The collection of octahedral sites between a pair of AB stacked close-packed Ti layers also forms a triangular lattice as illustrated in Figure 3.1 and has a C stacking sequence relative to the adjacent Ti AB layers. Every layer of octahedral sites has the same C stacking such that the octahedral sites by themselves form a simple hexagonal lattice within hcp Ti. The number of octahedral interstitial sites is equal to the number of Ti atoms forming the hcp crystal structure. Figure 3.1 also shows a side view of the hcp crystal with the interstitial octahedral layers labeled as C.

We enumerated 504 different oxygen vacancy orderings within symmetrically distinct supercells up to a volume of 6 hcp primitive unit cells. Figure 3.2(a) shows the calculated formation energies of these orderings. Also shown in Figure 3.2(a) is the global

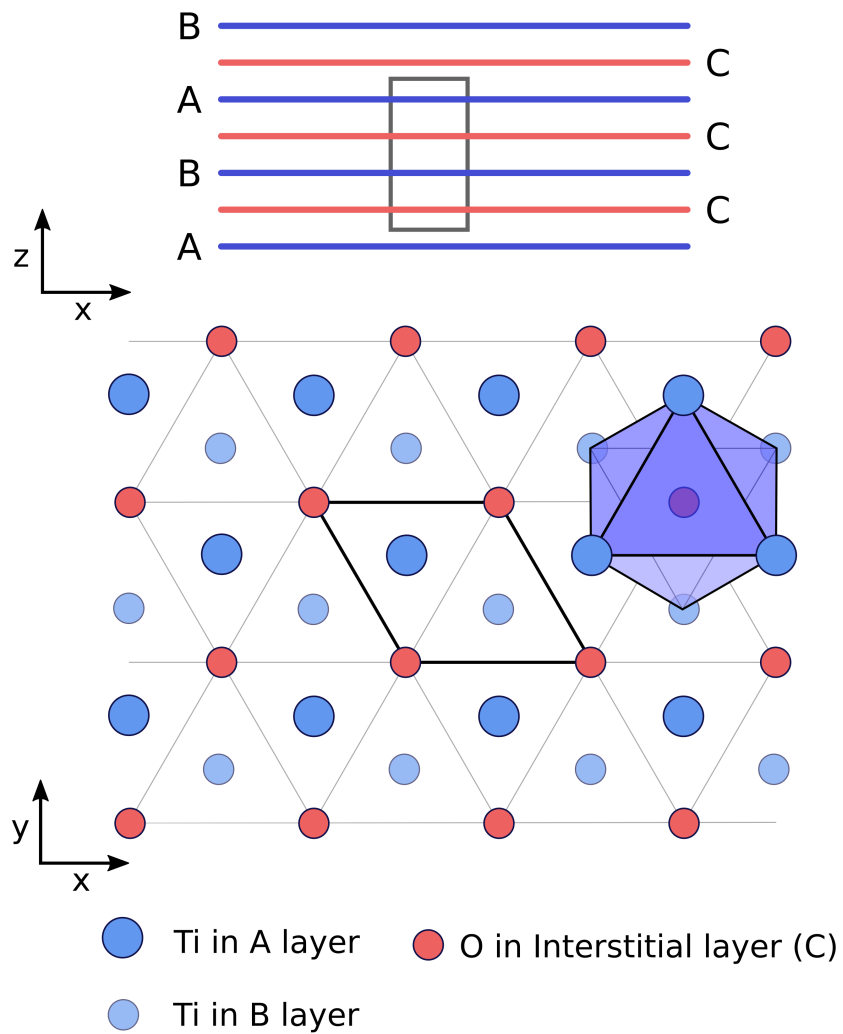


Figure 3.1: Depiction of the hcp crystal structure represented as an A-B stacking of close packed triangular lattices of metal atoms. Interstitial oxygen fills octahedral voids formed by the metal atoms in the interstitial layers. These sites also form a two-dimensional triangular lattice that has a C stacking relative to the hcp crystal

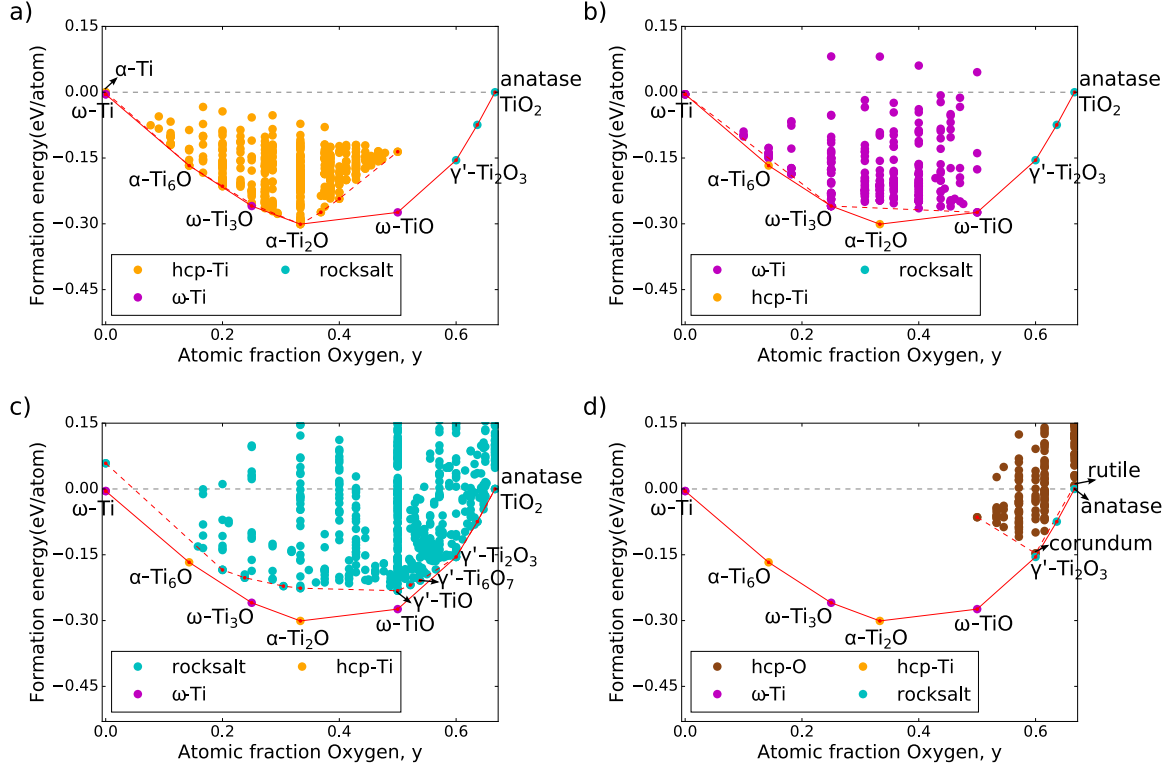


Figure 3.2: Formation energies of enumerated oxygen-vacancy and/or titanium-vacancy orderings within (a) hcp Ti (labeled α), (b) ω -Ti, (c) rocksalt and (d) hcp oxygen. The global convex is shown as solid lines and the metastable convex hulls of each parent crystal structure are shown using dashes lines. The formation energies are calculated relative to hcp Ti and anatase TiO_2 .

convex hull, connecting the lowest energy orderings over all four families of parent crystal structures considered in this work.

There are three ground state orderings when considering only the oxygen-vacancy configurations in hcp TiO_x : α - Ti_6O , α - Ti_3O and α - Ti_2O . The first ground state, α - Ti_6O , has oxygen filling one out of every six octahedral sites. They segregate to every other layer along the c -axis resulting in a staged ordering. The filled layers have an oxygen composition of $1/3$ with oxygen ordering on a $\sqrt{3}a \times \sqrt{3}a$ two-dimensional supercell of the triangular lattice. This ordering is shown in Figure 3.3(a). The second ground state, α - Ti_3O , is very similar to α - Ti_6O in that it is also staged along the c -axis and has oxygen

ordered on a $\sqrt{3}a \times \sqrt{3}a$ supercell within the filled layers. The filled layers, however, now have a composition of $2/3$ as illustrated in Figure 3.3(b). The two-dimensional supercells of each filled layer in Ti_6O and Ti_3O are staggered relative to each other along the c -axis. Both the Ti_6O and Ti_3O low energy orderings are consistent with those predicted to be ground states in previous first-principles studies [97, 98]. The third predicted ground state with the $\alpha\text{-Ti}_2\text{O}$ stoichiometry has $1/2$ of its octahedral sites filled by oxygen. This ordering is not staged but has oxygen instead filling each layer uniformly. Within each layer, the oxygens arrange in a zig-zag pattern separated by zig-zags of vacant sites as illustrated in Figure 3.3(c). The zig-zag rows are staggered when going from one interstitial layer to the next avoiding oxygen overlap between adjacent layers along the c -axis. This ordering was also found to be a ground state by Burton and van de Walle [97].

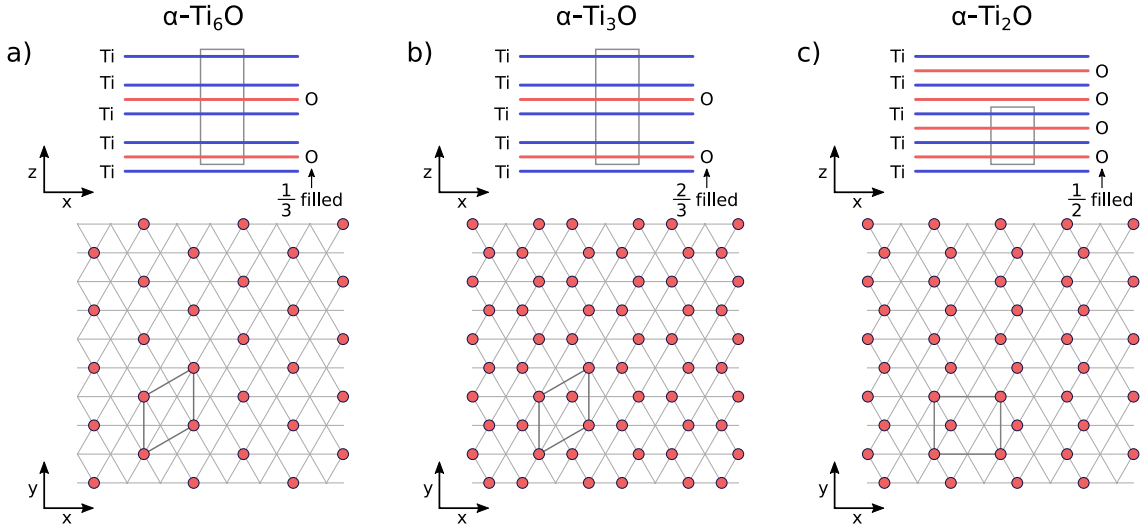


Figure 3.3: Ground state oxygen orderings over the interstitial sites of hcp Ti: (a) $\alpha\text{-Ti}_6\text{O}$, (b) $\alpha\text{-Ti}_3\text{O}$ and (c) $\alpha\text{-Ti}_2\text{O}$. In $\alpha\text{-Ti}_6\text{O}$ and $\alpha\text{-Ti}_3\text{O}$ the oxygen fills alternating layers and forms a $\sqrt{3}a \times \sqrt{3}a$ supercell parallel to the hcp basal plane. The oxygen of $\alpha\text{-Ti}_2\text{O}$ order as zig-zag rows.

3.3.2 Rocksalt based oxides

The rocksalt crystal structure consists of two fcc sublattices with the sites of one fcc sublattice filling the octahedral sites of the other fcc sublattice. Titanium and oxygen can form a rocksalt based crystal structure in which Ti occupies one fcc sublattice and oxygen the other. A rocksalt type phase is observed at high temperatures, which is reported to be stable in a wide concentration range ($0.45 < y < 0.6$ for $\text{Ti}_{1-y}\text{O}_y$). This phase is usually referred in the literature as γ -TiO and contains vacancies on both the Ti and O sublattices that are disordered at high temperature [99].

Remarkably, the low temperature, stoichiometric form of equiatomic TiO contains an equal number of oxygen and titanium vacancies on each fcc sublattice that order to form a supercell containing 6 primitive rocksalt TiO unit cells [100]. In this ordering, one out of every six Ti and O sublattice sites are vacant. The unit cell and vacancy ordering is illustrated in Figure 3.4. In the literature, this ordered rocksalt has been referred to as α -TiO, Ti_5O_5 or monoclinic-TiO [61, 101]. To avoid confusion with hcp Ti and its suboxides, which are also referred to as α , we will label the low temperature ordered rocksalt as γ' -TiO, where γ indicates that it is derived from rocksalt and the prime signifies that it is ordered.

The anatase form of TiO_2 is also related to rocksalt in that it consists of an fcc oxygen sublattice with Ti ordered over half the octahedral interstitial sites. It can be derived from perfect rocksalt TiO by replacing half the Ti with vacancies. In fact, it is well known that having a precursor rocksalt phase fosters the further formation of anatase as opposed to rutile during the oxidation of Ti alloys [81].

To explore phase stability in the rocksalt parent crystal structure as a function of concentration, we systematically enumerated 720 vacancy orderings over the Ti and O sublattices of rocksalt TiO in supercells that contain up to 12 rocksalt primitive cells. Figure 3.2(c) shows the calculated formation energies for all the rocksalt derived orderings. Also shown is the global convex hull over the four parent crystal structures. There are five orderings at oxygen rich concentrations that reside on the convex hull. These include anatase TiO_2 at a mole fraction of $y = 2/3$ and the experimentally observed vacancy ordered γ' -TiO (mole fraction $y = 1/2$). Three additional ground states are predicted that we label γ' - Ti_6O_7 (mole fraction $y = 0.538$), γ' - Ti_2O_3 (mole fraction $y = 0.6$) and γ' - Ti_4O_7 (mole fraction $y = 0.636$), with the prime again signifying that they are vacancy ordered rocksalt phases. The γ' - Ti_4O_7 ordering barely breaks the convex hull and is nearly degenerate in energy with a two-phase mixture of γ' - Ti_2O_3 and anatase- TiO_2 .

The three ground state orderings γ' -TiO, γ' - Ti_6O_7 and γ' - Ti_2O_3 exhibit very similar vacancy arrangements. Figure 3.4 illustrates the vacancy ordering within γ' -TiO. Both the oxygen and titanium vacancies coalesce on one out of every three parallel (110) planes of the parent rocksalt crystal. Within those planes they order into a checker board-like pattern also shown in Figure 3.4. The γ' - Ti_2O_3 ground state only has Ti vacancies and these again coalesce on one out of every three parallel (110) planes of rocksalt as illustrated in Figure 3.5(a).

The vacancy ordering in γ' - Ti_6O_7 is slightly more complex than in the two other ground states since the vacancies coalesce to every (110) plane. Within each (110) plane, however, there are strips with a Ti and O vacancy arrangement as in TiO and strips that contain no vacancies. This ordering within the (110) planes is illustrated in Figure 3.5(b). The (110) planes are then staggered in the three dimensional crystal such that a

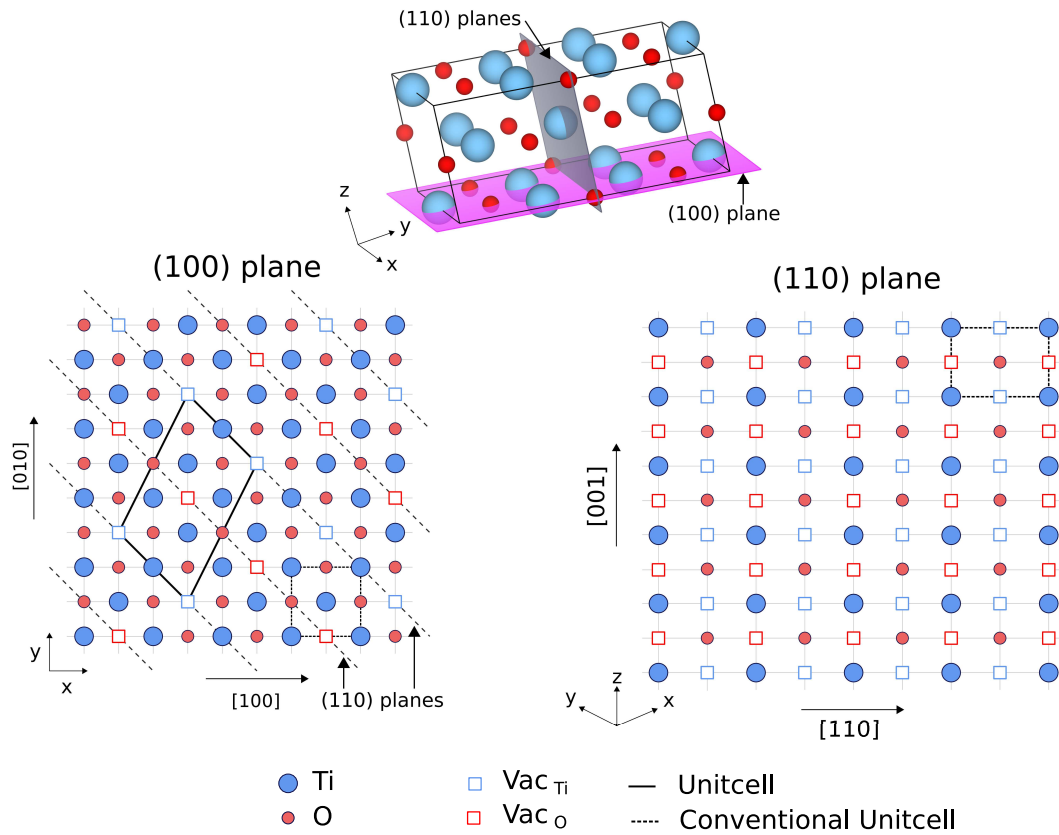


Figure 3.4: Illustration of the γ' -TiO structure. Titanium and oxygen vacancies coalesce on every third (110) plane.

strip containing vacancies neighbors strips that do not contain vacancies in the adjacent (110) planes.

3.3.3 ω -Ti based suboxides

Experimental studies have identified suboxides with an ω -Ti sublattice. The ω -Ti crystal structure is in fact the stable form of Ti at low temperatures and is predicted by PBE to have a lower energy than hcp Ti [102, 103]. The ω -Ti sublattice consists of two-dimensional honeycomb planes, labeled H, interleaved by triangular layers, labeled T (Figure 3.6). The unitcell has 3 Ti atoms. The Ti atoms of the triangular layers stack directly above and below the empty hexagonal rings of the honeycomb planes as illustrated in Figure 3.6. The ω -Ti sublattice has a variety of large interstitial sites all centered within the triangular T-layers that can be occupied by oxygen. One set of interstitial sites are coordinated by Ti forming a square pyramid. These are shown in Figure 3.6(b). There are two such sites for every Ti, however, pairs of pyramidal sites share faces, thereby, making it energetically very unfavorable to simultaneously occupy neighboring sites. Oxygen can also occupy the center of the square base between pairs of pyramidal sites. These are shown in Figure 3.6(c). There are a total of two square pyramidal sites and one square base site per Ti in the ω crystal structure.

We enumerated over 293 oxygen-vacancy configurations in ω -Ti with oxygen either in the square pyramidal sites or at the center of their base. Due to their close proximity, we never allowed simultaneous occupation of nearest neighbor pyramidal sites. Figure 3.2(b) shows the formation energies of the different configurations along with the global convex hull over all structures considered in this work. As is clear in Figure 3.2(b), two orderings having the ω -Ti sub-lattice reside on the global convex hull. The first is the ω -Ti₃O and has an atom fraction $y=0.25$ while the second has atom fraction $y=0.5$ corresponding to

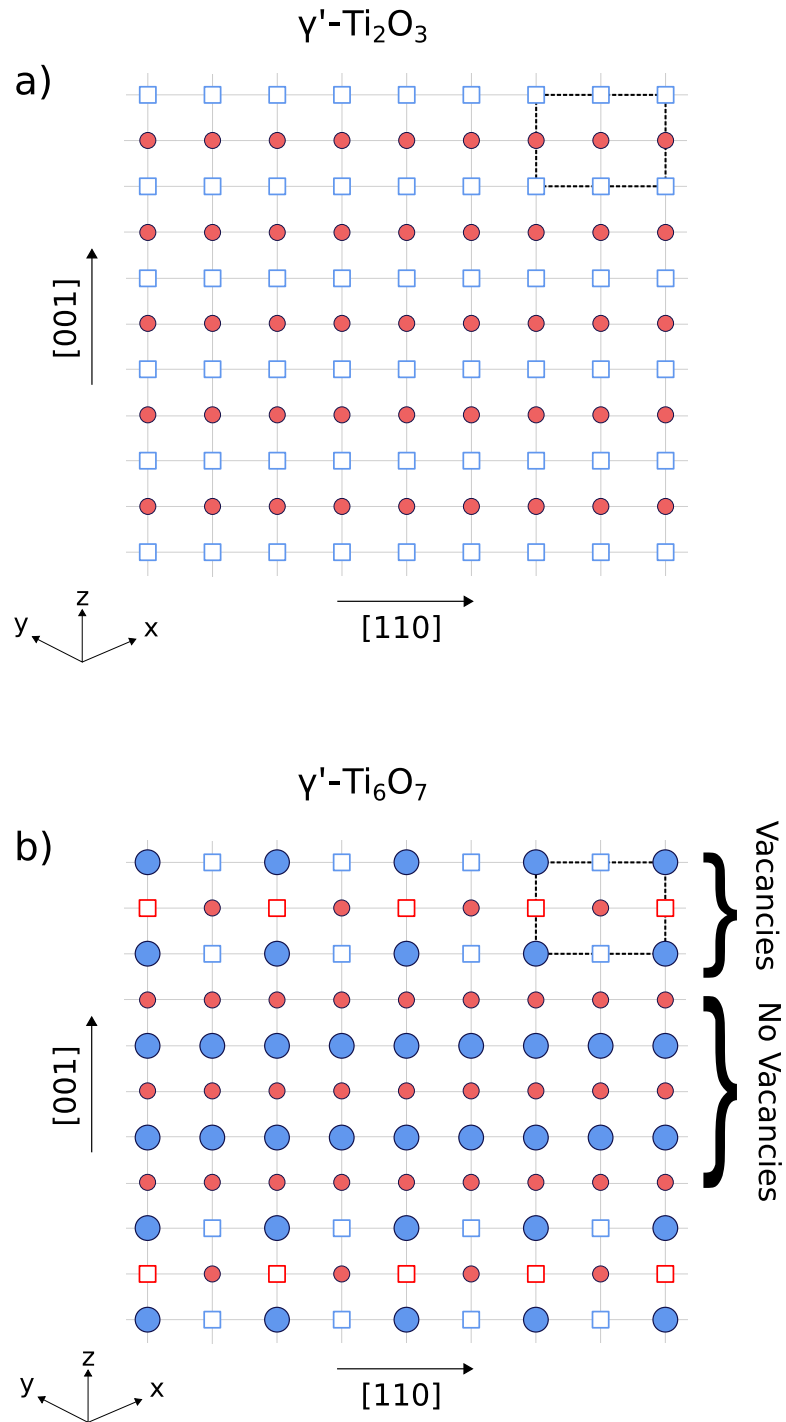


Figure 3.5: Vacancy orderings over the titanium and oxygen sites of a (110) plane of rocksalt for (a) γ' -Ti₂O₃ and (b) γ' -Ti₆O₇.

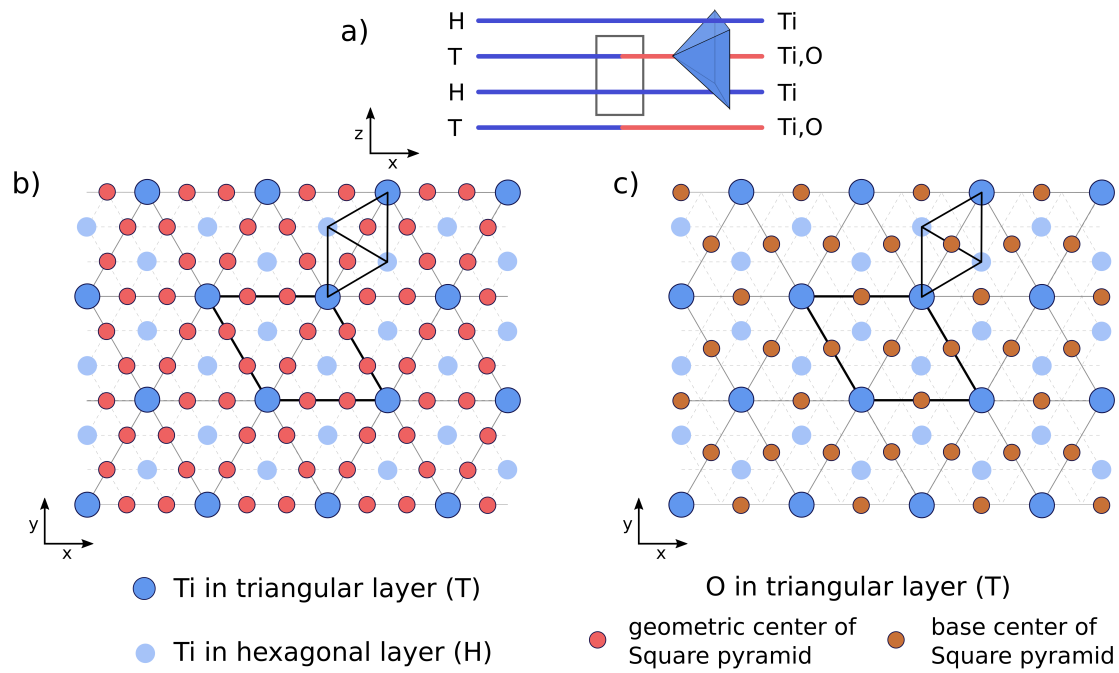


Figure 3.6: Illustration of the ω -Ti crystal and candidate interstitial sites. The ω crystal structure is made up of honeycomb (H) layers alternated by triangular layers (T) as shown in (a) and has square pyramidal interstitial sites that can be occupied by oxygen. Oxygen can also reside at the base center of a square pyramidal site. (b) and (c) show the arrangement of Ti and O atoms in the T and H layers respectively.

ω -TiO. There is, however, no ω -Ti based ground state having a stoichiometry of Ti_3O_2 as reported in early experimental studies [23, 96, 82].

In the ω -TiO ground state, the oxygen occupies half the Ti-square pyramidal sites. As is clear in Figure 3.7a), the oxygen in the ω -TiO ground state fill alternating pyramidal sites. There are two symmetrically equivalent variants of this ordering. One variant can be transformed into the other by passing each oxygen through the square base of its pyramidal site to its neighboring square pyramidal site. Figure 3.8 shows how the energy of the crystal varies along this path. In the ω -TiO ground state, the square base site, corresponding to the midpoint along this path, is an unstable position and coincides with a local maximum in the energy surface of Figure 3.8. Furthermore, the barrier to uniformly go from one ground state variant to the other is very large. The ground state ω -based TiO configuration is predicted to be more stable than the rocksalt γ' -TiO configuration. In fact the phase was recently synthesized by Amano *et.al* [63]. While they labeled it the ϵ phase, we will refer to it as ω -TiO to emphasize its relation to the ω crystal structure.

The other ω -Ti based ground state at lower oxygen fraction, ω - Ti_3O , has oxygen occupying one third of the square base sites. Its ordering is shown in Figure 3.7(b). Inspection of the relaxed oxygen-vacancy configurations within ω - TiO_x revealed a shift in the preference for the square pyramidal sites to the square base of the pyramidal sites as the oxygen concentration decreases. Figure 3.8 shows that the square base sites of ω - Ti_3O are a shallow minimum as a function of oxygen displacements that take it from the square base sites to the centers of the adjacent pyramidal sites.

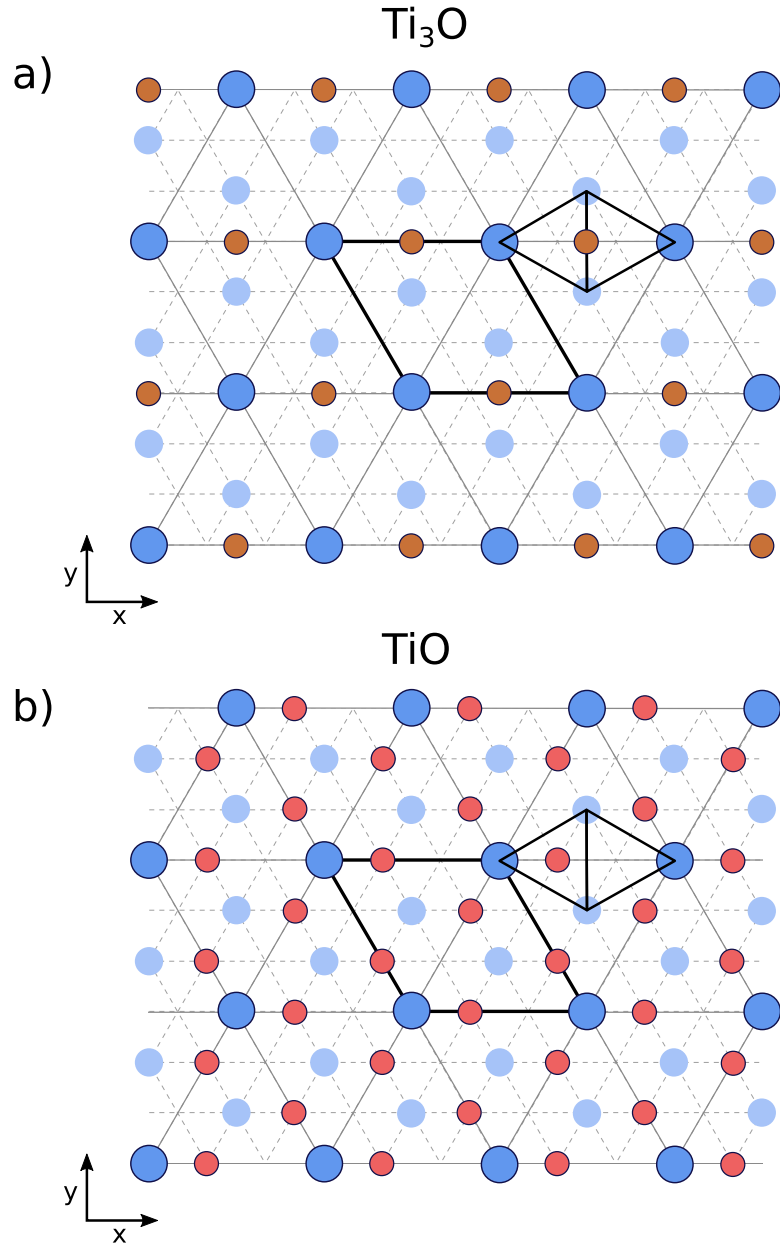


Figure 3.7: Oxygen orderings within the T layers of (a) $\omega\text{-Ti}_3\text{O}$ and (b) $\omega\text{-TiO}$.

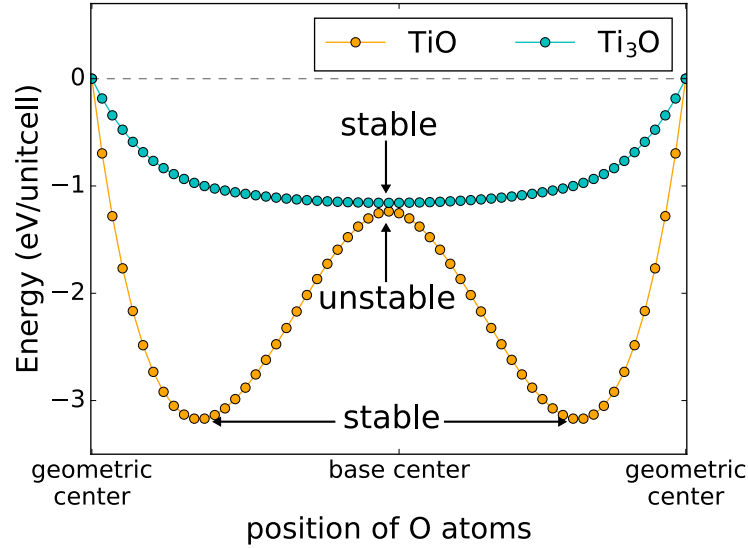


Figure 3.8: Energy landscape along the path joining pyramidal and base center interstitial positions in the ground state structures of ω - Ti_3O and ω - TiO .

3.3.4 Hcp oxygen based oxides

A large number of the oxygen rich oxides of Ti can be mapped onto structures having an hcp oxygen sublattice with different Ti-vacancy orderings over the interstitial octahedral sites of the oxygen sublattice. We enumerated 177 different Ti-vacancy configurations over the octahedral sites of hcp oxygen within supercells up to four times the primitive hcp cell. The calculated formation energies are shown in Figure 3.2(d). While all calculations were performed with spin polarization, only a fraction of the configurations maintained a finite (ferromagnetic) moment after relaxation. The corundum Ti_2O_3 and rutile TiO_2 structures, for example, relaxed to non-magnetic states. Two Magnéli phases, though, remained ferromagnetic (Ti_4O_7 and Ti_5O_9). Surprisingly none of the hcp oxygen based orderings reside on the global convex hull. While it is well known that most approximations to DFT predict that anatase is more stable than rutile TiO_2 [104, 105, 106, 107, 108, 109], Figure 3.2(d) shows that the corundum form of Ti_2O_3 is also predicted to be less stable than the predicted rocksalt based ground state, γ' - Ti_2O_3 .

Furthermore, none of the Magnéli based phases, which are derived from rutile, reside on the global convex hull.

3.4 Discussion

The Ti-O binary has a remarkably rich variety of stable and metastable oxides and suboxides. There are many qualitative similarities between the calculated and experimentally observed stable oxide orderings, but there are also subtle but important differences. For example, it has already been well-established that most approximations to DFT predict the anatase form of TiO_2 as having a lower energy than rutile [104, 105, 106, 107, 108, 109], while common interpretations of experiment indicate that the reverse should be true [110, 111]. The results of the present study suggest that additional discrepancies occur at lower Ti/O ratios. The corundum crystal structure of Ti_2O_3 has been reported in many experimental studies [96, 93]. Nevertheless, DFT-PBE predicts a vacancy ordering in rocksalt as the ground state at the Ti_2O_3 stoichiometry. We are unaware of any experimental reports of a rocksalt derived ordering having the same composition. At the TiO stoichiometry, the ω -TiO phase is predicted to be the ground state, while assessed phase diagrams include the rocksalt form of γ' -TiO as the equilibrium phase at low temperature (usually labeled α -TiO) [61, 17]. The vacancy ordered rocksalt form of γ' -TiO has been well characterized experimentally and studied theoretically [96, 100, 112, 113]. It is only recently that an ω -TiO phase has been successfully synthesized using indirect routes [63]. Early reports by Andersson [82] of the existence of Ti_3O_2 having an ω -Ti sublattice confuse matters further. The PBE convex hull of Figure 3.2(b) does not exhibit a ground state having a stoichiometry of Ti_3O_2 , with the formation energies of ω -Ti based orderings being well above the hull at this composition. Andersson, however, was not able to isolate the purported Ti_3O_2 line com-

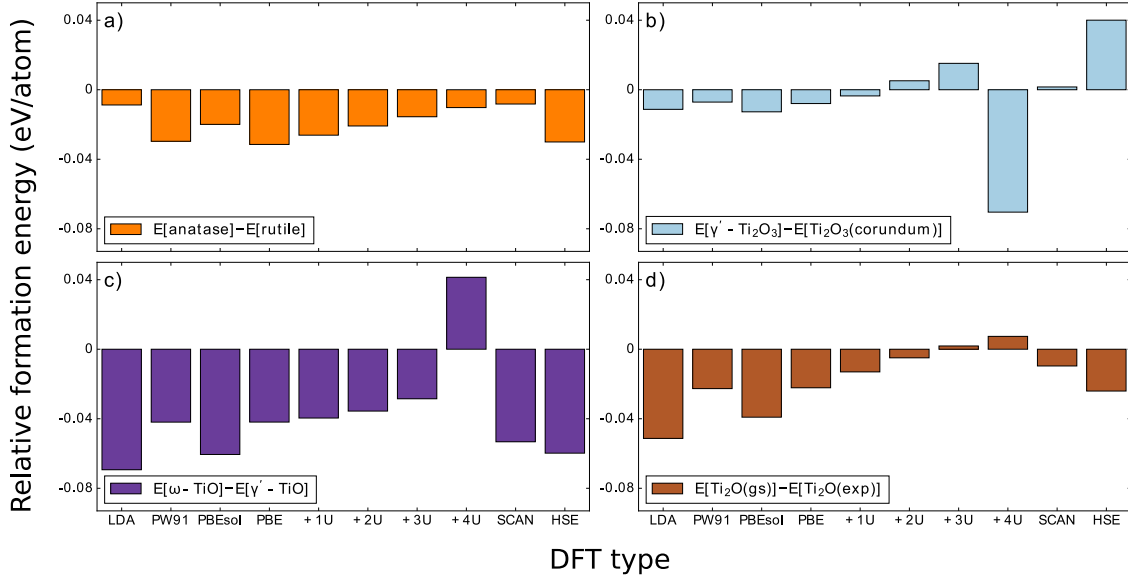


Figure 3.9: Dependence of the relative stability between competing polymorphs on the various approximations to density functional theory. (a) The energy difference between anatase and rutile TiO_2 (negative values signify anatase as a lower energy and stable polymorph), (b) energy difference between rocksalt γ' - Ti_2O_3 and corundum Ti_2O_3 (c) energy difference between ω - TiO and γ' - TiO and (d) energy difference between the ground state(gs) zig-zag ordered α - Ti_2O and experimental(exp) staged Ti_2O .

pound but rather studied multi-phase mixtures that may well have included an ω - TiO instead.

Discrepancies between DFT predicted ground states and experiment also exist for the suboxides. The diffraction patterns for the three ordered suboxides having an hcp Ti sublattice suggest stage ordering with oxygen filling alternating layers between close-packed Ti layers [114]. This is consistent with the ground state predictions for α - Ti_6O and α - Ti_3O , but the predicted ground state for α - Ti_2O is not staged. The oxygen ordering of α - Ti_2O consists of zig-zag oxygen rows separated by equivalent rows of vacancies within each oxygen layer (Figure 3.3(c)) and is predicted to have an energy that is 22 meV/atom lower than the stage-ordered form of Ti_2O .

The discrepancies between predicted ground states and experiment may be due to a failure of DFT-PBE. The relative stability between anatase and rutile TiO_2 has been studied extensively in the past using a wide variety of approximations to DFT and its extensions. This includes LDA, PBE, PW91, DFT+U, HSE and the random phase approximation (RPA) [104, 105, 106, 107, 108, 109, 115]. It is only with DFT+U employing values of U in excess of 6 eV or with the random phase approximation that the relative stability between anatase and rutile is reversed [115]. Figure 3.9 shows the sensitivity of the difference in energy between the competing polymorphs at the TiO_2 , Ti_2O_3 , TiO and Ti_2O stoichiometries as calculated with different approximations to DFT (i.e. LDA, PW91, PBE, PBESol, and the recently developed SCAN potential) and the extensions to DFT with +U and hybrid functional methods (HSE). All calculations in Figure 3.9 were performed spin polarized ¹.

Figure 3.9 shows that almost all approximations are qualitatively consistent with DFT-PBE, including the newly developed SCAN exchange-correlation functional. The results of Figure 3.9(a) are consistent with past studies [104, 105, 106, 107, 108, 109], showing that most approximations to DFT predict anatase as more stable than rutile. Even the newly developed SCAN exchange correlation functional predicts anatase as the ground state. Predictions with HSE are also consistent with PBE for Ti_2O , TiO and TiO_2 . Only in the case of Ti_2O_3 does HSE reverse the PBE predicted relative stability between corundum and the vacancy ordered rocksalt phase. SCAN predicts that corundum and the low energy vacancy-ordered rocksalt are essentially degenerate within the numerical

¹All ground states with the exception of the the Ti_4O_7 and Ti_5O_9 Magnéli phases were predicted to be non magnetic for the $U=0$ calculations. Several phases had finite magnetic moments for non zero U values. The rocksalt based γ' - TiO , Ti_6O_7 and Ti_2O_3 , for example, exhibited magnetic moments when $U=3$ eV and greater. Magnéli Ti_3O_5 was found to favor a finite magnetic moment when $U=2$ eV and greater. Corundum Ti_2O_3 was found to converge to both a non-magnetic state and a ferromagnetic state depending on how the magnetic moments were initialized. Surprisingly the lowest energy state for U values less than or equal to 4 eV was the non-magnetic state. All HSE calculations predicted non-magnetic ground states.

error of the VASP calculations, the difference between the two polymorphs of Ti_2O_3 being less than 1 meV/atom with SCAN. Figure 3.9 (c) and (d) show that large values of U (above 3-4 eV) within the DFT+ U approximation will reverse the relative stability between γ' -TiO and ω -TiO and between the staged and zig-zag row ordered α - Ti_2O . It is, however, questionable whether DFT+ U is an accurate description at these Ti rich concentrations, especially for Ti_2O .

3.5 Summary

In this chapter, we have performed a comprehensive first-principles study of phase stability in the Ti-O binary at zero kelvin. We have predicted new orderings of stable titanium oxides, namely ω - Ti_3O , ω -TiO, γ' - Ti_6O_7 and γ' - Ti_2O_3 , and reinforced the prediction in stability of hcp- TiO_x suboxides observed in previous first-principles studies in the literature. Our study also reveals important discrepancies between predicted ground state structures and experimentally observed phases. It is possible that more advanced electronic structure methods that go beyond DFT and its common extensions may be required to accurately describe the physics of several of the oxides in the Ti-O binary. The results of this study suggest a different ordering for α - Ti_2O than was inferred from past diffraction studies[114] and the possibility of additional vacancy ordered rocksalt phases.

Chapter 4

Ground state ordering of carbon and nitrogen atoms in titanium

4.1 Introduction

Titanium alloys are lightweight and high strength metals making them the default option for a diverse number of weight sensitive structural applications[10]. Titanium is also highly reactive, especially with interstitial elements such as oxygen[61, 17], nitrogen[16] and carbon[19]. In fact, a rich variety of compounds with both structural and functional applications can be formed by combining titanium with interstitial elements.

TiC, for example, has a high strength and a high melting point, making it an excellent structural material for coatings, tools and wear resistant applications[116]. It is often used in making cermets (ceramic and metal composites), which have attractive mechanical properties[116]. Ti-N compounds also have well-known structural applications and can

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serve as coatings for tools where wear resistance is a key requirement [117]. Furthermore, the unique optical properties of TiN make it suited for photovoltaic applications [118]. TiN is used as nano precipitates in dye sensitized solar materials[119] and can serve as a plasmonic material to help increase light trapping efficiency[120]. It is also used as a catalyst to improve the hydrogen storage efficiency of light metal complex hydrides[121].

In spite of their numerous structural and functional applications, there are many unknowns about the low-temperature thermodynamic properties of the compounds that form in the Ti-rich half of the Ti-C and Ti-N binaries. Similar to oxygen, both C and N can dissolve interstitially in the hcp crystal structure of Ti. Rocksalt based carbides and nitrides become stable at equi-atomic compositions, with Ti forming an fcc sublattice and C or N filling interstitial octahedral sites. The rocksalt based TiC and TiN compounds, however, are able to tolerate high concentrations of vacancies on the C or N sublattices. Experimentally very little is known about the low-temperature ordering tendencies of the vacancies and their order-disorder transitions.

In this chapter, we report on a comprehensive first-principles statistical mechanics study of phase stability in the Ti-C and Ti-N binary systems at zero kelvin. We identify low-temperature C-vacancy and N-vacancy orderings over the octahedral sites of hcp and fcc Ti and compare with the experimental observations.

4.2 Methodology

Density functional theory as implemented in the VASP package[45, 46, 47, 48] was used to calculate the zero Kelvin energies of a large number of C and N orderings over the octahedral interstitial sites of hcp and fcc Ti. The CASM software package[34, 35, 28, 36] was used to enumerate symmetrically distinct orderings in the fcc and hcp crystal

systems. The first-principles calculations were performed within the generalized gradient approximation of Perdew, Bruke and Ernzerhof (DFT-PBE) [50, 51] using the projector augmented wave (PAW) method [90, 91] to describe interactions between core and valence electrons. The PAW potentials treat the $3s$, $3p$, $3d$ and $4s$ orbitals of Ti (Ti-sv) and the $2s$ and $2p$ orbitals of C and N as valence states. The plane wave expansion of the electronic states had an energy cutoff of 550 eV. A $15 \times 15 \times 9$ ($16 \times 16 \times 8$) k-point grid was found to achieve convergence within 2 meV/unit cell for the primitive cell of the hcp Ti-C (Ti-N) system. A $17 \times 17 \times 17$ k-point grid was used for the primitive cell of rocksalt based Ti-C and Ti-N compounds. These k-point grids were centered around the Γ point and were scaled appropriately for supercells of the primitive unit cells. Each structure was fully relaxed with respect to lattice parameters and atomic coordinates. Partial occupancy during relaxation runs was treated with the Methfessel-Paxton scheme (of order 2) while the tetrahedron method with Blöchl corrections was used during the static runs. All the ground states predicted in the current study relaxed to a nonmagnetic state when starting from a ferromagnetically initialized configuration.

4.3 Ground state analysis

The search for ground state C-vacancy and N-vacancy orderings over the octahedral interstitial sites of hcp and fcc Ti was performed iteratively. The energies of an initial set of orderings within a particular parent crystal structure (i.e. hcp Ti or fcc Ti) were first calculated with DFT-PBE and used to train cluster expansion Hamiltonians for each parent crystal. The cluster expansions were then used to calculate the energies of a substantially larger set of orderings. Any cluster expansion predicted low-energy configurations that were not part of a previous training set were then included in a next batch of configurations whose energies were calculated with DFT-PBE. The iterative

process was continued until the cluster expansions no longer predicted new ground state configurations. Next chapter on finite temperature phase stability analysis describes the construction of these cluster expansion Hamiltonians.

The formation energies of most orderings in the Ti-C binary are negative when calculated relative to Ti and graphite. Experimental phase diagrams indicate that rocksalt TiN forms relative to Ti and N₂ gas [16]. To reveal subtle energy differences between the many low-energy orderings, we use hcp Ti and hcp TiX (where X=C or N fills all octahedral interstitial sites) as reference states. The calculated formation energies for the different configurations are shown in Figure 4.1(a) for the Ti-C system and in Figure 4.1(b) for the Ti-N system. As a measure of composition, we use atomic fractions defined as $y = N_X / (N_{Ti} + N_X)$, where N_{Ti} and N_X are the number of Ti and X atoms respectively. The value of y varies from 0 to 0.5 for configurations having compositions between Ti to TiX. The formation energy per atom, $E_f(y)$, for a configuration having a composition y (i.e. Ti_{1-y}X_y), is then defined as

$$E_f(y) = E(y) - (1 - 2y)E[\text{Ti}] - (y)E[\text{TiX}] \quad (4.1)$$

where $E(y)$ is the energy of the configuration Ti_{1-y}X_y, $E[\text{Ti}]$ is the energy of HCP Ti and $E[\text{TiX}]$ is the energy of HCP Ti with X filling all the octahedral sites.

The global convex hulls in Figure 4.1(a) and 4.1(b) show that both the Ti-C and Ti-N systems have a series of ground states that are stable at 0 K. The convex hull corresponds to the envelope of the lowest energy orderings. Any ordering that resides on the convex hull is a stable ground state at zero kelvin. Figure 4.2 illustrates the various ground state orderings. It is interesting to note that all the ground states are of the type Ti_nX_{n-1} with $n > 1$, although not all integer values of n correspond to ground state stoichiometries.

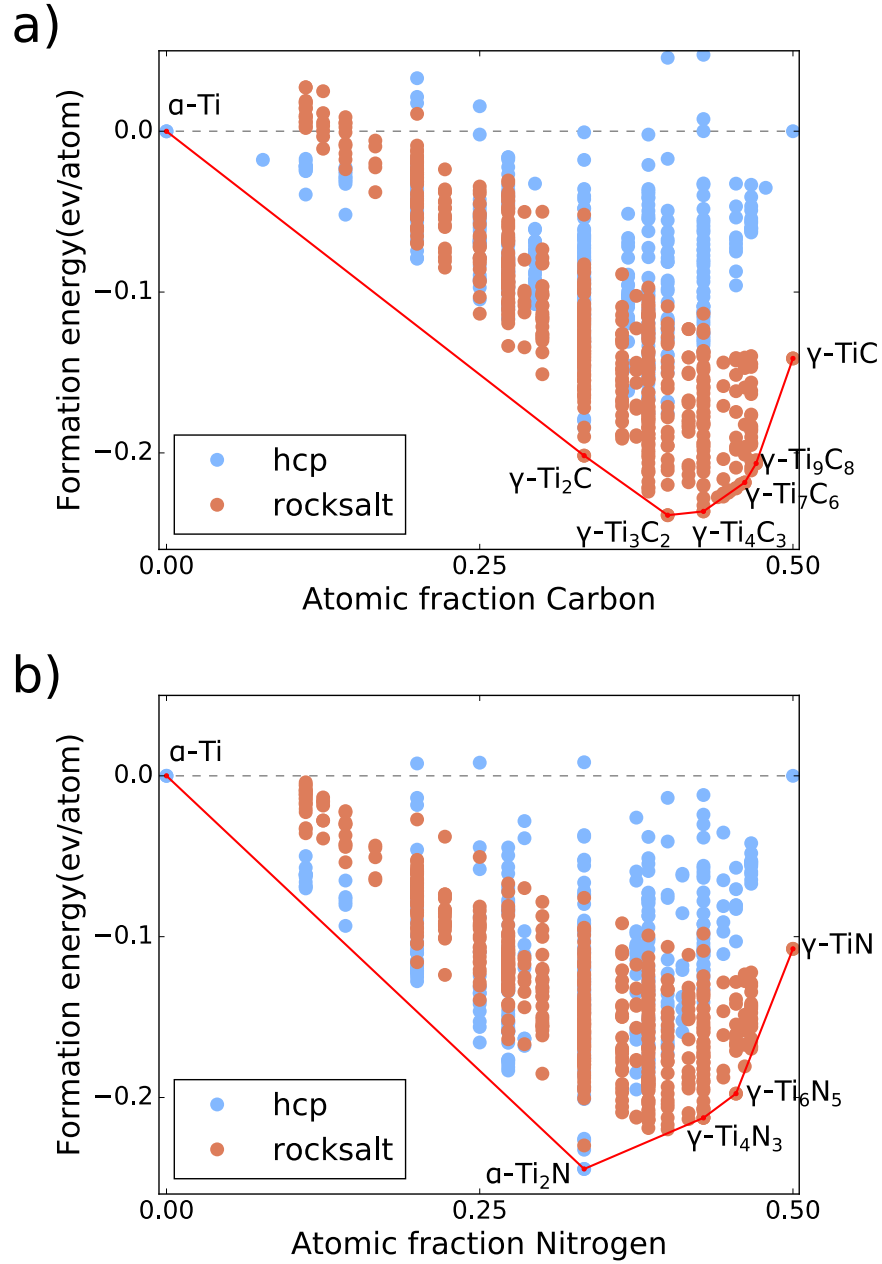


Figure 4.1: Formation energies of enumerated configurations in a) the Ti-C binary and b) the Ti-N binary. The red line corresponds to the global convex hull and connects the energies of the ground state orderings.

Both fcc and hcp consist of close-packed triangular layers having an ABC and an ABAB stacking respectively. The interstitial octahedral sites of fcc also form an fcc lattice. The interstitial octahedral sites of hcp form a simple hexagonal lattice in which triangular layers of octahedral sites stack in a CCC sequence between the ABAB close-packed layers of the hcp crystal. Figure 4.2 illustrates the different ground state orderings as 2-dimensional stackings of close-packed layers. We describe the orderings of Figure 4.2 in the next two sections.

4.3.1 Ti-C binary system

We enumerated 477 (645) C-vacancy configurations over the octahedral sites of hcp Ti (fcc Ti) in super cells having volumes up to 6 (9) times that of the primitive unit cell. The formation energies of Figure 4.1(a) show that only fcc Ti derived configurations with high carbon concentrations reside on the convex hull. There are no hcp based ground state orderings. The stoichiometric formulas for the ground states are Ti_2C , Ti_3C_2 , Ti_4C_3 , Ti_7C_6 , Ti_9C_8 and the pure rocksalt structure TiC at equi-atomic composition. The experimental literature refers to rocksalt TiC as the γ phase [122, 123]. We will use the prefix γ to indicate that a particular stoichiometry corresponds to a vacancy-ordered rocksalt phase.

The γ - Ti_2C ground state ordering is shown in Figure 4.2(b) and has cubic symmetry. The carbon concentration fluctuates between 3/4 and 1/4 in alternating (111) octahedral layers. The carbon ordering over the octahedral sites of fcc Ti in γ - Ti_2C is identical to that of the Al cations over the octahedral sites of the fcc oxygen sublattice of spinel MgAl_2O_4 . The γ - Ti_3C_2 ground state shown in Figure 4.2(c) consists of alternating octahedral (111) layers within fcc Ti that are 1/3 filled and fully filled. The carbon in the 1/3 filled layers order on a $\sqrt{3}a \times \sqrt{3}a$ super lattice, which is a common ordering on the triangular lattice.

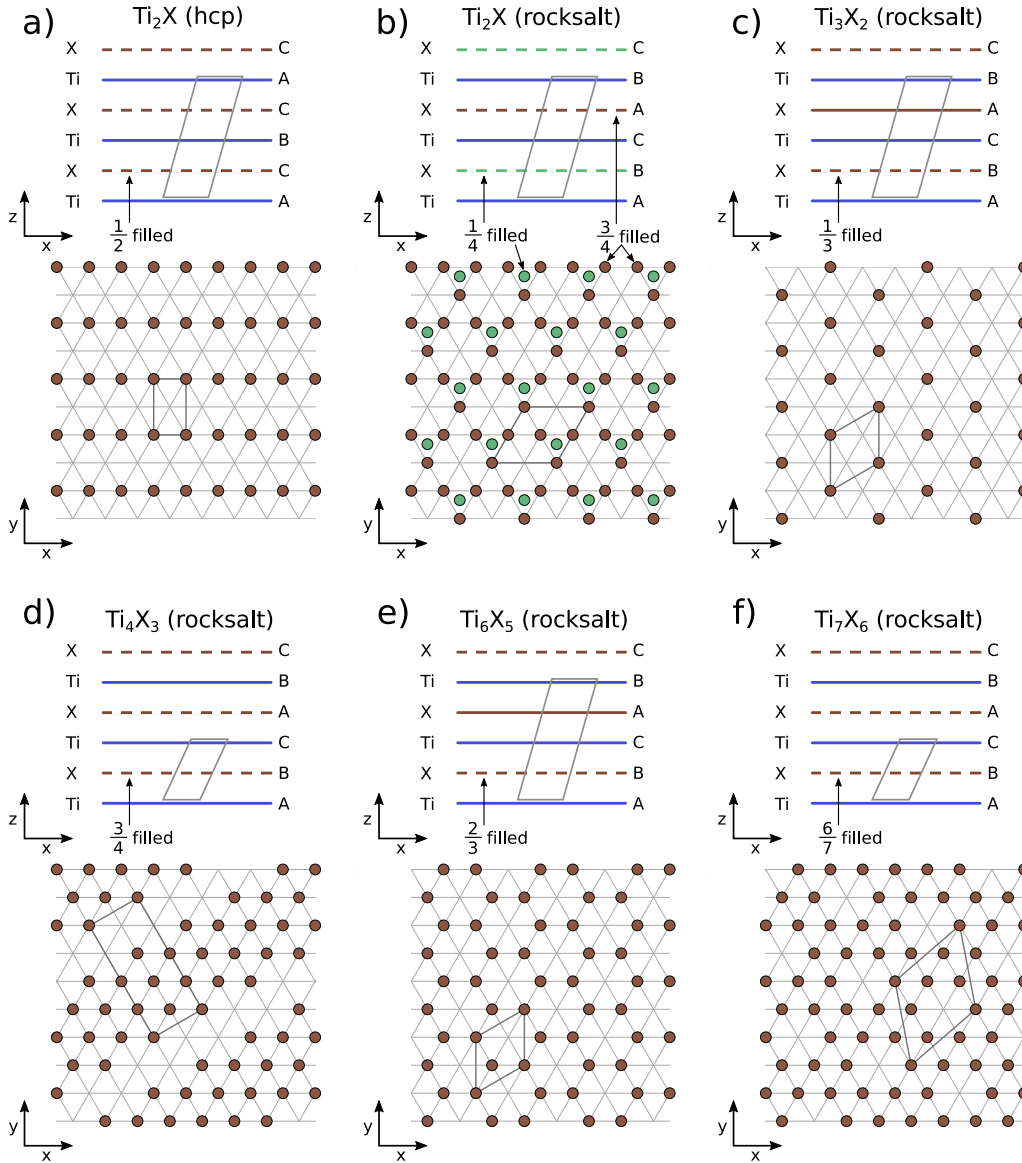


Figure 4.2: Interstitial-vacancy orderings within the ground states of the Ti-N and Ti-C binaries. Each ground state ordering can be generated by a particular stacking of two-dimensional interstitial-vacancy ordered layers. The top half of each subfigure shows the stacking of alternate metal and interstitial layers along the c-axis of hcp or along a (111) direction of fcc. Dashed lines indicate close-packed layers containing interstitial vacancies, while solid lines indicate completely filled layers. The bottom half of each subfigure shows the ordering of interstitial atoms over the triangular close-packed planes of octahedral sites in hcp and fcc. The black/grey boxes shows the unitcell of the ordered ground states.

This ordering maximizes the distance between carbon atoms within the $1/3$ filled (111) layer.

The γ -Ti₄C₃ ground state shown in Figure 4.2(d) has a uniform $3/4$ filling in each (111) plane of octahedral interstitial sites. The vacancies order into zigzag rows separated by three zigzag rows of carbon atoms. The γ -Ti₇C₆ ground state shown in Figure 4.2(f) has a uniform distribution of carbon in every (111) plane with vacancies ordering on a $\sqrt{7}a \times \sqrt{7}a$ super lattice. This superlattice ordering maximizes the distance between vacancies within each (111) layer when one out of every seven sites are vacant.

The final rocksalt derived ground state identified here with stoichiometry γ -Ti₉C₈ has a very dilute vacancy concentration. It consists of two completely filled (111) layers alternated by a $2/3$ filled (111) layer in which the vacancies order on a $\sqrt{3}a \times \sqrt{3}a$ super lattice. This ground state ordering is only marginally stable, barely breaking the common tangent between γ -Ti₇C₆ and stoichiometric γ -TiC.

4.3.2 Ti-N binary system

For the Ti-N system, we enumerated 393 (630) N-vacancy orderings over the octahedral sites of hcp (fcc) Ti in supercells up to volume 5 (9) of the primitive cell. In contrast to the Ti-C system, there is one hcp based ground state having a stoichiometry of Ti₂N in the Ti-N system. The ground state ordering of Ti₂N is shown in Figure 4.2(a). Every triangular layer of octahedral interstitial sites is half filled, with nitrogen ordering in rows separated by rows of vacancies. The in-plane row orderings in adjacent layers are translated relative to each other such that nitrogen atoms never share faces with each other. Experimental phase diagrams show the existence of an hcp based compound with at Ti₂N composition [16] and the ordering of nitrogen atoms match the first-principles

derived ground state.

The Ti-N system also has two rocksalt derived ground states having stoichiometries γ -Ti₄N₃ and γ -Ti₆N₅, where as before we use γ to denote that the compounds are derived from rocksalt. The nitrogen ordering within γ -Ti₄N₃ is identical to that of γ -Ti₄C₃ and is illustrated in Figure 4.2(d). The γ -Ti₆N₅ ground state consists of completely filled (111) layers of octahedral interstitial sites alternated by 2/3 filled (111) layers. The nitrogen vacancies in the 2/3 filled layers order on a $\sqrt{3}a \times \sqrt{3}a$ super lattice.

4.4 Summary

The zero kelvin analysis in the current study has shown that the the Ti-C and Ti-N binary systems contains stable ground state orderings that are not present in the experimental assessments [19, 16]. Although there are phase diagrams available in the literature[124, 125] that attempt to resolve the stability domains of Ti-C vacancy ordered hcp and rocksalt phases, they do not contain many of the ground states predicted here and previously[126]. DFT-PBE predicts a large number of vacancy ordered ground states, especially within the TiC_x and TiN_x rocksalt phases. The ordering of γ -Ti₂C has been determined experimentally [127] and matches that predicted in this study. Several other ground states have been predicted previously from first principles. These include the vacancy orderings in Ti₃C₂ and Ti₇C₆ [128, 129] and the Ti₆N₅ ground state ordering [130]. A ground state vacancy ordering has also been predicted for Ti₄N₃ [130], however, insufficient crystallographic detail was provided to enable a comparison with the ground state of this study at the same composition. New ground states discovered in this study include γ -Ti₄C₃ and γ -Ti₉C₈.

Chapter 5

Linking electronic structure to phase stability in Ti interstitial alloys

5.1 Introduction

The first-principles analysis in the last two chapters shows that the Ti-X (X= C, N, O) binary systems contain a diverse array of stable and metastable ground states orderings. In the Ti-rich region($x_{Ti} > 0.5$), hcp and fcc crystal based configurations are stable. Ground state configurations closer to pure Ti in composition are based on hcp hosts and the configuration around equiatomic composition are based on fcc or rocksalt crystal systems. There is a transition in phase stability from hcp to fcc hosts for the stable configurations in the three binary interstitial Ti-X (X=C, N, O) systems of interest. But the boundary between the stability domains for the hcp and fcc based configurations change as we go from C to N to O based alloy systems. Hcp crystal based configurations are stable up to 33 atomic percentage in the Ti-O system but we did not

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discover any stable configurations on hcp host crystal in the Ti-C system. Opposite is true for fcc based configurations, there are many stable fcc based configurations in Ti-C system compared to the N and O binaries. O promotes hcp host configurations whereas C stabilizes fcc host configurations. As C, N and O are adjacent on the periodic table and mainly differ in the number of electrons, we have used electronic structure of the ground state configurations to explain the shift in phase stability from hcp to fcc host crystal.

In this chapter, first we report on the type of bonding between the Ti and the interstitial atoms in the hcp and fcc crystal systems. Section 5.3 discusses the similarities and differences in the electronic structure of the low temperature stable orderings in the binary systems. Later in section 5.4, a finite temperature phase stability analysis exploring the order-disorder transitions in the Ti-C and Ti-N binary systems using cluster expansion approaches and Monte Carlo simulations is presented. Along with the Ti-O phase diagram discussed in the next chapter, we compare the calculated temperature versus composition phase diagrams to identify trends in Ti-X phase stability upon increasing the number of valence electrons when X goes from C to N to O. The high interstitial solubility of C, N and O in hcp and fcc Ti is rooted in the peculiar electronic structure of these compounds and section 5.5 presents the arguments linking the electronic structure to the phase stability of hcp and fcc crystal systems in titanium interstitial systems.

5.2 Methodology

Temperature dependent thermodynamic properties of Ti-X systems with X being carbon (C) or nitrogen (N) were calculated by combining first-principles electronic structure methods with statistical-mechanics approaches. The 0 K density functional theory(DFT)

energies of the configuration enumerated in previous chapter served as training data to parameterize cluster expansion Hamiltonians [52, 53, 54]. These models are capable of describing the configurational energy of a crystal with near first-principles accuracy. The expansion coefficients were determined with least squares regression techniques combined with a genetic algorithm to select an optimal set of cluster expansion basis functions [38].

The cluster expansions were implemented in grand canonical Monte Carlo simulations to calculate thermodynamic quantities as a function of temperature and chemical potential. Free energy descriptions of the various phases as a function of temperature and composition were obtained with standard free energy integration techniques applied to Monte Carlo generated data [59, 60, 131]. The CASM software package [34, 35, 28, 36] was used to construct and parameterize cluster expansion Hamiltonians and to perform Monte Carlo simulations.

5.3 Electronic structure

We analyzed the electronic structure of the ground state orderings described in the previous chapter. To reveal trends, we compare density of states plots of the Ti-C and Ti-N ground state orderings to those of similar Ti-O orderings. The three interstitial species, C, N and O, are neighbors in the periodic table, having the same valence shell, but differing in their number of valence electrons and nuclear charge.

The electronic structure of the rocksalt forms of TiO, TiN and TiC is well understood [132, 133, 134]. Each Ti atom in a rocksalt TiX phase is coordinated by an octahedron of X. The cubic symmetry of the rocksalt crystal structure breaks the degeneracy of the Ti d orbitals into t_{2g} levels (d_{xy} , d_{yz} and d_{xz} orbitals) and e_g levels ($d_{x^2-y^2}$ and d_{z^2} orbitals). Figure 5.1 shows the orientation of these orbitals along with the p-orbitals of

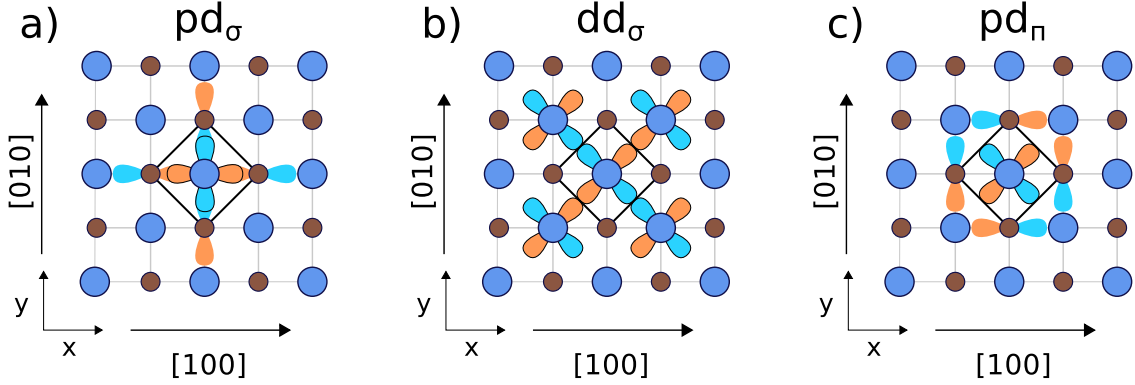


Figure 5.1: The orientation of metal host d orbitals and interstitial p orbitals in a) pd_σ , b) dd_σ and c) pd_π bonds projected on a (100) plane of conventional rocksalt unitcell.

the interstitial atoms on a (100) plane of the conventional rocksalt unit cell. The on-axis e_g orbitals point towards interstitial atoms and can hybridize with their p orbitals to form pd_σ bonds (Figure 5.1(a)). The off-axis t_{2g} orbitals point towards the neighboring Ti atoms to form dd_σ bonds (Figure 5.1(b)). They also form pd_π bonds with the p orbitals of the interstitial elements[132] as can be seen in Figure 5.1(c).

Figure 5.2 compares the calculated electronic density of states of fcc-Ti with those of rocksalt TiO, TiN and TiC. The density of states have been aligned using the core Ti 3s states. The energy levels of the 3s states are sufficiently deep that they are negligibly affected by the surrounding environment. In addition to showing the total density of states, Figure 5.2 also shows projected densities of states, with contributions from Ti t_{2g} (e_g) levels shown in green (orange) and contributions from X p levels shown in light green.

The insertion of O, N and C into the interstitial sites of fcc Ti to form rocksalt introduces p states well below the Fermi level (Figure 5.2). The p levels progressively increase in energy due to a decrease in nuclear charge when going from O to N to C. The p states hybridize with the Ti d orbitals to form bonding pd_σ and pd_π states below the

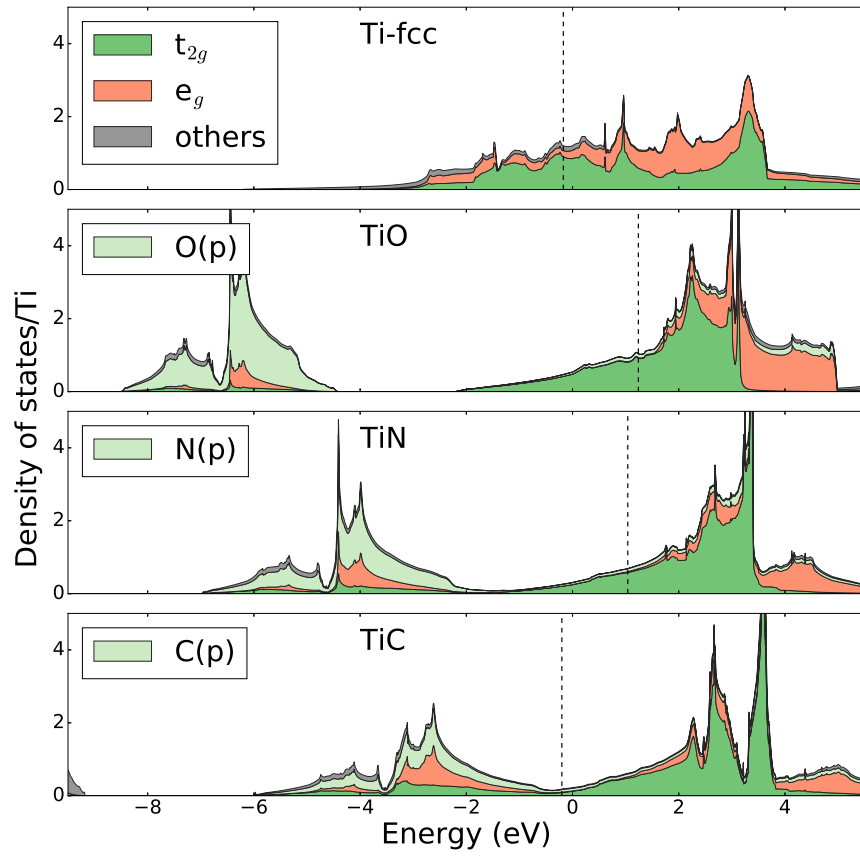


Figure 5.2: Projected density of states of fcc-Ti and rocksalt-TiX (X=C,N,O) compounds.

Fermi level and antibonding pd_σ^* and pd_π^* above the Fermi. Since the oxygen p states are much lower than the Ti d states there is little hybridization and the bonding pd_σ and pd_π states in TiO are primarily of p character localized on oxygen. The p levels of nitrogen are slightly higher than those of oxygen, leading to more hybridized bonding pd_σ and pd_π states in TiN. The carbon p levels appear at even higher energies allowing for significant overlap with the Ti d orbitals to produce clearly hybridized pd_σ and pd_π bonds in TiC.

Shifts in the intrinsic p levels and number of valence electrons when going from O to N to C also results in clear variations in the electronic structure at the Fermi level. In fcc-Ti there are no interstitial atoms and the states below the Fermi level are predominantly t_{2g} in character, suggesting the importance of directional dd_σ bonds between neighboring Ti atoms. Similar to fcc Ti, the levels at and immediately below the Fermi level in TiO and TiN also have t_{2g} character. The Fermi energy in TiC, in contrast, lies in a shallow valley separating the bonding pd_σ and pd_π states between Ti and C from the Ti d states having t_{2g} character. Bonding in TiC is, therefore, predominantly between Ti and C, with the majority of t_{2g} states necessary for dd_σ bonds residing above the Fermi level and unoccupied.

The introduction of vacancies into the rocksalt forms of TiO, TiN and TiC results in "vacancy states" below the Fermi level [135, 136]. These emerge from a realignment of d-orbitals of the Ti atoms next to interstitial vacancies. Figure 5.3 shows the density of states in substoichiometric Ti_2X rocksalt based compounds. The interstitial vacancy ordering is identical to that of the Ti_2C ground state configuration of Figure 4.2(b). The presence of vacancies does not qualitatively modify the nature of hybridization between Ti and interstitial atoms that is evident in perfect rocksalt. However, new states in the

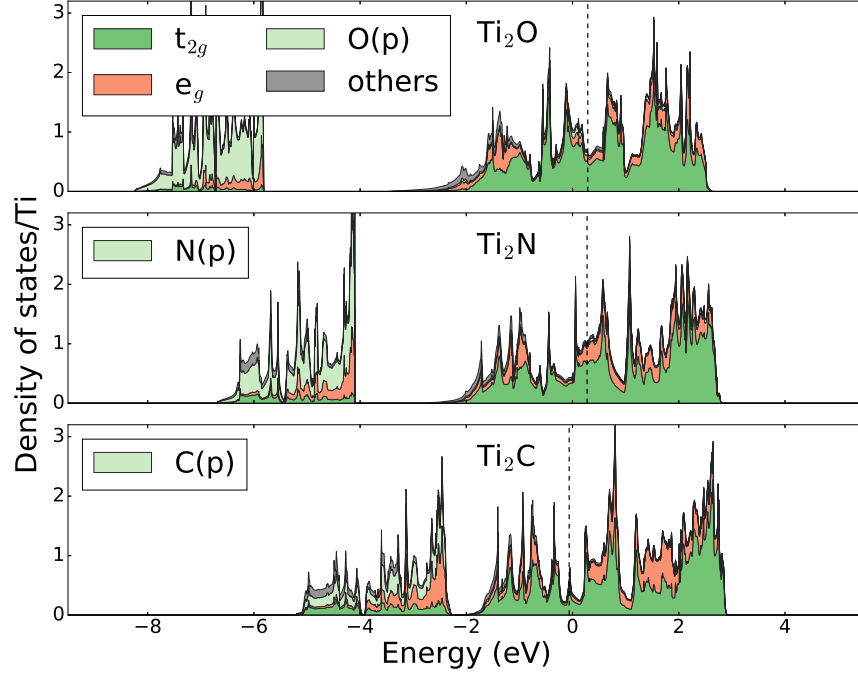


Figure 5.3: Projected density of states of rocksalt- Ti_2X ($\text{X}=\text{C},\text{N},\text{O}$) compounds.

density of states appear in the vicinity of the Fermi level. The removal of interstitial atoms from perfect rocksalt results in the partial elimination of $\text{Ti-X } \text{pd}_\sigma$ and pd_π bonds, which is then compensated by a strengthening of the dd_σ bonds between neighboring Ti [137]. This is evident in Figure 5.3 from the dominance of t_{2g} character in the peaks corresponding to vacancy states.

Figure 5.4 shows the effect of changes in the vacancy concentration on the density of states of TiC_x . Each compound in Figure 5.4 corresponds to a vacancy ordered rock salt ground state in the Ti-C binary. While the qualitative features of the interstitial/metal hybridization below the Fermi level does not change, more and more vacancy states emerge below the Fermi level with vacancy concentration. Furthermore, the peaks associated with the new states along with other states become sharper when going from TiC to Ti_2C , indicating an increase in localization. The introduction of C vacancies reduces the

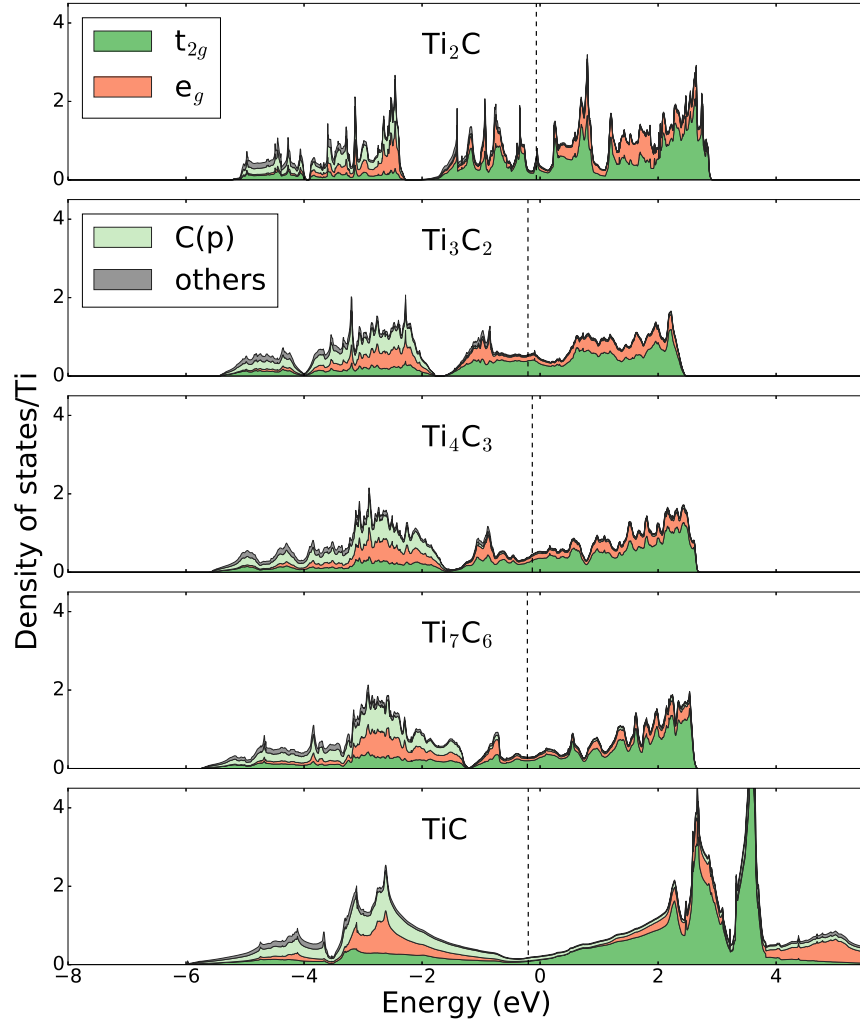


Figure 5.4: Projected density of states of ground state rocksalt titanium carbides.

number of Ti-C bonds that draw electrons from the Ti host, allowing for the filling of Ti d levels that have predominantly t_{2g} character.

Bonding in the hcp based compounds is more subtle than in the cubic rocksalt phases. The hexagonal symmetry of hcp splits the d-orbitals into 3 symmetrically distinct groups. One corresponds to the d_{z^2} orbital with lobes aligned along the z-axis. The second group consists of combinations of d_{xy} and $d_{x^2-y^2}$ to yield orbitals that point towards Ti nearest neighbors within the close packed planes. The remaining d_{yz} and d_{xz} orbitals point out

of the x-y plane and can hybridize with the Ti of adjacent close-packed planes. It is well known that the early transition metals Ti, Zr and Hf are stable in the hcp crystal structure at low temperature since their Fermi level resides within a valley in the electronic densities of state of the transition metal *d*-levels [138]. This is evident in Figure 5.5(a).

Figure 5.5 (b) shows the density of states in the hcp based α -Ti₂N ground state (Figure 4.2(a)) while Figure 5.5 (c) shows that of metastable hcp-TiN. The interstitial octahedral sites in hcp form a trigonal prism around the host metal atoms. The p orbitals of the interstitial species can hybridize with the d_{yz} and d_{xz} orbitals of Ti to form σ bonds and with the d_{xy} and $d_{x^2-y^2}$ to form π bonds[139]. Figures 5.5 (b) and (c) indicate that such hybridization does indeed occur in α -Ti₂N and hcp TiN. In fact, the partial densities of states in Figures 5.5 (b) and (c) are qualitatively similar to those of the rocksalt phases, with bonding states between N p levels and Ti d levels appearing below the Fermi level and with Ti d states dominating at and immediately below the Fermi level.

5.4 Phase diagrams

Predicting phase stability at finite temperature requires a statistical mechanics approach [54]. The formation energies for the Ti-C and Ti-N binaries were used to parameterize cluster expansions of the configurational energy. A separate cluster expansion was constructed for each parent crystal structure. The cluster expansion of the configurational energy of C-vacancy (N-vacancy) disorder over the octahedral sites of hcp Ti was parameterized by fitting to the formation energies of 477 (393) configurations using a genetic algorithm. The hcp based Ti-C (Ti-N) cluster expansion had a weighted root mean square (rms) error of 9.3 (9.7) meV/unit cell and weighted cross validation (cv) score of 13.5 (11.4) meV/unit cell. The cluster expansion of C-vacancy (N-vacancy) disorder in

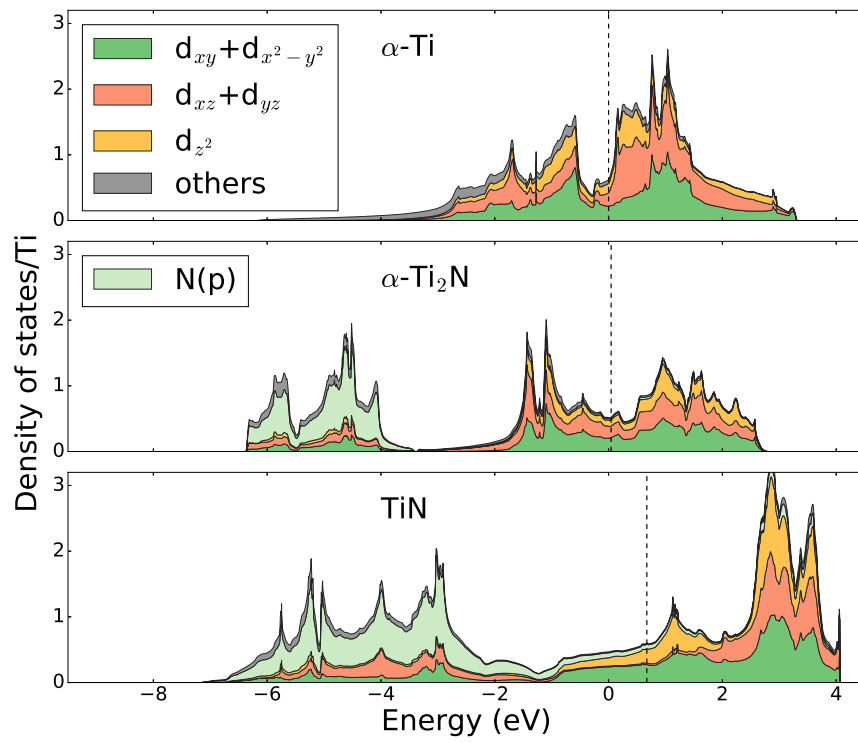


Figure 5.5: Projected density of states of α -Ti , the α -Ti₂N ground state and metastable hcp TiN.

the rocksalt was parameterized with 645 (629) formation energies and had a weighted rms of 5.1 (6.1) meV/unit cell and a weighted cv of 5.9 (7.0) meV/unit cell.

The Hamiltonians were then implemented in grand canonical Monte Carlo simulations to calculate the free energies needed to construct temperature versus composition phase diagrams. The average interstitial concentration and average grand canonical energy were calculated with grand canonical Monte Carlo simulations over a grid of temperatures and interstitial chemical potentials. Standard free energy integration techniques [59, 60, 131] were then applied to this data to calculate free energies as a function of interstitial composition over a range of temperatures. The phase diagrams were subsequently constructed using the common tangent method to map out two-phase coexistence regions.

Figures 5.6(a) and 5.6(b) show the calculated phase diagrams for the Ti-C and the Ti-N binaries respectively. For comparison, Figure 5.6(c) shows a phase diagram of the Ti-O binary calculated using similar approaches. Next chapter on Ti-O phase diagrams describes the derivation of the binary Ti-O phase diagram. Not included in the phase diagrams of Figure 5.6 is the high temperature bcc phase. This phase is stabilized by vibrational entropy and only appears at high temperature. The neglect of the high temperature bcc phase does not affect our predictions of carbide and nitride phase stability at intermediate to low temperatures. The hcp interstitial solid solutions are shown in light blue, while any hcp derived ordered phase is shown in dark blue. The disordered rocksalts (i.e. X-vacancy disorder over the interstitial octahedral sites of fcc Ti) are shown in light orange, while any vacancy ordered rocksalt phases are shown in light brown.

Figures 5.6(a) and 5.6(b) show an appreciable solubility of C and N in hcp Ti. The N solubility is substantially higher than that of C. A comparison of Figures 5.6(a) and

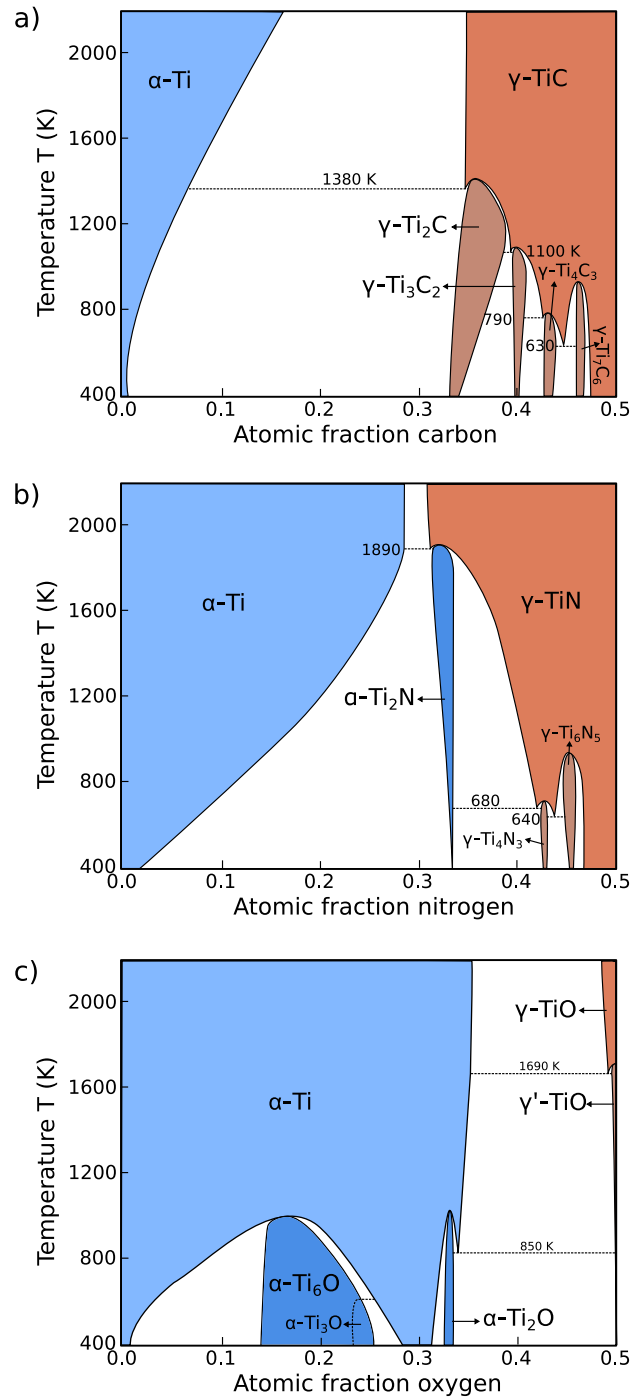


Figure 5.6: Computed phase diagrams for the a) Ti-C b) Ti-N and c) Ti-O binary systems. Single phase regions colored in shades of blue have an hcp parent crystal and those colored in shades of red are rocksalt based.

5.6(b) to Figures 5.6(c) reveals that oxygen has an even higher solubility in hcp Ti than both N and C. At 1200 K, for example, the solubility in hcp Ti is 5% for C, increasing to 20% for N and going as high as 33% for O. The number of hcp derived ordered phases also increases when going from C to N to O. In the Ti-C binary, there are no hcp based ordered phases. In the Ti-N binary, in contrast, the hcp based ordered Ti_2N phase [Figure 4.2(a)] is predicted to be stable to very high temperatures, transforming to a disordered rocksalt around 1900 K. The Ti-O binary has even more hcp derived ordered phases with stoichiometries Ti_6O , Ti_3O and Ti_2O . These suboxide phases disorder to an hcp Ti-O solid solution at around 1000 K.

The rocksalt phase is predicted to be stable over a wide concentration interval in both the Ti-C and Ti-N systems. Most of the ground state vacancy orderings in the Ti-C and Ti-N rocksalts remain stable to quite high temperatures, disordering at temperatures that range between 600 K and 1400 K. Only the $\gamma\text{-Ti}_9\text{C}_8$ vacancy ordered rocksalt phase is predicted to have its order/disorder transformation temperature below 400 K and hence it does not appear in the phase diagram shown in Figure 5.6(a). The disordered rocksalt phases, labeled $\gamma\text{-TiC}$ and $\gamma\text{-TiN}$ are stable over wide concentration intervals at elevated temperature, indicating that the carbide and nitride based rocksalts are able to tolerate high concentrations of C and N vacancies. Rocksalt derived phases in the Ti-O binary, in contrast, are only stable in a very narrow concentration interval. In fact, a comparison of Figures 5.6(a), (b) and (c) reveals that the concentration interval in which the rocksalt phase is predicted to be stable progressively decreases when going from C to N to O.

5.5 Discussion and Summary

The results of this first-principles study has shown that the the Ti-C and Ti-N phase diagrams are substantially more complex than is generally assumed based on experimental assessments [19, 16]. The calculated temperature-composition phase diagrams of Figure 5.6 show that the vacancy ordered rocksalt phases remain stable to high temperatures. Consistent with experimental observations [19, 16], the disordered TiC_x and TiN_x rocksalt phases can tolerate very high vacancy concentrations on the C and N sublattices respectively. Although our calculations have rigorously accounted for configurational degrees of freedom, they did not include contributions from vibrational excitations [140, 141]. The inclusion of vibrational excitations may alter the predicted transition temperatures, however, they are unlikely to modify the qualitative phase relations predicted in this work.

As is evident from Figure 5.6, titanium has a remarkable ability to dissolve large atom fractions of C, N and O within the octahedral sites of hcp and fcc. All three interstitial elements form bonding states (pd_σ , pd_π) and antibonding states (pd_σ^* , pd_π^*) upon hybridization with Ti d levels. The bonding states appear well below the Fermi level and are consequently completely filled (figures 5.2, 5.5). This ability to fill the bonding states and leave the high energy antibonding states unoccupied is one factor contributing to the high solubility of interstitial atoms in hcp and fcc Ti.

All three Ti-X (X=C, N and O) binaries favor an hcp Ti host at low interstitial concentrations and an fcc host at high concentrations (Figure 5.6). This trend likely has its origin in crystallographic differences between hcp and fcc. The octahedral interstitial sites of hcp Ti share faces with each other, while those of fcc Ti only share edges. Below the Ti_2X stoichiometry, the interstitial-vacancy orderings within hcp Ti minimize energy

by avoiding simultaneous occupancy of pairs of face-sharing octahedral sites. This becomes more difficult in hcp above the Ti_2X stoichiometry and the rocksalt phases with an fcc Ti sublattice become more stable.

Figures 5.6(a), (b) and (c) reveal a clear trend in the relative stability between hcp and rocksalt phases at intermediate interstitial compositions, with the rocksalt phases becoming more stable relative to hcp upon going from O to N to C. This behavior is likely rooted in the electronic structure that emerges upon insertion of interstitial elements into hcp and fcc Ti. The electronic levels at and immediately below the Fermi levels of the Ti-X compounds are dominated by Ti d states. More of these states are occupied in the Ti-O compounds than in Ti-C compounds with the same structure since O has more valence electrons than C. As a result, bonding pd_σ and pd_π states play a more important role in Ti-C compounds than they do in Ti-O compounds. This difference is likely in part responsible for the higher stability of rocksalt in the Ti-C system than in the Ti-O system. The cubic symmetry of fcc Ti and its interstitial network is well suited for the pd_σ hybridization that characterizes the TiC_x rocksalt phases. On the other hand the hcp Ti host of the TiO_x suboxides is more favored when the Ti d states play a more prominent role[138]. The Ti-N compounds have electronic structures that are intermediate to those of the Ti-O and Ti-C compounds. As a consequence, the degree with which rocksalt is favored at intermediate interstitial composition in the Ti-N binary is between that of the Ti-O and Ti-C binaries.

The variation in relative stability between hcp and fcc based compounds with the chemical identity of the interstitial guest species can be exploited in synthesis. For example, it is well known that pre treatment of Ti with carbon leads to a surface rocksalt TiC_x precursor phase that favors the subsequent formation of anatase TiO_2 as opposed

to rutile TiO_2 upon further oxidation [20]. The presence of N in air means that it plays an important role during the oxidation of Ti. Future work will focus on mixtures of O, N and C within hcp Ti and rocksalt. It is likely that low temperature O-N-C-vacancy ordered phases exist within hcp and fcc Ti with interesting structural and functional properties.

Chapter 6

Finite temperature analysis of Ti-O system

6.1 Introduction

The Ti-O system consists of a multitude of stable and metastable oxides that are used in wide ranging applications. In the previous chapters, we have investigated phase stability in the Ti-O binary system using first-principles analysis at zero kelvin. We have performed a systematic search for ground state structures as a function of oxygen concentration by considering oxygen-vacancy and/or titanium-vacancy orderings over four parent crystal structures: (i) hcp Ti, (ii) ω -Ti, (iii) rocksalt and (iv) hcp oxygen containing interstitial titanium. In this chapter, we explore the phase stability of ground state configurations at finite temperatures in Ti-O binary system.

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The first estimates of the finite temperature stability in Ti-O system were performed by Bumps et al.[23] and Schofield et al.[142] in the 1950's. They have since been refined but many of the features in current Ti-O phase diagrams [17, 61] rely on experimental studies that were performed almost a half century ago. These phase diagrams have not been able to resolve the stability of the ordered hcp-Ti suboxides and do not include the many rocksalt based orderings discovered in the current study. A similar study using first-principles was performed by Burton and van de Walle[97] but their study was restricted to the Ti-rich portion of the phase diagram. In the current study, we present a comprehensive analysis of phase stability in Ti-O system at finite temperatures across the entire composition range of the phase diagram and include the newly discovered rocksalt and ω -Ti based orderings.

In Section 6.3, we report on a statistical mechanics study of phase stability in the Ti-O system at finite temperature using cluster expansion approaches and Monte Carlo simulations. The calculations predict a high oxygen solubility in hcp Ti and the stability of suboxide phases that undergo order-disorder transitions upon heating. Vacancy ordered rocksalt phases are also predicted at low temperature that disorder to form an extended solid solution at high temperatures. Section 6.4 compares the predicted Ti-O phase diagrams to experimental observations and highlights several similarities and discrepancies in the predictions. Predicted stable and metastable phase diagrams are qualitatively consistent with experimental observations, however, important discrepancies are revealed between first-principles density functional theory predictions of phase stability and the current understanding of phase stability in this system. We conclude with a discussion of the possible role that vibrational excitations may play in affecting phase stability in the Ti-O system.

6.2 Methodology

The enumeration of different oxygen-vacancy and titanium-vacancy orderings over various parent crystal structures was performed with the CASM software package [34, 35, 28, 36]. CASM was also used to construct and parameterize cluster expansion Hamiltonians and to perform finite temperature Monte Carlo simulations.

Cluster expansion Hamiltonians [52, 143, 144, 53] were used to parameterize the dependence of the energies of the hcp Ti based suboxides and the rocksalt based oxides as a function of the degree of oxygen-vacancy and titanium-vacancy order. A cluster expansion is a natural parameterization of the energy of a particular parent crystal structure as a function of configurational degrees of freedom. The approach relies on the use of occupation variables σ_i assigned to each oxygen (titanium) sublattice site i that is 1 if the site is occupied and 0 if it is vacant (or vice versa depending on the reference configuration). The energy of the crystal can then be expressed as an expansion in terms of polynomials of occupation variables belonging to different sites of a cluster according to [52]

$$E_f\{\vec{\sigma}\} = \sum_{\alpha} V_{\alpha} \phi_{\alpha} \quad (6.1)$$

where the cluster functions, ϕ_{α} , are defined as the product of the site occupation variables belonging to a cluster α ,

$$\phi_{\alpha} = \prod_{i \in \alpha} \sigma_i \quad (6.2)$$

The expansion coefficients, V_{α} , referred to as effective cluster interactions (ECI), are to be determined by training on a large set of energies of different oxygen-vacancy and titanium-vacancy orderings. A wide variety of schemes are available to choose the degree of truncation (i.e. which basis functions are included in the expansion) and the numerical

values of the ECI [145, 38, 146, 147]. In this work, we used a genetic algorithm approach [38] to select the important basis functions and fit the ECI using a least squares approach picking an expansion that minimizes the cross validation score. The cluster expansions were implemented in lattice Monte Carlo simulations to calculate finite temperature thermodynamic averages. These were used to generate free energy curves with which temperature versus composition phase diagrams were constructed.

6.3 Finite temperature phase stability

Experiments suggest that hcp and rocksalt based suboxides form solid solutions that are stable over large composition ranges at high temperature [61, 17]. In hcp, the ordered suboxides undergo order-disorder transitions upon heating in which oxygen and vacancies disorder to form a high temperature solid solution [148]. The oxygen and titanium vacancies of the rocksalt based phases, which are ordered at low temperature, can also disorder to form a high temperature solid solution [149].

We investigated these order-disorder transitions and the high temperature disordered solid solutions by combining DFT-PBE parameterized cluster expansions with Monte Carlo simulations. For hcp based TiO_x we constructed a cluster expansion that describes the configurational energy for oxygen-vacancy disorder over the octahedral sites of the hcp Ti sublattice. The parameters of the expansion were fit to 350 DFT-PBE formation energies using a genetic algorithm to determine an optimal set of interaction coefficients. The cluster expansion fit has the weighted cv score of 3.2 meV/unit cell and a weighted rms of 2.9 meV/unit cell. The weights on the configurations reduce exponentially with increasing distance from the convex hull.

We also constructed a cluster expansion to describe the configurational energy of vacancies over both the Ti and O sublattices of rocksalt TiO. This cluster expansion is capable of describing the vacancy ordered γ' -TiO rocksalt phase as well as the other ground states that can be derived from rocksalt by introducing vacancies on the Ti and O sublattices. These include the ground states having Ti_6O_7 and Ti_2O_3 stoichiometries and anatase TiO_2 . The cluster expansion does not predict the marginally stable Ti_4O_7 ground state as residing on the convex hull. A total of 611 DFT-PBE formation energies were used to parameterize the interaction coefficients of the rocksalt cluster expansion. The cluster expansion fit has a cv score of 34 meV/unit cell and the weighted rms of 25 meV/unit cell with weights scaled towards compounds in the composition region of interest.

Grand canonical Monte Carlo simulations were performed on the two cluster expansions to calculate thermodynamic averages, including average concentrations, grand canonical energy, heat capacity and the covariances of the number of oxygen/vacancies within the crystal, all as a function of temperature and oxygen chemical potential. The thermodynamic averages were then used to generate free energies with conventional free energy integration techniques [150, 59, 151, 60]. Application of the common tangent construction to the Gibbs free energies then enabled the construction of finite temperature phase diagrams.

Figure 6.1(a) shows a calculated temperature versus composition phase diagram for hcp based TiO_x and rocksalt $\text{Ti}_{(1-y)}\text{O}_y$. The phase diagram does not include the ω -Ti based suboxides, which are on the global convex hull at zero Kelvin but were left out when applying the common tangent construction to calculated Gibbs free energies. This was done to facilitate comparison to experimental assessments which do not yet include the ω -

Ti based oxide phases[61, 17]. Furthermore, since none of the oxides having an hcp oxygen sublattice (i.e. rutile, Magnéli and corundum) are predicted as global ground states with PBE, they also do not appear in the calculated phase diagram. Hence the phase diagram of Figure 6.1(a) is a metastable phase diagram and represents phase stability under the assumption that the ω -Ti based suboxides are prevented from forming due, for example, to kinetic factors.

The metastable phase diagram of Figure 6.1(a) shows that the hcp Ti based suboxides, α -Ti₆O, α -Ti₃O and α -Ti₂O, disorder to form a solid solution at intermediate temperatures, with stoichiometric Ti₆O and Ti₂O having order-disorder transition temperatures of approximately 1000 K. The solid solution, however, is stable to lower temperatures at compositions away from the ideal ordering stoichiometries. The α -Ti₆O suboxide phase is also predicted to be stable over a wide oxygen concentration range. The excess oxygen is accommodated in the vacant sites of the filled oxygen layers of the α -Ti₆O ordering (Figure 3.3a) without disrupting the $\sqrt{3}a \times \sqrt{3}a$ super lattice periodicity. Inspection of the heat capacity and the covariance of the oxygen concentration as a function of temperature and chemical potential suggests the existence of a second order transition between α -Ti₃O and oxygen excess α -Ti₆O. This is represented by the dashed line in Figure 6.1(a). The high temperature hcp based solid solution is predicted to be stable up to an oxygen concentration of $y \approx 0.33$ before it decomposes into a rocksalt based oxide.

The calculated phase diagram of Figure 6.1(a) replicates the vast solid solution region of hcp TiO_x at higher temperatures as observed experimentally and provides more clarity about phase stability at low temperature. It is also consistent with a previous first-principles study of the hcp TiO_x portion of the phase diagram by Burton and van de Walle

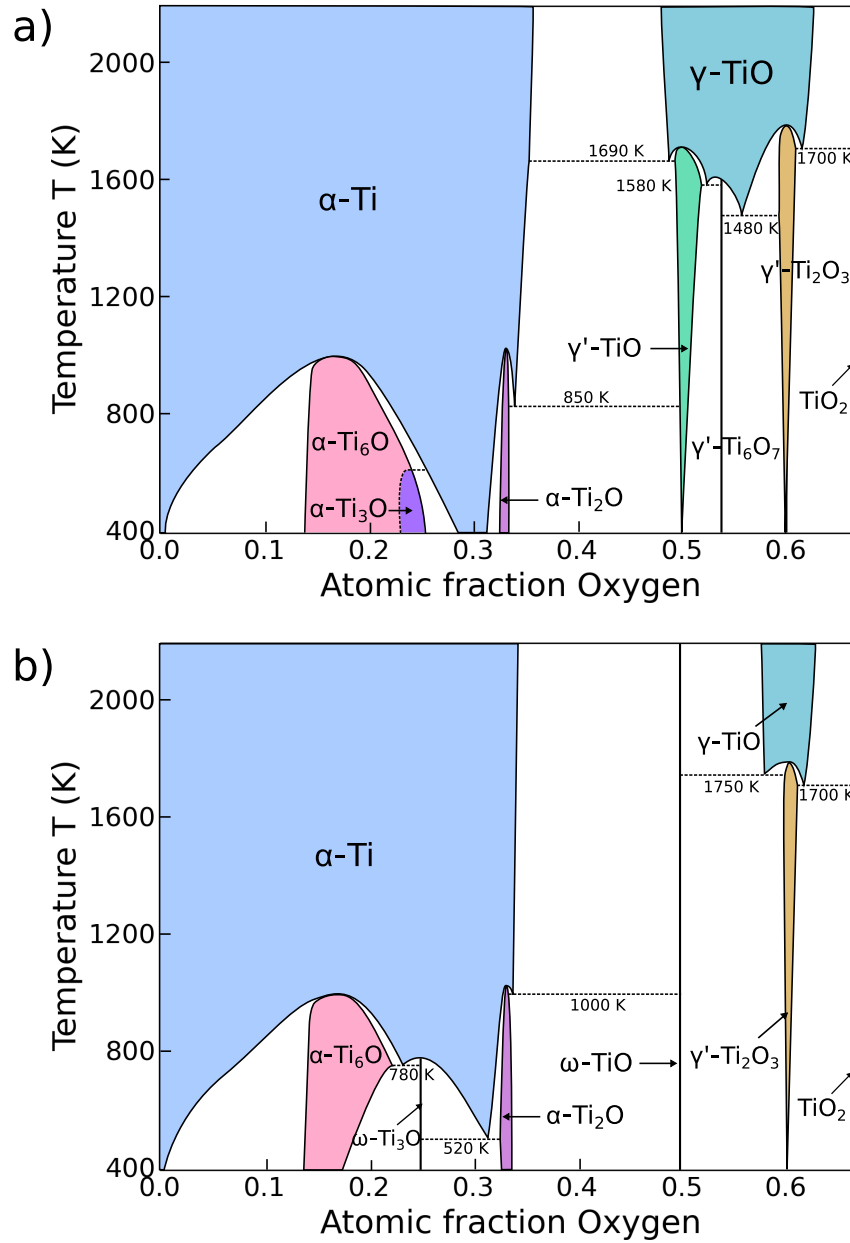


Figure 6.1: Calculated binary metastable and equilibrium Ti-O phase diagrams. (a) Metastable phase diagram calculated by excluding the ω -Ti based parent crystal structure. (b) Equilibrium phase diagram calculated by considering all four parent crystal structures.

[97], although there is a difference in the predicted order-disorder transition temperature of Ti_2O . The present study also predicts a second order transformation between the α - Ti_6O and α - Ti_3O , while such a transition is not predicted in the previous study. These disparities are likely due to differences in the parameterization of the cluster expansion Hamiltonian. The cluster expansion of the present study was parameterized with three times as many DFT calculations as were used in the earlier studies.

Figure 6.1(a) shows that the rocksalt orderings are predicted to disorder at temperatures between 1600 and 1700 Kelvin. This is substantially higher than the transition temperatures reported in assessed phase diagrams based on experimental measurements [152]. The disordered rocksalt phase is stable in a wide concentration range at high temperature, consistent with assessed phase diagrams of the Ti-O binary [61, 17].

Figure 6.1(b) shows a calculated phase diagram when all four parent crystal structures are considered and represents global phase stability as predicted with DFT-PBE. In constructing the phase diagram of Figure 6.1(b) all ω -Ti based suboxides were treated as line compounds. Configurational entropy favors hcp TiO_x at high temperature with ω - Ti_3O (treated as a line compound) transforming to an hcp TiO_x solid solution at approximately 800 K. Figure 6.1(b) also shows that configurational entropy within the rocksalt host is not large enough to overcome the energy difference between ω -TiO and γ' -TiO predicted at zero Kelvin with DFT-PBE, with ω -TiO predicted to be stable at all temperatures considered. The high temperature disordered γ -TiO rocksalt is still predicted to form, but only at concentrations where the oxygen content is higher than the Ti content.

6.4 Discussion

Our systematic investigation of phase stability over four parent crystal structures (i.e. α -TiO_x, ω -TiO_x, rocksalt derived oxides and oxides having an hcp oxygen sublattice) has shown that DFT is capable of accurately describing important features of the Ti-O binary phase diagram. The combination of DFT-PBE calculations and cluster expansion approaches to account for configurational degrees of freedom predict an oxygen solubility in hcp Ti of approximately 33%, in excellent agreement with experiment. Furthermore, the oxygen within hcp Ti is predicted to order at low temperature as observed experimentally [153, 114, 154]. DFT-PBE also predicts that the experimentally observed vacancy ordered rocksalt, γ' -TiO, is a ground state when considering all vacancy orderings over the Ti and O sublattices of rocksalt. Monte Carlo simulations show that the vacancy ordered rocksalt phases undergo order-disorder transitions to form a high temperature disordered rocksalt solid solution over an extended oxygen composition. This is again qualitatively consistent with experimental observations and assessed phase diagrams, although the predicted order-disorder transition temperatures are substantially higher than reported ones [152]. Another apparent inconsistency is the prediction that ω -Ti₃O and ω -TiO are global ground states that are stable at finite temperatures. Recently there is some evidence in the literature for the stability of the ω -TiO ground state over the γ' -TiO configuration[63], but there is no experimental evidence for the existence of an ω -Ti₃O suboxide.

While our study accounted for configurational degrees of freedom, vibrational excitations are also likely to be important at elevated temperature. The inclusion of vibrational degrees of freedom could qualitatively modify several of the predicted zero Kelvin relative stabilities. In fact, recent experimental and first-principles studies of TiO₂ have

demonstrated the importance of anharmonicity in rutile and have pointed to the possibility that vibrational excitations could reverse the relative stability between rutile and anatase at intermediate and high temperatures [155, 156]. Vibrational excitations are also likely important at low oxygen concentrations. The ω -Ti phase is the ground state in the absence of oxygen, but transforms to hcp α -Ti at intermediate temperatures due to a difference in vibrational entropy [157]. A similar difference in vibrational entropy may reverse the predicted relative stability between α -Ti₃O and ω -Ti₃O at intermediate temperatures considering that these two crystals differ in energy by only 4 meV/atom. Vibrational excitations may also affect the relative stability between ω -TiO and γ' -TiO. An investigation of phase stability in the chemically similar Zr-O binary showed that the ZrO monoxide having the same crystal structure as ω -TiO [28, 158] has less vibrational entropy than the other oxides in the Zr-O system [141]. The importance of anharmonic vibrational excitations in the oxides of the Ti-O system [155, 156] complicates the treatment of vibrational contributions to the free energy as it requires models that go beyond the quasi-harmonic approximation [159, 35, 160, 161].

The strong affinity between titanium and oxygen and the difficulty of eliminating other impurities such as hydrogen, carbon and nitrogen that also react to form compounds with titanium make this system especially challenging to study experimentally. Interstitial impurities such as carbon and nitrogen favor a rocksalt compound with Ti [162, 163] and if present as contaminants can play a role in selecting out the rocksalt form of TiO [20], which DFT calculations predict as being metastable relative to the ω -TiO. Intrinsic kinetic barriers between the hcp Ti sublattice of α -TiO_x and the ω -Ti sublattice of ω -Ti₃O and ω -TiO [164] may also play a role in suppressing the formation of what DFT predicts are equilibrium phases.

In summary, we have performed a comprehensive first-principles study of phase stability in the Ti-O binary both at zero Kelvin and at finite temperature by accounting for configurational degrees of freedom. Many qualitative features of the predicted equilibrium and metastable phase diagrams agree with experimental observations. This includes a prediction of an exceptionally high oxygen solubility in hcp Ti, the stability of oxygen ordering within hcp Ti at low temperature and the stability of rocksalt based oxides having high concentrations of both oxygen and titanium vacancies at intermediate concentrations. The inclusion of vibrational contributions to the free energy may rectify several of these discrepancies and should be the focus of future studies. Experimental studies are suggested to further refine the crystal structures of the oxides and suboxides in this complex system.

Chapter 7

Oxygen induced chemical short range ordering in Ti-Al based alloys

7.1 Introduction

Intermetallic Ti-Al based alloys are widely used in weight sensitive applications[165]. Refractory additions such as Ti enhance the high temperature properties of the alloys[10] whereas Al has low density and improves the corrosion resistance of the alloy by aiding in the formation of surface Al_2O_3 layer[166, 167, 168]. Ti is very reactive and can dissolve significant quantities of interstitial elements such as oxygen[17], nitrogen[16] and carbon[19]. It is interesting to understand the interaction of substitutional additions such as Al with the dissolved interstitial elements in Ti. The present chapter illustrates the effect of dissolved oxygen on Ti-Al alloys using pseudo-binary phase diagrams. Oxygen was found to induce chemical short range ordering in the disordered hcp solid solution phase and increase the relative stability of the disordered α -Ti over the ordered Ti_3Al phase. Ti and Al are used in the design of light weight high entropy alloys[169] and the insights from the current study can shed light on similar interactions between the solute

atoms in HEA's[8].

In this chapter, we have performed a comprehensive first principles based finite temperature analysis of the ternary Ti-Al-O system. We discovered a new stable ground state which is illustrated in section 7.3.1. Section 7.3.2 presents the cluster expansion based coarse grained thermodynamic model built for the Ti-Al-O system and also introduces the chemical short range ordering observed in the system at high temperatures. Section 7.3.3 describes the pseudo-binary Ti-Al phase diagrams obtained at different degrees of oxygen solubility. Finally section 7.4 discusses the implication of oxygen induced chemical short range ordering to the phases stability of the ordered and the disordered phases in the Ti-Al alloys.

7.2 Methodology

Finite temperature thermodynamic assessment for the Ti-Al-O system was performed using a combination of 0 K first principle calculations and statistical mechanics approaches. The following sections provide details regarding the setup used for running first-principles calculation, constructing basis functions and fitting ternary cluster expansion.

7.2.1 DFT calculations

Total energies for the enumerated configurations based on hcp and fcc crystal systems were calculated using density functional theory(DFT) as implemented in VASP[45, 46, 47, 48]. The calculations in the current study were performed within generalized gradient approximation(GGA).The exchange correlation term was parametrized using the Perdew, Burke and Ernzerhof(PBE) method[50, 51] and the interaction between core states and

valence states was done using projector augmented wave (PAW) method [90, 91]. The PAW-PBE potentials used in the current study kept 3s, 3p, 3d and 4s orbitals of Ti (Ti_sv) as valence. Also the 3s and 3p states in Al along with 2s and 2p states in O were as considered valence shells.

For running the VASP calculations, a plane wave energy cutoff of 550 eV was used. k-point convergence was performed on both primitive hcp and fcc structures to converge the energies to within 2 meV/atom. Γ -centered k-point mesh grids of size $14 \times 14 \times 8$ was used in hcp and mesh grid of size $22 \times 22 \times 22$ was used in fcc to achieve the desired convergence level. For configurations belonging to a supercell of the primitive structure, the k-point grid was scaled to keep the density of k-points in the reciprocal space constant. All the structures were allowed to relax from their ideal lattice parameters until a energy convergence of 10^{-6} eV for the configuration and force convergence of 0.02 eV/Å on each atom was achieved. After complete relaxation of a configuration, a static calculation was performed to obtain high accuracy total energies. Partial occupancy were treated using Methfessel-Paxton (order 2) method for relaxation runs and tetrahedron method with Blöchl corrections was used in static runs. The ground states predicted in the current study did not show any net magnetic moment after relaxation.

DFT energies of hcp-Ti (E_{Ti}^{hcp}), fcc-Al (E_{Al}^{fcc}) and O₂ molecule (E_{O_2}) were used as references to define the formation energy (E_f) for the configurations. Equation 7.1 provides the definition for the formation energy of the configurations in terms of the concentration of Ti, Al and O atoms. For this study we have used atomic fractions (x_M where M = Ti, Al, O) to define the composition of the enumerated configurations.

$$\begin{aligned}
E_f &= E_{tot}^{DFT} - x_{Ti}E_{Ti}^{hcp} - x_{Al}E_{Al}^{fcc} - x_O \frac{E_{O_2}^{corr}}{2} \\
x_M &= \frac{N_M}{N_{Ti} + N_{Al} + N_O}
\end{aligned} \tag{7.1}$$

where E_f and E_{tot}^{DFT} are the formation energy normalized per atom and DFT predicted total energy of the configuration normalized per atom respectively. x_M is the atomic fraction defined in terms of N_M the number of atoms of type M(Ti/Al/O) in the configuration. In case of O_2 molecule, a corrected total energy of the molecule($E_{O_2}^{corr}$) was used. DFT does not predict the binding energy of oxygen accurately and the correction proposed by Wang et al.[170] and Lee et al.[171] was implemented.

7.2.2 Ternary cluster expansion

Ternary cluster expansion Hamiltonians were used to parametrize the formation energy of the configurations[52, 53, 54]. Basis functions were constructed using degrees of freedom on the metal and interstitial sublattice. Every site has an occupation variable σ_i that depend on the degree of freedom on that site. For the metal sublattice, the value of σ_i is assigned to be 0 if the site is occupied by Ti atom and is assigned a value of 1 if the site is occupied by Al. Similarly on the interstitial sublattice, the value of σ_i is assigned to be 0 if the site is empty i.e. occupied by a vacancy and is assigned a value of 1 if the site is occupied by Al.

Clusters are a group of sites and each symmetrically unique cluster has a basis function attached to it. Basis function for a cluster α is obtained by multiplying the occupation

variables(σ_i) of the sites in the cluster as shown in the following equation

$$\phi_\alpha = \prod_{i \in \alpha} \sigma_i \quad (7.2)$$

The formation energy(E_f) of an enumerated configuration can be expressed in terms of polynomials of the clusters functions(ϕ_α). The equation describing the formation energy using the basis functions is as follows

$$E_f\{\vec{\sigma}\} = \sum_{\alpha} V_{\alpha} \phi_{\alpha} \quad (7.3)$$

where the terms V_{α} are the effective cluster interactions(ECI's). These are determined by training a large set of formation energy data of the enumerated configurations. In the current study a Hamiltonian was constructed on the ternary hcp system. A total of 1507 number of symmetrically unique clusters(57 pairs, 183 triplets, 1265 quadruplets) were enumerated. The ECI's for the clusters with no cross terms in the basis functions from the interstitial sublattice and the metal sublattice were fixed according to the previous studies done on the Ti-O[172] and Ti-Al systems[173]. This helps to keep the binary phase stability consistent with the previous studies[32]. For the remaining clusters a genetic algorithm was used to pick only the important clusters and the least squares method was used to obtain the ECI's [38].

Thermodynamic averages were obtained from Monte Carlo simulations performed on a supercell of size $12 \times 12 \times 12$ of the primitive hcp unit cell on grid of chemical potentials at each temperature. A convergence of 1 meV/atom in formation energy and 0.5% in atomic compositions were achieved in each of the Monte Carlo runs. To avoid hysteresis, the Monte Carlo runs at each temperature were performed starting from different stable ground state configurations. High temperature free energy used to

construct phase diagrams was obtained using standard free energy integration techniques [59, 60, 131].

7.3 Results

Finite temperature thermodynamic assessment of the Ti-Al-O ternary system has been performed to establish the influence of oxygen on the Ti-Al system. First we performed a 0 K analysis and discovered a new ground state. Next finite temperature thermodynamics was obtained using cluster expansion and Monte Carlo methods. Previous first-principles studies have looked at the individual binary systems namely Ti-O[172] and Ti-Al[173] systems. In the current study, the ternary composition space was explored in two parent crystal systems namely the hexagonal close packing(hcp) and the face centered cubic(fcc) systems.

7.3.1 Discovery of a new ternary ground state

We enumerated a large number of symmetrically unique configurations in the hcp and the fcc crystal systems using A Cluster Approach to Statistical Mechanics(CASM) software package[34, 35, 28, 36]. Configurations are enumerated by arranging the metal atoms(Ti and Al) on the triangular close packed planes and oxygen atoms on some of the octahedral interstitial sites in the crystal. The 0 K energy of the enumerated configurations was obtained using density functional theory(DFT) as implemented in the Vienna ab initio simulation package(VASP). The Figure 7.1a) shows the 0 K phase diagram of the Ti-Al-O system which provides the phase equilibrium of the ground states i.e. the configurations that are stable at 0 K.

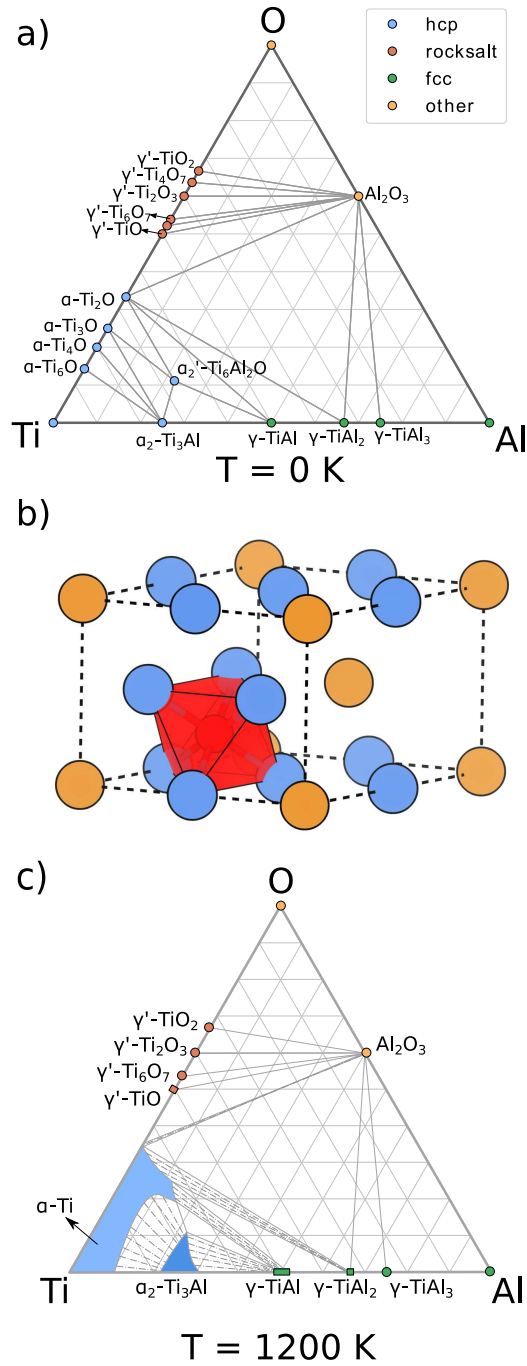


Figure 7.1: a) Ternary convex hull of the Ti-Al-O system showing ground state configurations based on the hcp, fcc and rocksalt crystal systems. b) Unit cell of the newly discovered ternary ground state α_2 '-Ti₆Al₂O. Ti, Al and O atoms are shown in blue, orange and red colors respectively. c) Calculated ternary phase diagram for Ti-Al-O system at 1200 K.

	Distance between Al and O defects (Å)	Formation Energy, E_f (eV)
1 st NN	2.06	0.754
2 nd NN	3.59	0.056
3 rd NN	3.88	0.033
4 th NN	4.63	0.0

Table 7.1: Formation energy of the configurations in hcp-Ti with dilute Al and O defects situated at different nearest neighbor(NN) distances.

The binary suboxides and oxides shown along the Ti-O axis are discussed in chapter 3. The Ti-Al axis consists of α_2 -Ti₃Al which is an ordering on the hcp crystal, while γ -TiAl, TiAl₂ and TiAl₃, are orderings on the fcc crystal[174]. Ordered Al₂O₃ compound on the Al-O axis has the corundum structure where O forms the hcp crystal and Al occupies the interstitial positions[175].

We have discovered a new ternary ground state ordering labeled as α_2' -Ti₆Al₂O as seen in the 0 K phase diagram in Figure 7.1a). The prime in the label indicates that the ordering is derived by adding oxygen to the α_2 -Ti₃Al crystal. Figure 7.1b) shows the unit cell of the ordered compound. The metal atoms in the compounds are in a DO₁₉ ordering similar to α_2 -Ti₃Al while O occupies the octahedral interstitial site coordinated by 6 Ti atoms. There is some evidence in the literature that in O occupies the interstitial sites in Ti₃Al crystal with first nearest neighbor Ti interactions and avoids Al atoms due to repulsion[176, 177], but there was no evidence of the new ternary ground state in the Ti-Al-O system.

The repulsion between the Al and O atoms in the Ti₃Al crystal was observed even at the dilute limit of the solute atoms. Defect configurations in hcp-Ti were enumerated by placing one Al defect and one interstitial O atom at different distances from each other. Formation energies for the defect configurations are shown in table 7.1 and the

energies are referenced to the configuration where the defects are the farthest. DFT calculations for these configurations are performed in a large supercell($3 \times 3 \times 3$ of the hcp-Ti unitcell) to avoid interaction with periodic images.

From the table we can see that the formation energy is highest for the configuration where the defects are the closest. Also there is a significant drop in energy when the defects are pushed away into the second nearest neighbor(NN) position. But the energy stabilizes if we move the defects further apart to third and fourth neighbors. Due to the repulsion between the Al and O atoms, the Al-O first neighbor bond is high in energy. These bonds are not present in the configurations where defects are further apart thereby lowering the formation energy of these configurations. This behavior is reflected in the newly discovered α'_2 -Ti₆Al₂O ground state, O avoids the high energy Al-O bonds by occupying octhedra formed the titanium atoms.

7.3.2 Finite temperature ternary phase stability

At higher temperatures, the ground state configurations can disorder and may go through a order-disorder phase transition. Experimentally drawn finite temperature phase diagrams for the Ti-Al-O system show extensive solid solubility for the hcp based Ti rich phases[178]. We have investigated the finite temperature solubility using the cluster expansion method along with grand canonical Monte Carlo sampling. To fit the formation energies of the hcp based configurations, a ternary cluster expansion was parametrized using formation energies of 2050 configurations. The fit had a weighted rms of 0.036 eV/atom, but in the Ti rich region($x_{Ti} > 0.66$) where the hcp based phases are stable, the weighted rms comes down to 0.007 eV/atom.

The calculated ternary Ti-Al-O phase diagram at 1200 K is presented in Figure 7.1c). The Phase diagram was calculated by applying common tangent construction to free energies calculated with Monte Carlo simulations and standard free energy integration techniques[59, 60, 131]. The phase diagram in Figure 7.1c) shows large solid solution regions for the hcp based disordered α -Ti and ordered α_2 -Ti₃Al phases and a wide two phase region between the single phase fields. The α_2 -Ti₃Al phase exhibits partial disorder due to the formation of antisite defects on the metal sublattice and it can dissolve up to 11 atomic percentage oxygen. Also around 20 atomic percent oxygen, α -Ti phase field has a deep solubility range into the composition triangle. This indicates simultaneous solubility of oxygen and aluminum atoms in the disordered α -Ti phase.

The topology of the ternary phase diagram can be understood by the inspection of the ordering in the system. Figure 7.2 shows the snapshots of the equilibrated Monte Carlo simulation cell at 1200 K. The snapshots were taken from a grand canonical Monte Carlo run while passing through the two phase region between the disordered α -Ti and the ordered α_2 -Ti₃Al phases. In Figure 7.2a), the Al atoms(shown in orange) and the Ti atoms(shown in blue) are ordered on the metal sublattice with the O atoms(shown in red) spread in random throughout the interstitial sublattice. Conversely the snapshot in Figure 7.2b) is taken in the disordered α -Ti phase that is in equilibrium with the ordered phase across the two phase region. The metal sublattice of the system in this configuration is completely disordered and the number of oxygen atoms in the adjoining layer is higher than the ordered phase. Importantly oxygen atoms are found to be next to a Ti atom and avoid Al atoms.

Monte carlo sampling performed at finite temperatures showed short range ordering of Al and O atoms in the hcp crystal. Due to the repulsion, O atoms avoid occupying

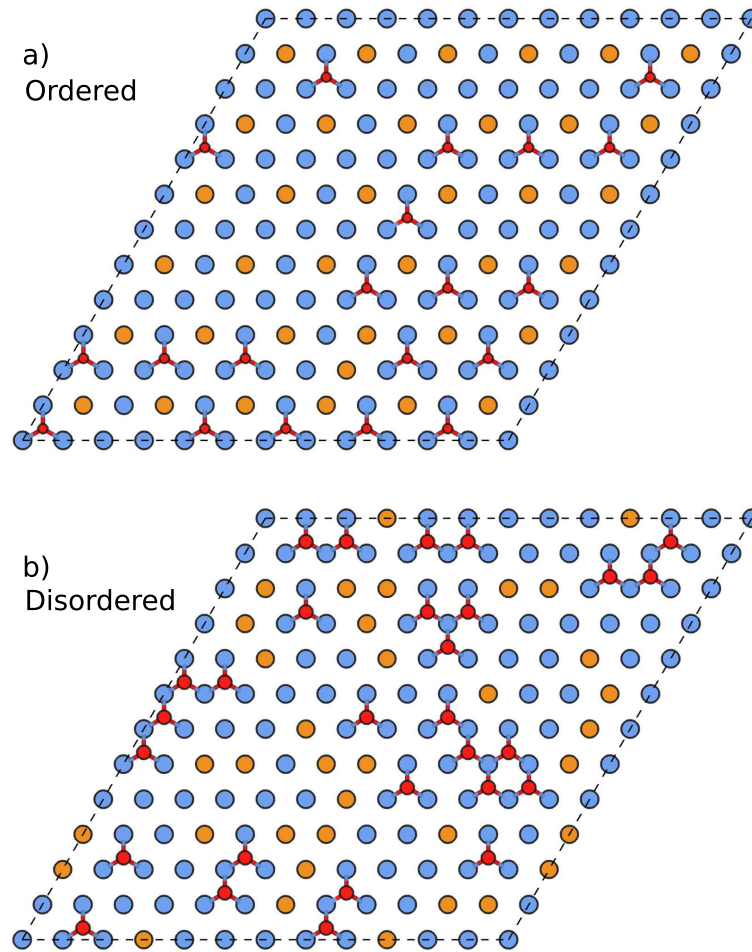


Figure 7.2: Monte carlo snapshots of the equilibrated simulation cells at 1200 K. The snapshots show one of the close packed planes in the metal sublattice and an adjoining interstitial sublattice plane containing oxygen atoms. Sub figure a) is a snapshot when the system is disordered and b) is a snapshot when the metal sublattice is ordered as in α_2 -Ti₃Al phase.

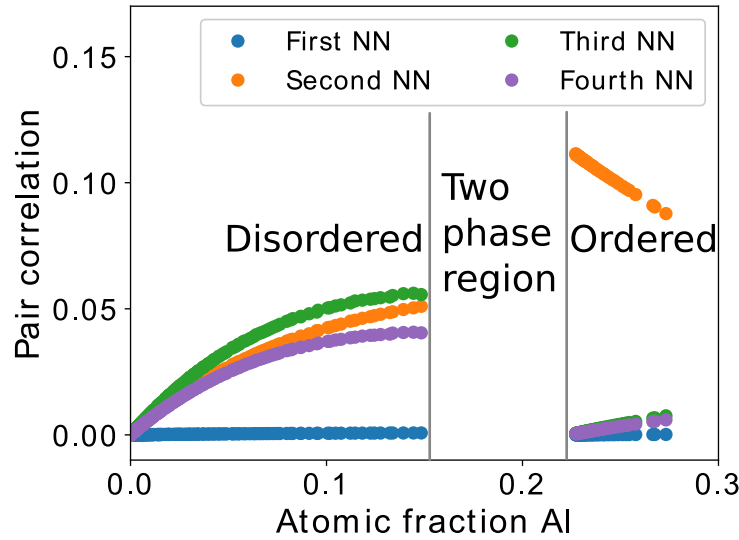


Figure 7.3: Average pair correlation along the constant oxygen chemical potential Monte Carlo run at 1200 K

any octahedron formed by one or more Al atoms. This is evident from Figure 7.3 which provides the average pair correlation of the Al-O pairs during the Monte Carlo simulation. Pair correlation is the probability of finding Al-O bonds and is zero at first neighbor distance in the disordered α -Ti and the ordered α_2 -Ti₃Al phases. This indicates that there are no high energy first neighbor Al-O bonds in the system. The Al atoms are ordered in the α_2 -Ti₃Al phase which otherwise restricts the number of sites for oxygen. The α -Ti phase has higher oxygen solubility as its metal sublattice is disordered increasing the number of sites where Al and O atoms avoid first neighbor pairs. The difference in the solubility of oxygen between the ordered and the disordered phases will have significant impact on the binary Ti-Al equilibrium and is further explored in the next section.

7.3.3 Effect of dissolved oxygen on the binary Ti-Al phase stability

The pseudobinary Ti-Al phase diagrams will depend on the amount of dissolved oxygen, which in turn is dependent on the oxygen chemical potential of the environment. We can calculate pseudobinary phase diagrams at constant oxygen chemical potentials by minimizing the Legendre transformed free energy(Λ)[179] expressed as

$$\Lambda(T, P, N_{Ti}, N_{Al}, \mu_O) = \frac{G - \mu_O N_O}{N_{Ti} + N_{Al}} \quad (7.4)$$

Figure 7.4a) shows the Ti rich part of the calculated ternary phase diagram overlapped with the data of equilibrium atomic composition at different oxygen chemical potentials. Increase in oxygen chemical potential leads to an increase in the dissolution of oxygen in the hcp based α -Ti and α_2 -Ti₃Al phases. Each pseudo-binary phase diagram in Figure 7.4b)-e) is obtained by solving for the phase equilibrium of the Ti-Al system at a fixed oxygen chemical potential. The value of the oxygen chemical potential goes up as we go from Figure 7.4b) to 7.4e) thereby increasing the dissolution of oxygen in the system. The color coding in binary phases diagrams in Figure 7.4 denotes the equilibrium oxygen composition in the single phase regions. Blue represents no oxygen solubility in the phase and red represents the maximum oxygen solubility of O in Ti(33 atomic percentage O). The two phase regions are color coded as white in the phase diagrams and the dashed lines represent the boundary between the α_2 -Ti₃Al and the α -Ti phases where the system goes through a order-disorder phase transition.

The phase diagram in Figure 7.4b) corresponds to a very low oxygen chemical potential. The single phase regions in this phase diagram are fully blue which means that this is

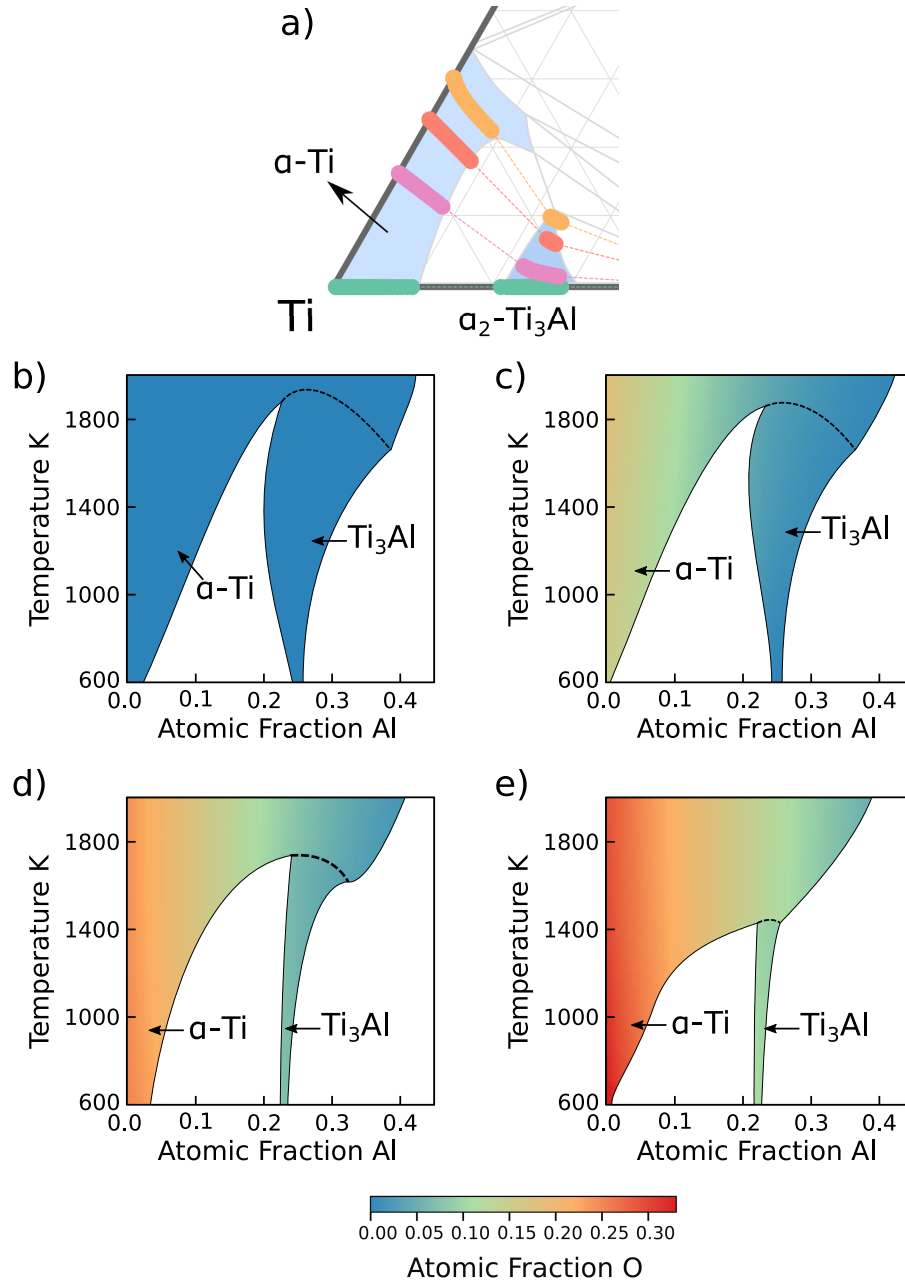


Figure 7.4: a) Ti rich section of the ternary Ti-Al-O phase diagram showing equilibrium concentrations at different oxygen chemical potentials. b-e) Pseudo-binary Ti-Al phase diagram drawn at different degrees of oxygen solubility. The chemical potential of the oxygen increases as we go from b) to e). The color in the single phase fields correspond to the equilibrium oxygen composition. The color bar at the bottom of the Figure maps the color onto atomic fraction of $O(x_O)$.

close to the true Ti-Al phase equilibrium when the amount of O is negligible. At low oxygen environments, there is a large single phase field for the ordered α_2 -Ti₃Al phase. As the chemical potential of O goes up, the oxygen dissolution in the ordered phase goes up and the width of the single phase region decreases (Figures 7.4c-e). The ternary phase diagram in Figure 7.1c) shows the decreasing width of the ordered α_2 -Ti₃Al phase with increasing oxygen composition of the phases in equilibrium. Hence as the ordered phase dissolves higher quantities of oxygen, the composition range where the phase is stable decreases.

The pseudo-binary phase diagrams suggest that the order-disorder transition temperature is very sensitive to the oxygen chemical potential. This is due to the ability of the disordered α -Ti phase to dissolve high concentration of oxygen. The transition temperature from the ordered α_2 -Ti₃Al to the disordered α -Ti with out any oxygen is around 1900 K (Figure 7.4b), but at oxygen solubility limit of α -Ti it drops down to 1450 K (Figure 7.4e). At higher oxygen dissolution, α_2 -Ti₃Al phase disorders into α -Ti phase at much lower temperature.

The phase diagrams also show that in the disordered α -Ti phase, as the composition of Al goes up the equilibrium concentration of O comes down. At higher Al concentration, the number of sites for O is restricted because Al and O atoms avoid each other due to repulsion. This behavior in O solubility leads to a difference in oxygen composition between the α -Ti and α_2 -Ti₃Al phases across the two phase equilibrium. A tie line at finite temperature on the phase diagrams (Figure 7.4c-e), shows that the ordered α_2 -Ti₃Al phase is in equilibrium with the disordered α -Ti phase that has higher O dissolution. Hence at constant temperature the system can disorder the metal sublattice to dissolve more oxygen. This phenomenon in Ti-Al system has important consequences on the

thermodynamic stability of the ordered α_2 -Ti₃Al phase and is discussed in the next section.

7.4 Discussion

We have investigated the influence of oxygen on the phase stability in the Ti-Al system. Zero kelvin analysis of the configurations enumerated in the Ti-Al-O ternary system revealed a previously unknown stable ground state ordering α'_2 -Ti₆Al₂O (Figure 7.1b). Finite temperature phase equilibrium obtained using the cluster expansion model and Monte Carlo sampling was used to explore phase stability in the system. O induced chemical short range ordering in the system while making the disordered α -Ti phase more stable.

An experimentally drawn phase diagram at similar temperature by Kelkar et al.[180] is available in the literature. Both the experimental phase diagram and the computational phase diagram presented in the current study have similarities in their prediction of the hcp based solid solution phases. As an example, in the current study we also predict a big two phase region between the disordered α -Ti and the ordered Ti₃Al phase and at maximum oxygen solubility in α -Ti (about 33 atomic percent O) there is no Al dissolution. The difference is that we predict a lower oxygen solubility (about 11 atomic percent of O) in Ti₃Al than the literature (about 20-25 atomic percentage oxygen[180]). Also around 20 atomic percent oxygen, the disordered α -Ti phase has a deep solid solution region into the composition triangle suggesting simultaneous solubility of Al and O which disagrees with experimental observations. High energy Al-O bonds and the short range ordering that occurs at finite temperatures in the disordered α -Ti phase are at the origins of the disparities.

The calculated pseudo-binary phase diagrams at different oxygen chemical potentials provide insight as to the origin of the large discrepancies between different experimental phase diagrams of the Ti-Al binary system[174]. This may be due to the different oxygen partial pressures at which the experiments are performed thereby changing the amount of the dissolved oxygen in the samples. The presence of oxygen lowers the stability of the ordered α_2 -Ti₃Al phase when compared to the disordered α -Ti phase. The ternary phase diagram in Figure 7.1c) shows the reducing solid solution range for the α_2 -Ti₃Al phase as the oxygen composition goes up. Also the pseudo-binary Ti-Al phase diagrams in Figures 7.4b)-e) shows that the maximum stable temperature for the ordered α_2 -Ti₃Al phase goes down with increasing oxygen solubility. This indicates that the disordered α -Ti phase is more stable at higher oxygen concentrations. Hence the amount of dissolved oxygen dictates the relative stability of the ordered and the disordered phases.

We have observed that the repulsion between the Al and O atoms causes high energy first neighbor Al-O bonds. Monte Carlo snapshots in Figures 7.2a-b) and pair correlation data in Figure 7.3 shows that the repulsion causes the oxygen atoms to pick sites that are far away from Al. The disordered α -Ti phase has short range ordering in the disordered metal sublattice which helps accommodate excess amount of oxygen atoms while avoiding first neighbor Al interactions. But the ordered α_2 -Ti₃Al phase has its metal sublattice intact and cannot accommodate excess oxygen. Hence at a constant temperature, a transformation from ordered α_2 -Ti₃Al phase into a disordered α -Ti phase will increase the oxygen solubility of the system. This means that the system can disorder the metal sublattice and dissolve higher concentration of oxygen atoms while making the ordered phase less stable.

7.5 Summary

We have performed first-principles statistical mechanics analysis to determine the influence of substitutional Al addition on the solubility of interstitial oxygen in hcp-Ti. We discovered a new ternary ordered compound in the Ti-Al-O system using density functional theory calculations. Due the repulsion between the solute atoms, O prefers to occupy interstitial sites that avoid first neighbor interaction with Al atoms in the Ti rich matrix. Finite temperature analysis shows that O induces chemical short range ordering in the disordered α -Ti phase at high temperatures. The solubility of oxygen in was limited in the α_2 -Ti₃Al phase due to the ordered metal sublattice thereby restricting the number of favorable O interstitial sites.

Pseudo-binary Ti-Al phase diagrams at different levels of oxygen solubility were constructed to analyze the effect of dissolved oxygen on the binary phase stability. Difference in oxygen solubility across the two phase equilibrium between the ordered α_2 -Ti₃Al and the disordered α -Ti phase meant that the system can disorder the metal sublattice to accommodate higher oxygen concentration in the alloy. The Pseudo-binary phase diagrams suggests at higher oxygen dissolution the disordered α -Ti phase is much more stable than the ordered α_2 -Ti₃Al phase.

Chapter 8

Conclusion

Ever since its discovery in late 18th century, there has been a growing interest in using titanium for industrial, aerospace and biological applications. Interstitial solutes play a vital role in strengthening mechanisms present in the material, such as precipitation hardening and solid solution strengthening. Titanium is a very reactive metal which can dissolve significant amounts of interstitial elements and form diverse ordered compounds with many substitution additions. In this dissertation, we use a combination of first-principles and statistical mechanics methods to build finite temperature thermodynamic models for titanium interstitial alloys. Interaction between hcp α -Ti stabilizing interstitial and substitutional solutes was investigated in the present work.

In the first part of the dissertation, the orderings of C, N and O interstitial elements in Ti at 0 K were determined. Chapter 3 discussed the phase stability of ordered compounds in the Ti-O binary system, whereas in chapter 4 the orderings of Ti carbides and nitrides were presented. Using first-principles methods, a series of stable and metastable ground states were discovered in various crystal structures of Ti such as hcp, ω and rocksalt crystals. In the hcp-Ti crystal system, a series of stable suboxide (Ti_xO) ground states

in the Ti-O binary and ordered α -Ti₂N compound in Ti-N binary were found to be stable. In the rocksalt crystal structure, newly discovered Ti-rich orderings include γ -Ti₄N₃, γ -Ti₄C₃ and γ -Ti₉N₈. In the Ti-O system, O-rich rocksalt based oxides containing vacancies on both the metal and interstitial sublattices were found to be stable. Experimental observations do not contain any ω -Ti crystal based orderings but DFT predicted oxides that were globally stable. As Standard DFT-PBE methods are known to fail at predicting the right Ti orderings, especially at high O concentration, a sensitivity analysis using other well known dft extensions was performed to analyze the relative stability of oxides predicted in the current study.

In the next part of the dissertation, the finite temperature phase stability in the binary interstitial systems was explored. Using a combination of coarse grained DFT parametrized cluster expansion models and Monte Carlo simulations accurate phase diagrams were calculated. Chapter 5 resolves the phase stability of ordered compounds based on the hcp and fcc crystals systems that are stable in the Ti-rich section of the binary Ti- X ($X = \text{C, N, O}$) phase diagrams. Carbon stabilized a lot of rocksalt based orderings, whereas oxygen stabilized hcp based orderings, with nitrogen having an intermediate effect on the phase stability. This behavior was linked to the electronic structure of the ordered compounds and the change in the number of valence electrons between the interstitial elements. Chapter 6 works out the complete phase diagram of the Ti-O binary system. Many of the features in the phase diagram agree with experimental observations but there are some subtle and important differences in the phase stability predicted using thermodynamic models. While the disagreement at higher O concentrations can be associated with the failure of standard DFT methods, the chapter presents arguments for other factors that can be at work affecting the phase stability of lower oxides and suboxides.

Finally in the last part of the dissertation, the ternary Ti-Al-O system with both substitutional and interstitial solutes was explored. The solubility of interstitial O with the addition of substitutional Al on the Ti sublattice was investigated. The 0 K analysis using first-principles methods discovered a new ground state ordering in the ternary composition space. O in this ordering was found to preferentially occupy positions away from the first neighbor shell of Al atoms. This is due to the repulsion of Al and O atoms in the Ti-rich matrix present even at dilute concentrations of defects. The calculated high temperature phase diagrams showed simultaneous solubility of Al and O in the disordered α -Ti phase. O solubility in the ordered α_2 -Ti₃Al phase was limited as there are fewer sites for O to occupy that avoid the first nearest neighbor shells of Al atoms. Pseudo-binary phase diagrams of the Ti-Al system at different degrees of O solubility were used to understand the effect of O on phase stability. O was found to induce short range ordering in the disordered α -Ti phase and also increased the relative stability of the disordered α -Ti phase over the ordered α_2 -Ti₃Al phase.

Materials design is a complex process and understating the thermodynamics of interstitial alloy systems is fundamental for predicting mechanical response of structural materials. The insights developed in this dissertation can shed light on other alloy systems such as HEAs where similar interactions between interstitial solutes and metal atoms are important. As demonstrated in this dissertation, models generated using first-principles statistical mechanic methods can provide significant guidance in predicting phase stability at finite temperatures. The thermodynamic information generated for describing interstitial systems is crucial for building a multiscale model to predict oxidation sequences in titanium alloys. This dissertation provides links between the electronic structure of the materials and the predicted phase stability to answer some open questions in titanium alloys.

Appendix A

Ternary Ti systems of interest

A.1 Ti-O-C and Ti-O-N systems

We have enumerated around 200 configurations in the hcp crystal system with Ti on the metal sublattice while O and C/N were allowed on the interstitial sublattice. Figure A.1 shows the convex hulls for the Ti-O-C and the Ti-O-N systems. There were no stable ground states discovered in the hcp crystal. In the rocksalt crystal system, both metal and the interstitial sublattice are in the fcc crystal. In the Ti-O binary, the fcc-Ti sublattice contains vacancies while the Ti-C system does not have any vacancies on the metal sublattice. There were a few ternary ground states in the Ti-O-C fcc system but more work needs to be done to figure out the true grounds in the Ti oxycarbide and oxynitride systems.

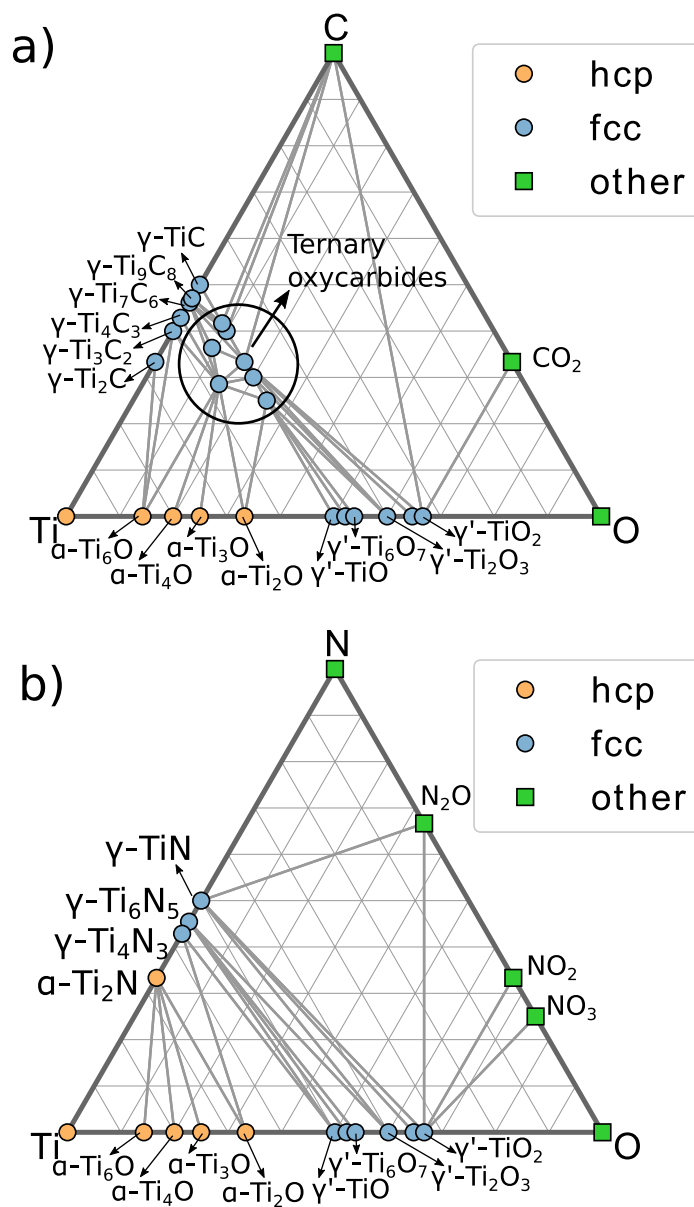


Figure A.1: Convex hull for a) Ti-O-C and b) Ti-O-N systems

A.2 Ti-Al-X (X=C, N, O) systems

The convex hulls in figures 7.1a) and A.2 shows the stable ground state orderings in the Ti-Al-X (X= C, N, O) systems. As discussed in chapter 7, we have discovered a new ternary ground state ordering (α_2' -Ti₆Al₂O) in the hcp crystal system. There is some experimental evidence for a ternary ground with cubic crystal usually referred as Z-phase with formula Ti₅Al₃O₂[181, 182, 183, 184, 185, 186]. We have performed DFT calculations using stable orderings with similar formula from other metallic systems, but we did not find any stable orderings in the Ti-Al-O system at the composition of the Z-phase.

The Ti-Al-C and the Ti-Al-N systems have ground states of the composition Ti_{n+1}AlX_n referred as MAX phases[187]. In the MAX phases, there is a slab of TiC or TiN rocksalt crystal sandwiched by Al layers. We have enumerated new MAX type configurations by changing the size of slab and the symmetry around Al layers. None of the newly enumerated MAX type phases were stable on the ternary convex hulls.

The stable Ti₃AlC ordering has antiperovskite structure with space group $Pm\bar{3}m$. The structure is similar to the perovskite structure, but the anion and cation positions are exchanged. In the CsXY₃ systems, ground states with tilted octahedron were found to more stable[188]. Figure A.3a) shows the structure of a Ti₃AlX structure with tilted octahedron, where the space group of the structure after tilting is $Im\bar{3}$. Energies of the Ti₃AlX structures with 15 different types of the octahedral tilts are shown in figure A.3b)-d). The Ti₃AlC structures have degenerate energies indicating no effect of the octahedral tilting. There were a few tilted octahedral Ti₃AlN and Ti₃AlO structures lower in energy than the untilted structures but the energy is not low enough to be stable ground states.

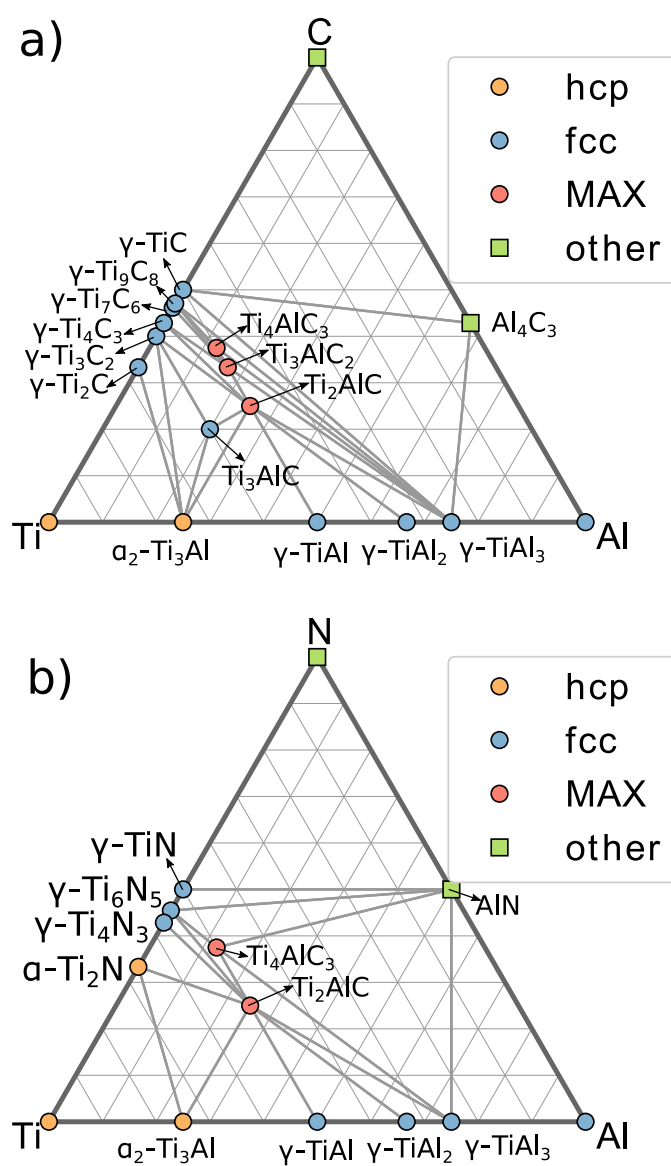


Figure A.2: Convex hull for a) Ti-Al-C and b) Ti-Al-N systems

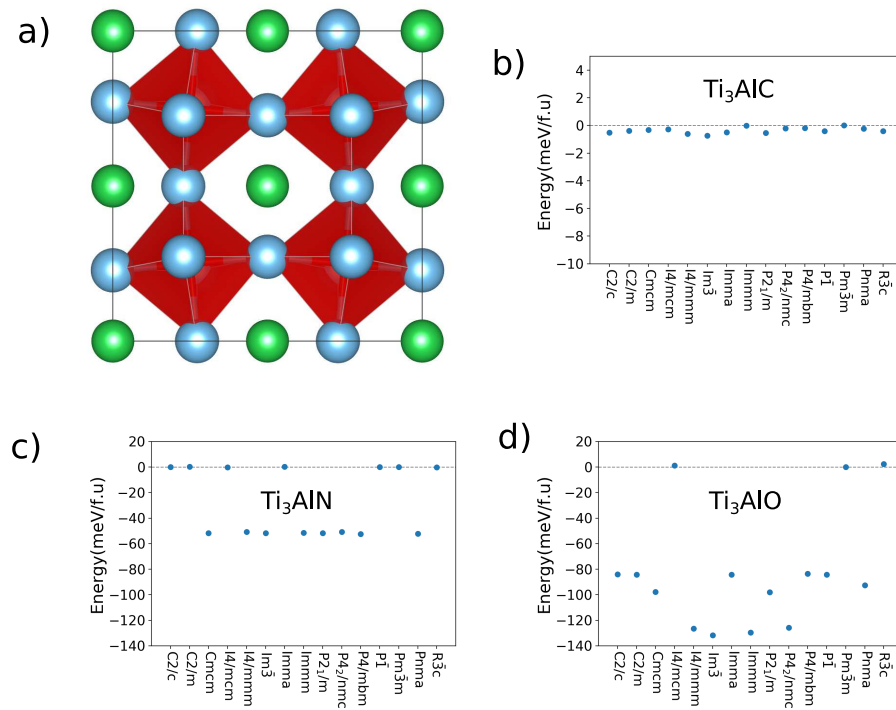


Figure A.3: a) Example of a Ti_3AlX structure with tilted octahedra. Energy of the b) Ti_3AlC , c) Ti_3AlN and d) Ti_3AlO crystals with tilted octahedra. The X-axis shows the space group of the tilted crystals.

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