First-principles thermodynamic investigation on the $\alpha$ phases in TiO and TiNb binary system

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O and Nb are two representative alloying elements of Ti to form high-temperature and corrosion resistance $\alpha$ Ti alloys. The investigation on the thermodynamic characteristics of $\alpha$ Ti-O and Ti-Nb has attracted much attention in recent years. However, in this regard, a satisfied experimental technique or modeling scheme is still yet to be developed due to the appearance of a variety of oxides in Ti-O and the mechanical instability present in Ti-Nb. Herein, we combined first-principles calculations with the cluster expansion method to investigate the ground-states characteristics for $\alpha$ Ti-O and $\alpha$ Ti-Nb systems. The atomic bonding interactions in these two systems were first revealed based on the calculated electronic structures. Afterwards, Debye-Grüneisen model and Monte Carlo simulations were employed together to investigate the thermodynamic properties of $\alpha$ phases in these two systems and the effect of vibrational entropy on the order-disorder transition temperatures of the phases in $\alpha$ Ti-O system was first examined. A good agreement with experimentally reported phase boundaries is obtained in Ti-Nb system through handling the mechanical instabilities introduced by the highly-distorted structures. Additionally, the cluster expansion coefficients for the Ti-O and Ti-Nb system offer a good starting point to investigate the phase equilibrium in Ti-Nb-O ternary alloy. We also believe the insights provided here would be helpful for those who would like to seek an efficient scheme they are confident with to investigate the phase thermodynamic properties of other hcp Ti-based alloys.

I. INTRODUCTION

Titanium is a well-known refractory metal which has a hcp crystal structure at lower temperatures, transitioning to bcc structure at $\sim 1155$ K. It is widely used in various sectors such as aerospace, chemical processing and biomaterials industries, after alloying with a small number of other elements which can be classified as $\alpha$-stabilizers (e.g. Al, O, N, C) and $\beta$-stabilizers (e.g. Nb, Mo, V, Cr, Fe).\textsuperscript{1–6}

In the last few decades, multicomponent $\alpha$ Ti alloys have gained considerable attention since they have high strength to weight ratio, good corrosion resistance and high temperature properties.\textsuperscript{7–9} Therefore, having a good understanding of the thermodynamic stability of binary $\alpha$ Ti alloys and ternary $\alpha$ Ti alloys is important to assist alloy design efforts. Alloying elements in these systems can occupy either interstitial or substitutional sites. Oxygen, occupying interstitial sites, can dissolve up to 33 at.% in hcp Ti,\textsuperscript{10} and can lead to the formation of a variety of compounds, which affect the phase equilibrium and thermodynamic properties of hcp Ti over a wide concentration range. Compared to $\alpha$ interstitial stabilizers such as oxygen, the addition of substitutional stabilizers, especially strong $\beta$ stabilizers like Nb, makes it more complicated to study the phase stability of the $\alpha$ phase due to the mechanical instability introduced by these elements.

First-principles calculations are increasingly used by many researchers to investigate the thermodynamic characteristics of $\alpha$ Ti-X alloys.\textsuperscript{11–13} In recent years a few studies have made gains in understanding the effect of the addition of interstitial O and $\beta$ stabilizers on the $\alpha$ phase stability and kinetic characteristics.\textsuperscript{14–18} For instance, Burton et al. and Gunda et al.\textsuperscript{16,17} reported the phase stability in the Ti-O binary system by ab initio calculations, but observed significant differences in their calculated transition temperatures. In addition, the calculated phase transition temperatures appear to diverge from the experimental data, which can be explained by the fact that vibrational entropy was not considered in these studies. Chinna\textsuperscript{19} et al. investigated the phase equilibrium in Ti-V, Ti-Nb, Ti-Ta binary alloys taking into account the phonon free energy using transferable force constants. The Ti-Nb system posed a particular challenge due to the fact that hcp and bcc Ti-Nb structures are mechanically unstable at high Nb content and high Ti content respectively. This resulted in a limited number of structures used for the fitting of the cluster expansion, which may have an effect on its accuracy when used to predict thermodynamic stability. Recently, the mechanical and thermodynamic properties of Ti$_2$O, were examined by Tang et al.,\textsuperscript{19} however some disagreements can be found regarding stable ground-states in the Ti-O system. For example, Tang et al. assumed the ground state of Ti$_2$O to have a P-3M1 space group while other studies suggest this should be Pbn. Furthermore, the effects of solute additions on electronic structures are not discussed in these articles and are scarcely reported anywhere else. A large body of experimental work has been published to investigate phase stability in binary, ternary and multicomponent $\alpha$ Ti alloys.\textsuperscript{20–22} However, it can be difficult to gain a comprehensive understanding of the alloying effects in these systems due to the formation of multiple phases and the complicated nature of the resulting microstructures. Therefore, a comprehensive understanding on the effects of chemistry on phase stability is desirable, and modern computational approaches can deliver this.

Herein, the effect of the separate addition of octahedral interstitial O and substitutional Nb on the phase stability and thermodynamic properties of hcp Ti was studied using first-principles simulations to fit a cluster expansion, and using the
effective cluster interaction coefficients in Monte Carlo simulations. The contribution of vibrational entropy to the phase equilibrium in hcp Ti-O and Ti-Nb was also examined by the combination of the Debye-Grüneisen model and Monte Carlo simulations. More importantly, the bonding interactions of Ti with O and Nb were also analyzed in depth by performing electronic structure calculations.

II. COMPUTATIONAL DETAILS

A. Total energy calculations

The total energy calculations of all the structures with different composition for the hcp Ti-O and Ti-Nb systems were performed using the projector augmented-wave (PAW) method as implemented in Vienna Ab-initio Simulation Package (VASP). \(^{23-27}\) The exchange-correlation functional was described by the generalised gradient approximation parametrised by Perdew-Burke-Ernzerhof (PBE). \(^{28}\) The PAW potentials of Ti\(_{sv}\) with 12 valence electrons, Nb\(_{sv}\) with 13 valence electrons and O with 6 valence electrons, recommended in the VASP manual, were used to treat valence states. Energy cutoff of 550 eV and 400 eV, 5000 and 8000 k-points per reciprocal atom were used which were tested as sufficiently large to have a good calculation convergence for all the hcp Ti-O and Ti-Nb structures respectively, achieving convergence to 1 meV or lower. For each structure, all the degrees-of-freedom were first allowed to relax (i.e. full relaxation) with ions relaxing using a conjugate-gradient algorithm, followed by a static calculation with reaching the structural convergence criteria, ensuring residual forces on each atom are below 0.02 eV/Angstrom. All electronic self-consistent loops were stopped when the difference in total energy between subsequent iterations dropped below \(10^{-6}\) eV. The second-order Methfessel-Paxton scheme \(^{29}\) with the smearing width of 0.1 eV was used to treat the partial occupancy for relaxation calculations, meanwhile the tetrahedron method with Blöchl corrections \(^{30}\) was employed for static calculations. No previous paper reported that magnetism exists in any Ti-O and Ti-Nb compounds, therefore all the calculations were performed with non-spin polarization.

B. Cluster expansion formalism

The cluster expansion (CE) method \(^{31,32}\) was used to express the total energy of any configurations created in Monte Carlo simulations. The alloy theoretical automated toolkit (ATAT) \(^{33-35}\) was used to enumerate the structures and fit the cluster expansion to data obtained from first-principles calculations (DFT calculations). More details about the CE can be found in, \(^{34}\) a brief explanation is given here. For example, for a binary alloy, a specific configuration can be represented by a vector \(\sigma\) containing the occupation variable \(\sigma_i = -1\) or +1, depending on the type of atom occupying the site \(i\). Then, the CE can parameterize the energy of this configuration as a combination of the corresponding occupation variables through: \(^{33,36,37}\)

\[
E(\sigma) = \sum_{\alpha} m_{\alpha} J_{\alpha} \left( \prod_{i \in \alpha} \sigma_i \right)
\]

where \(\alpha\) is a cluster consisting of a set of sites, such as pairs, triplets and quadruplets, \(\alpha'\) denotes all the clusters that are equivalent to the cluster \(\alpha\) through symmetry and the multiplicity \(m_{\alpha}\) represents the quantity of them. \(J_{\alpha}\) denotes the effective cluster interaction (ECI) coefficient of cluster \(\alpha\), determined by fitting clusters to the energy of the enumerated configurations obtained from first-principles calculations. ECIs reflect the strength of the interactions between the internal sites, embodying the information regarding the energetics of the system. Generally, it is expected to decay with the increase of the cluster diameter and the number of sites that the cluster contains.

The goodness of the fit of the cluster expansion can be clearly quantified through the cross-validation (CV) score: \(^{34}\)

\[
CV = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (E_i - E_{i(CE)})^2}
\]

where \(n\) is the number of all the configurations used to fit the cluster expansion. \(E_i\) and \(E_{i(CE)}\) indicate the calculated energy of structure \(i\) and CE predicted energy obtained from a least-squares fit to the \(n - 1\) other calculated energies, respectively. Similar to the root-mean-square error, the CV score, which is sensitive to outliers, averages deviations between DFT energies and CE predicted energies on all configurations. A small CV score in most cases indicates a highly accurate and predictive CE, and it can generally be lowered by increasing the number of the enumerated configurations, and by selecting an appropriate number of clusters. A different weight can be assigned to each structure, thereby giving more importance to structures that are closer to the convex hull, which can also help reduce the CV score.

Although there are many interstitial sites in the hcp lattice, such as octahedral, tetrahedral, and hexahedral interstitial sites, the fact that oxygen occupies the octahedral interstitial site compared to occupying other metastable interstitial sites has been demonstrated in many studies. \(^{14,15}\) In this paper, for the hcp Ti-O system, various configurations containing no more than 6 hcp Ti unit cells with oxygen-vacancy random ordering over the octahedral sites were enumerated. For the hcp Ti-Nb system, the non-equivalent structures containing at most 4 hcp Ti unit cells with Nb atoms random ordering over the substitutional sites were enumerated. It should be noted that, in the configuration enumeration process for both systems, the symmetry operations performed in the factor group calculated by ATAT ensure that all the enumerated configurations are unique in terms of symmetry.

C. Vibrational free energy and other thermodynamic properties

Many thermodynamic models have been developed to account for the vibrational degrees of freedom in solids with dif-
different precision. Here, the widely-applied Debye-Grueneisen model, \(^{38,39}\) implemented in Gibbs2, \(^{40,41}\) was employed to estimate the vibrational free energy \((F_{\text{vib}})\) for those relaxed structures close to convex hull over the whole composition region. These data was used to fit another CE for \(F_{\text{vib}}\) to obtain vibrational ECs. Within this framework, the volume- and temperature-dependent \(F_{\text{vib}}\) of a configuration can be calculated by:

\[
F_{\text{vib}} = \frac{9}{8}nk_b\Theta_D + 3nk_bT\ln(1 - e^{-\Theta_D/T}) - nk_bT\left(D(\Theta_D/T)\right)
\]  

(3)

where \(n\) is the number of atoms in primitive cell, \(k_b\) the Boltzmann’s constant and \(D\) the Debye function given by:

\[
D(x) = \frac{3}{x^3} \int_0^x \frac{y^3 e^{-y}}{1 - e^{-y}} dy
\]  

(4)

and \(\Theta_D\) denotes the Debye temperature calculated at the static equilibrium volume \(V_0\) by:\(^{38}\)

\[
\Theta_D(V) = \Theta_D(V_0) \cdot \left(\frac{V_0}{V}\right)\gamma
\]  

(5)

where \(\gamma\) is the Gruneisen parameter, which can be obtained by:\(^{42}\)

\[
\gamma = a + b \frac{dB_{\text{sta}}}{dp} = a - b \frac{d\ln B_{\text{sta}}}{d\ln V}
\]  

(6)

where \(B_{\text{sta}}\) is the static bulk modulus, factor \(a\) and \(b\) can be approximated using the expression by Slater \((a = -1/6, b = 1/2),^{43}\) Dugdale-McDonald \((a = -1/2, b = 1/2),^{44}\) Vaschenko-Zubarev \((a = -5/6, b = 1/2),^{45}\) and the mean free volume gamma \((a = -0.95, b = 1/2).^{46}\) There is little difference when testing each of the above expressions in this study, we adapt in the value of \(a = -5/6, b = 1/2\). The \(\Theta_D(V_0)\) can be expressed by:

\[
\Theta_D(V_0) = \frac{1}{k_B} (6\pi^2 V_0^{1/2}/n)^{1/3} f(\sigma) \sqrt{\frac{B_{\text{sta}}}{M}}
\]  

(7)

where \(M\) is the molecular mass of the primitive cell and \(\sigma\) the Poisson ratio at equilibrium state. The function \(f(\sigma)\) can be represented by:

\[
f(\sigma) = \left\{ 3 \left[ 2 \left( \frac{2(1 + \sigma)}{3(1 - 2\sigma)} \right)^{3/2} + \left( \frac{1 + \sigma}{3(1 - \sigma)} \right)^{3/2} \right]^{1/3} \right\}
\]  

(8)

Other thermodynamic properties of a configuration can be derived directly from the Helmholtz free energy, obtained from the configurational and vibrational free energies, according to the following equation:

\[
F(V; p, T) = F_{\text{config}}(V) + pV + F_{\text{vib}}(V; T)
\]  

(9)

As an input, a series of energy-volume \((E-V)\) data of the full relaxed structures were calculated and fit to the Birch-Murnaghan equation of state.\(^{47}\) Then, the obtained equilibrium volume at a given temperature and pressure can be used to derive the linear thermal expansion \(\lambda\) by:

\[
\lambda = \frac{1}{3V} \left(\frac{\partial V}{\partial T}\right)
\]  

(10)

The constant pressure and constant volume heat capacity can be calculated by:

\[
C_p = \left(\frac{\partial H}{\partial T}\right)_p, C_v = \left(\frac{\partial U}{\partial T}\right)_p
\]  

(11)

where \(H\) and \(U\) are the enthalpy and internal energy of the configuration respectively which can be derived from the Helmholtz free energy. In order to calculate the free energy of phases as a function of composition and temperature with the inclusion of vibrational entropy, the temperature-dependent ECs obtained by summing up ECs calculated from CE of configurational and vibrational free energies respectively were used as input (Hamiltonian) in Monte Carlo simulations. The Monte Carlo simulations implemented in emc2 and phb code of ATAT\(^{45}\) were performed to get the thermodynamic averages. Up to 2000 average and equilibrium passes were performed by the program to evaluate thermodynamic quantities at each step of these simulations.

III. RESULTS AND DISCUSSION

A. Hcp Ti-O system

1. Ground-states characteristics

A total of 365 configurations were enumerated over the whole O concentration range to search the ground-states and obtain a good CE prediction. All of these relaxed structures remain hcp, as confirmed using the common neighbor analysis (conventional, adaptive and interval CNA).\(^{48-50}\) The calculated and CE fitted formation energies \((E_f)\) of all the enumerated configurations and the residuals of the CE fit are plotted in Fig. 1, here the pure \(\Omega\) and \(\Omega\) are treated as the reference states and the O concentration in the oxygen-vacancy sublattice is taken as the \(x\)-axis. It is evident that the \(E_f\) of all the structures are well fitted by CE, having achieved a CV score of 6.13 meV/atom. With the exception of two end points, there are 5 ground-states found, namely \(\text{Ti}_6\text{O}, \text{Ti}_3\text{O}, \text{Ti}_2\text{O}, \text{Ti}_2\text{O}_2, \text{and Ti}_2\text{O}_2,\) and a new unreported compound, \(\text{Ti}_{12}\text{O}_5\). Since the two octahedral sites in the hcp Ti unit cell are highly energetic for oxygen occupation simultaneously,\(^{10,51}\) the enumerated structures with \(X_0\) larger than 0.5, including the ground-state \(\text{Ti}_2\text{O}_2\), are excluded during the CE, such that a very low weighted CV score of 2.45 meV/atom was obtained by fitting to the remaining 236 structures. The crystal structures and lattice parameters of these 4 ground-states are shown in Fig. 2 and Table I, respectively. Except for the fact that the \(\text{Ti}_2\text{O}_2\) has an orthorhombic Pbcn space group, all the other three ground-states have trigonal \(R\bar{3}\) symmetry. The lattice constants of...
FIG. 1. (a) DFT Calculated and CE fitted formation energies of the enumerated structures in hcp Ti-O system, the DFT ground-state orderings are connected as convex hull and (b) Residuals of the CE fit.

<table>
<thead>
<tr>
<th>Ground-state</th>
<th>Structure</th>
<th>Space group</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>(\alpha^\circ)</th>
<th>(\beta^\circ)</th>
<th>(\gamma^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ti}_6\text{O})</td>
<td>trigonal</td>
<td>R3</td>
<td>5.588</td>
<td>—</td>
<td>—</td>
<td>54.45</td>
<td>54.45</td>
<td>54.45</td>
</tr>
<tr>
<td>(\text{Ti}_3\text{O})</td>
<td>trigonal</td>
<td>R3</td>
<td>5.604</td>
<td>—</td>
<td>—</td>
<td>54.83</td>
<td>54.83</td>
<td>54.83</td>
</tr>
<tr>
<td>(\text{Ti}_{12}\text{O}_5)</td>
<td>trigonal</td>
<td>R3</td>
<td>10.029</td>
<td>—</td>
<td>—</td>
<td>29.78</td>
<td>29.78</td>
<td>29.78</td>
</tr>
<tr>
<td>(\text{Ti}_2\text{O})</td>
<td>orthorhombic</td>
<td>Pbcn</td>
<td>4.79</td>
<td>5.111</td>
<td>6.01</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

FIG. 2. Crystal structures of the DFT ground-states in hcp Ti-O system: (a) \(\text{Ti}_6\text{O}\), (b) \(\text{Ti}_3\text{O}\), (c) \(\text{Ti}_{12}\text{O}_5\), and (d) \(\text{Ti}_2\text{O}\) (red balls are oxygen atoms occupying hcp octahedral sites).

The nearest neighbor O-Ti distance in these ground-states becomes larger than the Oct-Ti distance in pure Ti, which indicates that the oxygen enlarges the interstitial radius of the octahedral site. The ECI of the optimized clusters including 20 pairs, 34 triplets and 26 quadruplets are shown in Fig. 3. A high ECI value of 142 meV for the smallest pairwise cluster, with a radius of 2.34 Å, was calculated, which represents a strong oxygen-vacancy interaction. The magnitude of all the ECIs decays to

FIG. 3. The effective cluster interactions (ECIs) of the optimized 20 pairs, 34 triplets and 26 quadruplets in \(\alpha\text{TiO}\) CE.
zero with the increase of the cluster diameter and the number of the sites it contains, which is due to the fact that the interaction strength between the sites in a structure should drop off with the increase of the site spacing.

2. Electronic structure of the ground-states

The total density of states (DOS) and O and Ti orbit-projected DOS are illustrated in Fig. 4, with the energy of Fermi level ($E_{\text{fermi}}$) set to 0. It can be seen that all the ground-states show metallic characteristics, since the Fermi Energy resides in the middle of the d band. The states around 20 eV below $E_{\text{fermi}}$ are contributed by the oxygen 2s orbital when the oxygen is introduced in hcp Ti. Moreover, the p orbitals of oxygen hybridize with the d orbitals of Ti below the $E_{\text{fermi}}$ to form $\sigma$ and $\pi$ bonds, and notably the bond strength enhances with the increase of oxygen concentration, which can be demonstrated by the variation trend of the $E_f$ of these ground-states, shown in Fig. 1. The DOS in the energy interval spanning the $E_{\text{fermi}}$ is dominated by the d orbitals of Ti.

3. Thermodynamic properties of ground-states

Thermodynamic properties are essential to describe the state of a solid system at various temperatures. Here, the thermal expansion and heat capacity of the ground-states, indicating their anharmonicity and heat retention or loss ability, were calculated by the Debye-Grüneisen model. Except for the inclusion of the configurational degrees of freedom, the $F_{\text{vib}}$ was also determined to view its effects on phase stability. The ordering Ti$_2$O$_3$ was not observed in experiments since our study shows it decomposes on heating into Ti$_3$O and Ti$_2$O at very low temperature ($\sim$50 K), its thermodynamic properties are not discussed here. The $F_{\text{vib}}$ and the linear thermal expansions of Ti$_3$O, Ti$_2$O and Ti$_2$O are shown in Fig. 5. With the increase of temperature, the $F_{\text{vib}}$ of these three ground-states gradually drops, this can be interpreted by the well-known volume effect which is basically attributed to thermal expansion: the volume expansion of a given compound stretches chemical bonds, which in turn makes them softer, leading to an increase in vibrational entropy. It also can be seen that the Ti$_2$O has the largest reduction rate over the whole temperature range since it has the biggest growth rate of linear thermal expansion (shown in Fig. 5(b)), indicating the anharmonic contributions are non-negligible especially at higher temperatures. On the other hand, the number of the bonds between unlike atoms determines the stiffness of a structure or phase in a system. In this work, it is obvious that Ti$_2$O has a larger number of Ti-O bonds than the other ground-states. Though oxygen atoms fill alternating layers of octahedral sites in both Ti$_3$O and Ti$_2$O, oxygen occupies more sites in Ti$_2$O in the same layer. The increase in bonds not only contributes to the stiffness of the structure and the reduction of the $E_f$ (as shown in Fig. 1(a)), but also leads to a decrease in vibrational entropy, and therefore a stiffer structure. Therefore, as shown in Fig. 5(a), the vibrational free energy of the three ground states over a wide temperature range (0 $\sim$ 950 K) show the ordering: Ti$_2$O$\rangle$Ti$_3$O$\rangle$Ti$_6$O.

The effects of lattice vibration on the order-disorder transition temperature of Ti$_6$O, Ti$_3$O and Ti$_2$O were also examined by performing Monte Carlo simulations, as shown in Table II. It is evident that vibrational entropy lowers the transition temperatures for all the phases, and this effect has a much larger number of structure. The most stable Ti$_6$O structure at 0 K found by Burton contains 18 Ti atoms and 3 O atoms with the similar R3 symmetry, and its formation energy (-0.1471 eV/atom) is slightly higher than that of Ti$_6$O (-0.1489 eV/atom) consisting of 6 Ti atoms and 1 O atom found in this work. It is worth noting that the transition temperatures of Ti$_6$O reported by Burton and Ruban et al. reach 1612 K and 2860 K, respectively, which is 479 K and 1727 K higher than that reported here. The difference of 1727K is possibly due to the higher accuracy of our cluster calculation. The ground-state structure as obtained from the first-principles simulations. The most stable Ti$_6$O structure was not observed in experiments since our study shows it decomposes on heating into Ti$_3$O and Ti$_2$O at very low temperature ($\sim$50 K), its thermodynamic properties are not discussed here. The $F_{\text{vib}}$ and the linear thermal expansions of Ti$_3$O, Ti$_2$O and Ti$_2$O are shown in Fig. 5. With the increase of temperature, the $F_{\text{vib}}$ of these three ground-states gradually drops, this can be interpreted by the well-known volume effect which is basically attributed to thermal expansion: the volume expansion of a given compound stretches chemical bonds, which in turn makes them softer, leading to an increase in vibrational entropy.

<table>
<thead>
<tr>
<th>Phase</th>
<th>w/o $F_{\text{vib}}$</th>
<th>w/ $F_{\text{vib}}$</th>
<th>Gunda et al.</th>
<th>Burton et al.</th>
<th>Expt $^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_6$O</td>
<td>913</td>
<td>745</td>
<td>999</td>
<td>1120</td>
<td>700</td>
</tr>
<tr>
<td>Ti$_3$O</td>
<td>689</td>
<td>656</td>
<td>609</td>
<td>860</td>
<td>780-850</td>
</tr>
<tr>
<td>Ti$_2$O</td>
<td>1133</td>
<td>914</td>
<td>1027</td>
<td>1612</td>
<td>—</td>
</tr>
</tbody>
</table>

The specific heat at constant pressure ($C_p$) and constant volume ($C_v$) of the ground states are shown in Fig. 6. Similar to other metal compounds, their heat capacity increases with the increase of temperature, and the higher the temperature, the slower the change rate. In addition, the heat capacity of Ti$_6$O is significantly higher than that of the other two ground states.
FIG. 4. DOS of the ground-sates Ti, Ti$_6$O, Ti$_3$O, Ti$_{12}$O$_5$ and Ti$_2$O: (a) Total and O projected DOS; (b) Total and Ti projected DOS.

FIG. 5. Temperature dependence of the (a) vibrational free energy and (b) linear thermal expansion for the ground-states Ti$_6$O, Ti$_3$O and Ti$_2$O. The data of the Ti$_3$O with P-31C structure and the Ti$_2$O with P-3M1 structure used in$^{19}$ is plotted here for comparison.

FIG. 6. The constant-pressure (a) and constant-volume (b) heat capacities of the ground-states Ti$_6$O, Ti$_3$O and Ti$_2$O as a function of temperature.
Unfortunately, the simulation and experimental reports on the temperature dependence of the thermodynamic properties of these three ground-states are extremely scarce, hence the thermodynamic properties of Ti$_2$O and Ti$_3$O with respective P-3M1 and P-31C space groups examined by Tang et al.$^{19}$ were used for comparison. Our calculated $C_p$ and $C_v$ for Ti$_3$O and Ti$_2$O are in good agreement with those reported by Tang, due to the little difference in formation energy of the corresponding ground-state. For instance, the formation energy of the P-31C Ti$_3$O found in our CE is -0.248 eV/atom which is slightly higher than that of ground-state R3 Ti$_3$O (-0.25 eV/atom).

B. Hcp Ti-Nb system

1. Ground-states characteristics

Unlike oxygen, Nb is a strong β stabilizer that can introduce mechanical instability in hcp Ti, making it more challenging to construct a good converged CE. In this CE, 166 configurations in total were enumerated in the range of Nb concentration from 0 to 1, however many configurations relaxed too far from the ideal hcp crystal, with some transforming to bcc. CNA methods were employed first to exclude the structures that relaxed to bcc and other geometries, then the structures with the relaxation amount (RA) > 0.1 were also excluded from the CE in order to avoid the noise introduced by highly distorted structures.$^{59}$ The checkrelax utility in ATAT,$^{60}$ which measures the distortion of a structure after relaxation, was employed to compute RA for each configuration by:

$$RA = \left\| \frac{D+D^T}{2} - I \right\|_F$$

(12)

where $I$ and $F$ denote the identity matrix and the Frobenius norm, respectively. $D$ refers to the matrix that represents the distortion between the original and relaxed configuration, and it can be derived from:

$$D = \left( \frac{\det(A)}{(\det(A))^{1/3}} \right)^{-1} \times \frac{\det(B)}{(\det(B))^{1/3}}$$

(13)

here $A$ and $B$ are the matrix composed of lattice vectors of the structures before and after relaxation, respectively. Fig. 7 exhibits the RA of all the 166 enumerated structures with the excluded structures marked as red symbols. A total of 42% of the 166 enumerated structures were excluded. As it can be seen, the higher the Nb content of a structure, the higher the possibility that its RA is larger than 0.1. A total of 92% of those over-relaxed structures (RA > 0.1) have Nb concentration larger than 50%, and 80% of the structures that relax to bcc or other geometries (red triangle) have RA above 0.1. As a result, 97 structures were left to construct the hcp TiNb CE, and the CV score was reduced from 19.1 meV/atom to 5.03 meV/atom before and after excluding the unstable structures. Their DFT calculated and CE fitted $E_f$ are shown in Fig. 8(a) where pure hcp Ti and Nb are taken as reference states, and the residuals of the fit are plotted in Fig. 8(b). It is obvious that, after tuning the CE, all the calculated $E_f$ are well reproduced by the approach, and the residuals for most structures are less than 5 meV/atom. A compound having stoichiometry TiNb with orthorhombic Pmmn is predicted to be a ground-state, the inset of Fig. 8a shows its crystal structure. A weighted CV score of 2.59 meV/atom, which is much lower than that reported by Chinnappan et al.$^{18}$ was obtained by assigning higher weights to structures closer to the convex hull. The $E_f$ of the structures with the Nb concentration larger than 0.5 are further from the convex hull, indicating the introduction of stronger mechanical instability. The optimized clusters include 13 pairs, 15 triplets and 10 quadruplets and their ECIs are illustrated in Fig. 9. The largest value for pairwise and triple-wise ECIs in this CE appearing at the cluster diameter of 5.1 Å and 2.946 Å respectively is about 10 meV which is much lower than that for pairwise (139.9 meV) calculated in hcp TiO CE. In addition, the values of some ECIs in triplets and quadruplets are comparable to those in pairs at cluster diameter around 5 Å, indicating there are some non-negligible complex Ti-Nb interactions in this system. We note that the magnitude of ECIs decays with the increase of the number of sites contained, as generally expected. The bcc TiNb CE, which is not shown here, was also investigated in this report, 60 clusters were used to fit 241 configurations. It is found that only 7 structures relaxed away from bcc symmetry and 4 structures have RA larger than 0.1, resulting in a weighted CV score of 1.71 meV/atom.

Our finding that, compared to the addition of Ti to bcc Nb, adding Nb to hcp Ti can introduce more mechanical instabilities since DFT calculations indicate more structures in the bcc TiNb system present larger RA and distortion, is contrary to that found by Chinnappan et al.$^{18}$ This discrepancy may be due to the smaller number of structures calculated in the Chinnappan study and the different calculation settings used in this study. To be specific, in their DFT calculations of hcp TiNb system, the larger convergence criteria ($10^{-4}$ eV) set for the electronic self-consistent loop results in some structures maintaining the metastable hcp crystal structure. Different
FIG. 8. (a) DFT Calculated and CE fitted formation energies of the structures used for CE in hcp Ti-Nb system, the DFT ground-state TiNb are connected with two end points as convex hull (the inset is the crystal structure of the ground-state TiNb, with blue balls shown as Ti atoms). (b) Residuals of the CE fit.

FIG. 9. The ECIs of the optimized 13 pairs, 15 triplets and 10 quadruplets in αTiNb CE.

PAW potentials were also used, which leads to small differences in formation energies for some structures. In this study, we opted to use the Ti_{sv} and Nb_{sv} potentials, which respectively treat 12 and 13 electrons as valence electrons. This leads, for instance, to the formation energy of TiNb to be 6.8 meV/atom higher than when using T_{pv} and Nb_{pv}.

2. Electronic structure analysis

The total and projected DOS of the ground-state TiNb and pure Ti are shown in Fig. 10(a), to reveal trends, the DOS of Ti_{3}Nb and TiNb_{3} with the lowest $E_f$ at their respective composition are also plotted. We can see, from Fig. 10(a), that the addition of Nb into hcp Ti parent cell changes the overall shape of each TDOS, and it is more evident with the increase of Nb concentration. The TDOS of ground-state TiNb exhibits fewer sharp peaks than pure Ti, indicating stronger metallic bonding present in TiNb thereby a lower obtained $E_f$. This trend was also captured by Zhou et al.

Although their study investigated this using special quasi-random structures. For the ground-state TiNb, the $d$ orbitals of both Ti and Nb contribute to the electronic states of the bonds, whereas antibonding was dominated by Ti $d$ orbitals alone, implying that the repulsion interaction between the nuclei is mainly caused by Ti. The $d$ orbitals of the ground-state TiNb can be split into three separate directional groups, namely $d_{xy}$, $d_{x^2−y^2}$, $d_{yz}$ and $d_{xz}$, and $d_{z^2}$. The $d_{xy}$ and $d_{x^2−y^2}$ orbitals, lying on the $x−y$ plane, facilitate the bonding between the nearest neighbor Ti and Nb atom within the closed-packed plane. The $d_{yz}$ and $d_{xz}$ orbitals, vertical to the $x−y$ plane, promote the hybridization of the Ti and Nb atoms on the $x−y$ plane with those nearest neighbor atoms sitting on the adjacent $x−y$ planes. The $d_{z^2}$ orbitals with lobes pointing along the $z$ axis are responsible for the interactions between atoms on the $x−y$ plane and their second neighbor along the $z$ direction, however this interaction is weaker than that of the first two groups. This can also be confirmed from Fig. 10(b), the contribution to PDOS by $d_{xy}$ and $d_{x^2−y^2}$ orbitals are comparable to that by $d_{yz}$ and $d_{xz}$ orbitals, both of which are greater than that of the $d_{z^2}$ orbitals, although the electron states of all these three groups spread over the entire energy interval around $E_{\text{fermi}}$.

3. Finite temperature phase stability

Since the ground-state TiNb turns to be unstable and disordered at lower temperature (~20 K), it is unnecessary to discuss its order-disorder transition temperature and thermodynamic properties. Here, in order to verify the precision of
FIG. 10. (a) DOS of the pure Ti, ground-state TiNb and ordered Ti$_3$Nb and TiNb$_3$; (b) Projected DOS of the ground-state TiNb.

FIG. 11. Computed phase boundaries between the $\alpha$ and $\beta$ phase in TiNb alloy without and with the inclusion of vibrational CE, DFT and experimental results in $^{18}$ and $^{62}$ respectively are plotted for comparison.

IV. CONCLUSIONS

For $\alpha$Ti-O oxides, an unreported ground-state compound with stoichiometry Ti$_{12}$O$_5$ was first identified in the $\alpha$Ti-O CE. The electronic structures of the ground-states were further analyzed, and found that bonding strength of the formed $\sigma$ and $\pi$ bonds enhances with the increase of interstitial oxygen concentration. This bonding interaction appearing on the nearest-neighbor Ti and O atoms is attributed to the hybridization between oxygen $p$ orbitals and Ti $d$ orbitals. In addition, the thermodynamic properties of the ground-state phases were also investigated for the first time. It was shown that Pbn $\text{Ti}_2\text{O}$ has the largest $F_{\text{vib}}$ than the other ground-states. Furthermore, the vibrational CE was also constructed and the order-disorder transition temperatures of these oxide phases were calculated without and with the inclusion of lattice vibration. It is found that vibrational entropy yields downward corrections to the computed transition temperatures for all the phases, although, compared with experimental data, our results still slightly overestimate and underestimate the transition temperatures for $\text{Ti}_6\text{O}$ and $\text{Ti}_3\text{O}$, respectively.

Unlike interstitial oxygen, substitutional Nb introduces more mechanical instabilities to the hcp Ti crystal, which makes it harder to obtain a converged CE. RA and CNA were performed to identify the highly distorted and over-relaxed structures such that a good converged CE was obtained by excluding these structures from the CE. The ground-state TiNb shows stronger metallic bonds than other compounds, thereby a lower $E_f$. With the inclusion of $F_{\text{vib}}$, our computed phase boundaries between $\alpha$ and $\beta$ phase are consistent with experimental results, indicating vibrational entropy plays a significant role.
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