First-principles study of phase equilibrium in Ti-V, Ti-Nb, and Ti-Ta alloys

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Abstract

The subsolidus equilibrium phase diagrams of Ti-V, Ti-Nb and Ti-Ta alloys have been computed through cluster expansion, lattice dynamics and Monte Carlo modeling methods combined with Density Functional Theory total-energy calculations. Computed phase boundaries in Ti-V alloy are found to be in good agreement with reported CALPHAD assessed experimental boundaries. For Ti-Ta system, the computed phase boundaries agree well with CALPHAD boundaries for Ta-rich alloys. For Ti-rich alloys, the transformation temperatures are overestimated by up to 200 K. In the case of Ti-Nb system, the calculated boundary of the bcc-solid-solution phase decreases rapidly in temperature with increasing Nb concentration compared to CALPHAD boundary, deviating from the latter by up to 600 K at 80% Nb. Our calculation gives qualitatively correct hcp-solid-solution regions for all the three alloy systems (i.e., solubility of V/Nb/Ta in hcp Ti). A key difficulty in modeling these systems is the presence of mechanical instability in the bcc phase at high Ti concentration. In this work, we circumvent this difficulty by excluding structures exhibiting instability in the cluster expansion construction process. We find that, while such a scheme is often appropriate (as in the Ti-V and Ti-Ta systems), it can become unreliable when the result exhibit a too strong sensitivity to the exclusion rule used (as in the Ti-Nb system). In all systems, we find that the inclusion of lattice vibration effects is crucial to obtain even qualitative agreement with experiment.

Keywords: Cluster expansion method; Monte Carlo simulations; Phase boundaries

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1. Introduction

Titanium and its alloys are strong, light, durable, corrosion resistant, and bio-compatible[1]. They are used in aerospace, automotive, energy and chemical industries[2, 3]. Titanium alloys are also used worldwide as bone and joint replacements, dental implants and cardiovascular devices[4–7]. Further, Ti-Nb and Ti-Nb-Ta alloys are used as superconducting magnets for magnetic resonance imaging, particle accelerators, mine sweeping, ore separation, levitated trains, and energy storage[8, 9].

Pure titanium transforms martensitically from the high-temperature bcc phase to the hcp phase below 1155 K. That is, it is not possible to retain the pure bcc Ti below 1155 K. Titanium alloys nevertheless transform reversibly from bcc (β) to hcp (α) crystal structures with variation in temperature. This property allows changes in microstructure and strengthening opportunities. Elements which raise or lower the transformation temperature are referred to as α stabilizers (like Al, O, N, C, Ge, La) or β stabilizers (like V, Fe, Cr, Nb, Ta, Mo), respectively[10]. With increasing content of β stabilizing elements, the nature of the β to α transformation changes from martensitic to nucleation and growth. The β to α transformation is however sluggish, allowing many metastable transformations to occur. Two martensites, α' and α'' , have been identified in alloys rapidly quenched from the β phase, the composition of the alloy determining which martensite is formed[10]. Precipitates known as ω phase may also form during a slow quench from the β phase or during isothermal aging[10, 11].

The β stabilized titanium alloys are classified as α , $\alpha+\beta$, and β alloys based on their position in the phase diagram[10]. The α alloys include commercially pure titanium as well as alloys containing minor amounts of β phase. The α alloys do not generally respond to heat treatments. They are highly corrosion resistant and preferentially used in hot and chemically aggressive environments[10]. Indeed, corrosion studies have found that the Ti-5Ta-1.8Nb alloys are a better alternative to stainless steels for nuclear fuel reprocessing vessels[12]. The $\alpha+\beta$ alloys range from the $\alpha/(\alpha+\beta)$ phase boundary up to the intersection of the α' or α'' martensitic transformation line with room temperature.

The β alloys are metastable and contain sufficient β stabilizers to completely retain the β phase upon quenching (and do not transform martensitically upon fast cooling from the β phase field)[10]. The β alloys can be solution treated and aged to achieve significant increases in strength. An attractive feature of β Ti alloys is their low elastic modulus, which is below that of the conventional α or $\alpha+\beta$ Ti alloys. This property is of particular relevance because an important requirement of orthopedic implants is a low elastic stiffness approximating that of the surrounding bone tissue. The Ti-V, Ti-Nb, Ti-Ta or Ti-Mo based bcc titanium alloys are found to have low elastic moduli[13–16]. Shape-memory effect and super elasticity have also been achieved in β Ti alloys[17].

Several theoretical studies on the phase equilibrium of Ti-V, Ti-Nb, and Ti-Ta alloys can be found in the recent literature[8, 18–20]. Nevertheless, the first-principles computational study of phase equilibrium of these alloys is lacking.

In this work, we model the equilibrium phase diagram of Ti-V, Ti-Nb and Ti-Ta alloys using the cluster expansion and Monte Carlo simulation techniques combined with the Density Functional Theory total-energy calculations.

The equilibrium phase diagrams of Ti-V, Ti-Nb and Ti-Ta alloys are apparently simple. These phase diagrams have only three phases, namely the liquid, the α and the β phases. The α solid-solution phase, based on the hcp Ti, dissolves only a few percent of V or Nb or Ta over 670-1100 K. The β solid-solution phase, derived from the high-temperature bcc Ti with the addition of sufficient amount of V or Nb or Ta which reinforces the stability of bcc Ti, exists at all compositions. At low temperatures, the β phase becomes unstable, leading to a miscibility gap spanning the whole concentration range. The solubility of V in α - and β -Ti defining the $\alpha/(\alpha + \beta)$ and $\beta/(\alpha + \beta)$ phase boundaries (α and β transus) respectively have been determined through microprobe and metallography techniques[21]. The maximum solubility of V in α -Ti is about 3.7 at.% over 773-873 K. The β transus continuously decreases in temperature with increasing vanadium content.

The cluster expansion method combined with Monte Carlo simulations have been widely used in the first-principles calculation of phase equilibrium in alloys. The cluster expansion method constructs an effective Hamiltonian for the configurational energy of a crystal in terms of polynomials of occupation variables describing the arrangement of atoms on the crystal sites[22]. With such Hamiltonian constructed separately for each of the phases of an alloy, free energies and phase boundaries are then computed through Monte Carlo simulations[23]. A large number of studies based on such techniques can be found in the literature[24–36]. These studies deal with alloys made of elements with different as well as same crystal structures (e.g. Al-Li, Al-Ti, Mg-Li, Al-Nb, and MgO-ZnO versus Cu-Au, Cd-Mg and V-Nb). However, they have typically considered coherent phase equilibrium. That is, phase equilibrium on a give lattice. For example, phase stability of Al-Ti alloy is studied either for the Al-rich alloys based on fcc structure of Al or for the Ti-rich alloys based on hcp structure of Ti. Combining them and constructing the complete phase diagram is tedious and uncommon. Further, in these earlier phase diagram calculations, the phonon contributions have been obtained generally through empirical methods. This is because of the lack of efficient and robust computational scheme for the phonon free energy of alloys with arbitrary compositions. On the other hand, phonon contribution is known to be important for accurate calculation of phase equilibrium[24, 25, 27].

For the phonon free energy of alloys, an approximate computational scheme have however been devised based on the observation that the effective springs of a Born-von Karman model are often transferable from one structure to another[37–40]. This technique has been used successfully in several studies[41–44]. But for alloys, such as, Ti-V, Ti-Nb and Ti-Ta where the constituent elements have different structures, the transferable force constants method of phonon free energies has not been applied. In this work we compute the sub-solidus phase equilibrium of these alloys through cluster expansion Hamiltonian of the systems constructed on hcp and bcc lattices, with the transferable

force constants method for phonon, and Monte Carlo simulations. The paper is organized into four sections. Followed by the introduction in section 1, the computational scheme is outlined briefly in section 2. In section 3, we discuss the calculated phase equilibria. Conclusions are given in section 4.

2. Computational methods

2.1. Cluster expansion

To compute the phase diagram of an alloy, free-energy of all the constituent phases should be known as a function of composition and temperature. Constructing these free energy functions entirely through DFT calculations is quite demanding. The cluster expansion (CE) method constructs a generalization of the Ising Hamiltonian for the energies of the different atomic configurations of an alloy. Detailed illustration of the method can be found in many papers[45–49]. Here a brief description is given. In the cluster expansion, the binary alloy $A_{1-x}B_x$ is treated as a lattice problem in which each of the N sites of a given lattice is assigned a spin or occupation variable $\hat{S}_i$ ($i = 1, 2, \dots, N$) with $\hat{S}_i = -1$ or $+1$ depending on the site i being occupied by an A or a B atom. Any configuration σ of the alloy is then defined by specifying the occupation variable $\hat{S}_i$ of the N sites of the lattice. For a lattice with N sites, the energies of the 2^N possible configurations σ can be exactly mapped into a generalized Ising Hamiltonian:

$$E(\sigma) = J_0 + \sum_i J_i \hat{S}_i(\sigma) + \sum_{j < i} J_{ij} \hat{S}_i(\sigma) \hat{S}_j(\sigma) + \sum_{k < j < i} J_{ijk} \hat{S}_i(\sigma) \hat{S}_j(\sigma) \hat{S}_k(\sigma) + \dots (1)$$

where the J 's are the interaction energies of various order, also known as effective cluster interactions. The first summation is over all sites in the lattice, the second over all pairs of sites, the third over all triplets, and so on.

Equation (1) defines a set of linear equations, in which a $2^N \times 2^N$ matrix of spin products multiplies a 2^N vector of J 's, giving a vector of the energies of the 2^N configurations. The J 's can then be solved exactly, as the matrix of spin products is proven to be orthogonal[46]. Although the cluster expansion Eq. (1) contains many interactions, the energetics of bonding is usually determined by relatively short length scales. Therefore, a finite number of interaction parameters is expected to provide the desired mapping of energetics with sufficient accuracy. The J 's can then be determined from the energies of a small set of ordered configurations through a least-squares fit minimization. The selection of which interactions to include in the fit is performed via minimization of the cross-validation score, as explained in [22].

A challenging aspect of the systems considered here is the presence of mechanical instability in the bcc phase at high Ti concentration. In this work, we circumvent this difficulty by merely excluding structures that relax too far from the starting ideal bcc geometry in the cluster expansion of energy. Our exclusion criterion is that the strain tensor the unit cell experience during relaxation should not have a norm that exceeds 0.05 (where the norm is defined as the

square root of the sum of the squares of each element of the tensor). The rationale for this approach is that, if the relaxed structures differ significantly from a bcc geometry, they would logically belong to the cluster expansion corresponding to another lattice and including them into bcc expansion would result in double-counting of some states. For the lattice dynamics calculations used to fit the vibrational free energy cluster expansion (described subsequently), we further exclude any structure with unstable phonon modes. This general approach relies on the assumption that if the cluster expansion is able to successfully describe the energy or phonon contributions over a large set of structures, it should also provide a reasonable predicted energy or vibrational free energy for structures not included in the fit. This scheme is similar in spirit to the extrapolations often performed in CALPHAD modeling of metastable or unstable phases, but is not without risks of loss of accuracy if too many data points are extrapolated rather than calculated.

While the above approach is quite simple to implement, one may be reasonably concerned by its accuracy since its precision is hard to quantify a priori based on purely theoretical grounds. The Ti-V, Ti-Ta and Ti-Nb systems, which are well-characterized experimentally, offer an opportunity for quantifying the accuracy of this approach.

2.2. Density functional theory (DFT) calculations

Electronic structure total energy calculations of ordered configurations required for the construction of cluster expansion Hamiltonian were performed using Vienna ab initio simulation package (VASP)[50, 51] with the generalized gradient approximation[52] and the projector augmented wave basis[53, 54] with an energy cutoff of 400 eV. The first-order Methfessel-Paxton method[55] of electronic occupancy has been used with a smearing width of 0.2 eV. Brillouin zone integration is carried out using a Monkhorst-Pack k-points mesh[56]. The total energies were tested for convergence with respect to the number of plane waves in the basis set and the number of k-points used in the sampling of the Brillouin zone. A $19 \times 19 \times 12$ mesh (280 k-points in BZ) for hcp Ti and equivalent meshes for CE on hcp lattice and a $20 \times 20 \times 20$ mesh (256 k-points in BZ) for bcc Nb and equivalent meshes for CE on bcc lattice have been used.

2.3. Phonon free energy

The conventional cluster expansion gives energies of arbitrary lattice configuration at 0 K and ignores vibrational excitation. Phonon contributions are however essential for accurate calculation of alloy phase equilibrium[57–59]. Vibrational effects can be formally included in the cluster expansion Hamiltonian by fitting to vibrational free energies, rather than ground state energies. This requires computation of the force-constants tensor and phonon spectrum for all the input structures, which is computationally demanding. On the other hand, calculation of phonon property of Pd-V alloys has revealed that the variation in the stiffness of a given chemical bond across different structures can be explained by changes in the bond length[60]. Based on this, Axel van de Walle and Ceder

identified that the bond stiffness versus bond length relationship is transferable and shown that a linear relationship can be used as a first approximation[61]. This method, known as stiffness versus length method, proceeds by parameterizing the bond-length dependence of the stiffness for each type of nearest-neighbor chemical bond. This is achieved by calculating the reaction forces from various imposed atomic displacements away from their equilibrium positions, which is done for a few ordered super cells for a range of lattice parameters. In the present work, three structures, consisting of the two end-members and a binary ground state structure, were considered. The parameters defining the bond-length-dependent transferable force constants relation are then obtained from a polynomial fit of the calculated forces as a function of bond length.

2.4. Monte Carlo simulations

The free energies of constituent phases as a function of composition and temperature and phase boundaries are calculated using Monte Carlo (MC) simulations in which the energetics is specified by the cluster expansion Hamiltonian. The Monte Carlo simulations were performed using the EMC2 program[23] of ATAT. EMC2 samples a semi-grand canonical ensemble in which the chemical potential and the temperature are specified externally. The composition $x \equiv \{\frac{N_i}{N}; i = 2, \dots, c\}$ is allowed to vary with the constraint of fixed total number of particles $\sum_{i=1}^c N_i = N$. The method of thermodynamic integration is used to determine the grand canonical potential ϕ^α of each phase α as a function of the chemical potential. The grand canonical potential at the starting point of the integration path is obtained from either the high or low temperature series expansion. We have used a 2366 (2197) atoms hcp (bcc) supercell for the Monte Carlo simulations. The EMC2 program automatically determines the number of equilibration and the averaging passes for a specified precision on the concentration of the alloy.

3. Results and discussion

3.1. Ground-states and transferable force constants

3.1.1. Ti-V system

Figure 1 shows the static formation energies from DFT computations that were used in fitting the cluster expansion Hamiltonians, and the corresponding formation energies predicted from cluster expansions for the hcp (α) and bcc (β) solid solution phases of Ti-V system (Figs. 1a and 1c). The effective cluster interactions involved in the respective cluster expansions are shown in Figs. 1b and 1d.

The ground-state search of both the hcp and bcc phases included all configurations of Ti and V with 6 or fewer atoms per unit cell. Cross validation scores of 24 and 9 meV were achieved in the respective cluster expansions. It is evident that the convergence of the hcp Ti-V cluster expansion requires 7 two-atoms and 3 three-atoms cluster interaction parameters. The bcc Ti-V cluster expansion reaches convergence with 6 two-atoms cluster interaction parameters.

Figure 1: Ground-state search and effective cluster interaction parameters in Ti-V system. Graphs (a) and (b) show the ground-state search and effective cluster interaction parameters for the hcp α -Ti_{1-x}V_x phase. Graphs (c) and (d) are for bcc β -Ti_{1-x}V_x phase. The formation energies in graphs (a) and (c) are with respect to hcp Ti and bcc V crystals. The abscissa in (b) and (d) are the cluster diameters, defined as the largest distance between any two points in the cluster (note that distinct clusters can share the same diameter).

Figure 2: Nearest neighbor stretching and bending force constants versus bond length in hcp Ti-V system. Symbols are ab initio data points and lines are linear fits defining the parameters of the transferable force constants relation which are used to compute the phonon spectrum of an arbitrary atomic configuration.

Figure 3: Nearest neighbor stretching and bending force constants versus bond length in bcc Ti-V system. Symbols are ab initio data points, and lines are linear fits defining the parameters of the transferable force constants relation which are used to compute the phonon spectrum of an arbitrary atomic configuration.

It is further evident that the formation energies of all the ordered structures are positive. This is consistent with the experimental phase diagrams which exhibit no ordered intermediate compounds. Formation energies for the hcp phases are larger (more positive) than for bcc phases. This suggests that more mixing is possible in the bcc phase rather than in hcp phase.

The dependence of the stretching and bending force constants on bond length are shown in figures 2 and 3 for the hcp and bcc Ti-V solid solution phases respectively. Like formation energies, the stiffness of force constants are relatively smaller in bcc phase than in hcp phase. In both the phases, stretching constants decrease monotonically with increasing bond length; bending terms, by contrast, are relatively insensitive. Linear fits through the data points, defining the parameters of the transferable force constants relation, were then used to compute the phonon spectrum and free energy of arbitrary atomic configurations.

3.1.2. *Ti-Nb system*

The formation energies from DFT computations that were used in fitting the cluster expansion Hamiltonians, and the formation energies predicted from cluster expansions for the hcp (α) and bcc (β) solid solution phases of Ti-Nb system are shown in Figs. 4a and 4c respectively. The effective cluster interactions involved in the respective cluster expansions are shown in Figs. 4b and 4d.

The ground-state search of both the hcp and bcc phases included all configurations of Ti and Nb with 6 or fewer atoms per unit cell. Cross validation scores of 14 and 8 meV were achieved in the respective cluster expansions. The convergence of the hcp Ti-Nb cluster expansion requires 8 two-atoms and 3 three-atoms cluster interactions while the bcc Ti-Nb cluster expansion reaches convergence with 8 two-atoms cluster, 4 three-atoms cluster and a four-atoms cluster interactions. It is evident that the formation energies of all the ordered structures are positive. This is consistent with the experimental phase diagram which exhibit no ordered intermediate compounds. Formation energies for the hcp phase is larger (more positive) than for bcc phase which suggests that more mixing is possible in the bcc phase rather than in hcp phase.

The dependence of the stretching and bending force constants on bond length are shown in figures 5 and 6 for the hcp and bcc Ti-Nb solid solution phases respectively. Like formation energies, the stiffness of force constants are relatively smaller in bcc phase than in hcp phase. In both the phases, stretching constants decrease monotonically with increasing bond length; bending terms, by contrast, are relatively insensitive. Linear fits through the data points were then used to compute the phonon spectrum and free energy of arbitrary atomic configurations.

3.1.3. *Ti-Ta system*

The ground-state search of both the hcp and bcc phases of Ti-Ta alloys are shown in figure 7. The static formation energies from DFT computations that were used in fitting the cluster expansion Hamiltonians, and the corresponding formation energies predicted from cluster expansions for the hcp (α) and bcc (β)

Figure 4: Ground-state search and effective cluster interaction parameters in Ti-Nb system. Graphs (a) and (b) show the ground-state search and effective cluster interaction parameters for the hcp α -Ti_{1-x}Nb_x phase. Graphs (c) and (d) are for bcc β -Ti_{1-x}Nb_x phase. The formation energies in graphs (a) and (c) are with respect to hcp Ti and bcc Nb crystals. The abscissa in (b) and (d) are the cluster diameters, defined as the largest distance between any two points in the cluster (note that distinct clusters can share the same diameter).

Figure 5: Nearest neighbor stretching and bending force constants versus bond length in hcp Ti-Nb system. Symbols are ab initio data points, and lines are linear fits defining the parameters of the transferable force constants relation which are used to compute the phonon spectrum of an arbitrary atomic configuration.

Figure 6: Nearest neighbor stretching and bending force constants versus bond length in bcc Ti-Nb system. Symbols are ab initio data points, and lines are linear fits defining the parameters of the transferable force constants relation which are used to compute the phonon spectrum of an arbitrary atomic configuration.

Figure 7: Ground-state search and effective cluster interaction parameters in Ti-Ta system. Graphs (a) and (b) show the ground-state search and effective cluster interaction parameters for the hcp $\alpha\text{-Ti}_{1-x}\text{Ta}_x$ phase. Graphs (c) and (d) are for bcc $\beta\text{-Ti}_{1-x}\text{Ta}_x$ phase. The formation energies in graphs (a) and (c) are with respect to hcp Ti and bcc Ta crystals. The abscissa in (b) and (d) are the cluster diameters, defined as the largest distance between any two points in the cluster (note that distinct clusters can share the same diameter)

solid solution phases of Ti-Ta system are shown in Figs. 7a and 7c respectively. The effective cluster interactions involved in the respective cluster expansions are shown in Figs. 7b and 7d.

The ground-state search of both the hcp and bcc phases included all configurations of Ti and Ta with 6 or fewer atoms per unit cell. Cross validation scores of 25 and 4 meV were achieved in the respective cluster expansions. The convergence of the hcp Ti-Ta cluster expansion requires 8 two-atoms cluster interactions while the bcc Ti-Ta cluster expansion reached the convergence with 11 two-atoms cluster and 9 three-atoms cluster interactions. It is evident that the formation energies of Ti-Ta alloys are also positive like Ti-V and Ti-Nb alloys. This is consistent with the experimental phase diagrams which exhibit no ordered intermediate compounds. Similar to Ti-V and Ti-Nb systems, formation energies for the hcp phase is larger (more positive) than for bcc phase.

The dependence of the stretching and bending force constants on bond length are shown in figures 8 and 9 for the hcp and bcc Ti-Ta solid solution phases respectively. Like formation energies, the stiffness of force constants are relatively smaller in bcc phase than in hcp phase. In both the phases, stretching

Figure 8: Nearest neighbor stretching and bending force constants versus bond length in hcp Ti-Ta system. Symbols are ab initio data points, and lines are linear fits defining the parameters of the transferable force constants relation which are used to compute the phonon spectrum of an arbitrary atomic configuration.

Figure 9: Nearest neighbor stretching and bending force constants versus bond length in bcc Ti-Ta system. Symbols are ab initio data points, and lines are linear fits defining the parameters of the transferable force constants relation which are used to compute the phonon spectrum of an arbitrary atomic configuration.

Figure 10: The calculated phase boundaries in Ti-V system compared with CALPHAD assessed experimental boundaries.

constants decrease monotonically with increasing bond length; bending terms, by contrast, are relatively insensitive. Linear fits through the data points were used in the calculation of the phonon free energies.

3.2. Computed phase boundaries

Phase boundaries in Ti-V alloy computed without and with phonon free energy (F_{vib}), compared with the CALPHAD assessed experimental boundaries, are shown in figure 10. It is evident that the phase boundaries computed without F_{vib} (red curves labeled with CE-MC-Without F_{vib}) diverge while computation including F_{vib} (blue curves labeled with CE-MC-With F_{vib}) gives closed phase boundaries in good agreement with CALPHAD boundaries. This demonstrates that phonon free energy contributions are essential for obtaining formally correct phase boundaries. Our ab initio calculated transformation temperatures for the bcc solid solution phase at the Ti- and V-rich regions match with CALPHAD results and agree within 80 K in the intermediate region of the phase diagram. Our computed $\alpha/(\alpha + \beta)$ boundary is in good agreement with the CALPHAD boundary with regard to transformation temperatures though the solubility of V in hcp Ti is predicted to be relatively less. The dramatic effect of vibrational contributions to the free energy can be traced back to the well-known tendency of Ti to soften some phonon modes in the bcc phase [62]. These soft modes are actually responsible for the mechanical instability that develops as composition approaches pure Ti. But even before the instability occurs, they still lead to a large vibrational entropy.

Phase boundaries in Ti-Nb alloy computed with phonon free energy (F_{vib}), compared with the CALPHAD boundaries is shown in figure 11. Phase bound-

Figure 11: The calculated phase boundaries in Ti-Nb system compared with CALPHAD assessed experimental boundaries.

Figure 12: The calculated phase boundaries in Ti-Ta system compared with CALPHAD assessed experimental boundaries.

aries computed without phonon free energies exhibited divergence similar to Ti-V system for similar reasons and are therefore omitted. It is evident that the solubility of Nb in hcp Ti and transformation temperature at the Ti-side are predicted satisfactorily. Whereas the $\beta/(\alpha + \beta)$ boundary decreases rapidly in temperature with increasing Nb concentration compared to CALPHAD boundary. The CE and CALPHAD boundaries differ by about 600 K, for instance, at 80% Nb. Phase boundaries in Ti-Ta alloy computed with phonon free energy (F_{vib}), compared with the CALPHAD boundaries is shown in figure 12. Like in Ti-V and Ti-Nb, phase boundaries computed without phonon free energies exhibited divergence and are omitted. Unlike Ti-Nb system, the transformation temperatures of $\beta/(\alpha + \beta)$ boundary in Ti-Ta system are predicted accurately at the Ta-side while it is overestimated by up to 200 K at the Ti-side although the solubility of Ta in hcp Ti predicted accurately.

3.3. Discussion

The reduced solubility of V and Nb in Ti, compared to respective CALPHAD results, can be interpreted as follows. As described in the methods section (Sec.2.1), in our cluster expansion Hamiltonian construction, we avoided the problem of mechanical instability of bcc Ti by merely excluding structures that relaxed too far from the starting ideal bcc geometry. Nevertheless, within the exclusion criterion, structures close to Ti may relax relatively far away from bcc and that unphysically pushes down the energies near Ti. The bcc Ti itself is constrained by symmetry, so its energy is not pushed down due to the instability. The net effect is that point defects in bcc Ti may be assigned a small formation energy which drives the bcc configurational free energy down near Ti. The magnitude of that effect exhibit some sensitivity to the number of structures that were removed, and hence the inaccuracies introduced are somewhat system-dependent.

It can be seen from Fig.1c and Fig.4c that the cluster expansions of β -Ti_{1-x}V_x and β -Ti_{1-x}Nb_x phases respectively have fewer calculated structures near Ti side than in Ti-Ta system (Fig.7c). This means that the bcc Ti-V and Ti-Nb lattices are relatively less stiff (by avoiding strongly relaxing structures and hence un-physically strong lattice) compared to bcc Ti-Ta lattice. This in turn means that the former two systems can accommodate more defects than the later. This is what we see in the phase diagrams as reduced solubility of V and Nb in hcp Ti.

In order to gain further insight into the discrepancies between the CALPHAD and CE-MC phase boundaries, we computed the difference in the free energies of bcc and hcp Ti ($G_{Ti}^{bcc} - G_{Ti}^{hcp}$). Figure 13 shows the result. The difference likely arises both from our simplified treatment of mechanical instabilities and from the fact that the experimental curve below the transition temperature is based on an extrapolation. Our larger calculated vibrational entropy difference (between bcc and hcp phases of Ti) is probably due to the fact that a harmonic model tends to over-estimate vibrational entropy close to mechanical instabilities (i.e., for bcc Ti). Our larger heat of transformation is likely due to the fact that the symmetry-constrained bcc structure has a higher energy than

Figure 13: The difference in the free energies of bcc and hcp Ti ($G_{Ti}^{bcc} - G_{Ti}^{hcp}$). The Calphad free energies were computed using the thermodynamic parameters given in Table 1 of Ref.[18]. First principles free energies correspond to our cluster expansions of Ti-Nb system.

the true dynamically stabilized bcc structure (where the bcc structure manifests itself only in an average sense). The fact that the transition temperature agrees better than the absolute accuracy of the calculated free energy suggests that formation enthalpies and formation entropies tends to be positively correlated (higher energy phases tends to have less stable and thus less stiff bonds, which results in a higher vibrational entropy)[61].

4. Summary and conclusion

Computed phase boundaries in Ti-V are found to be in good agreement with reported CALPHAD assessed experimental boundaries. For Ti-Ta system, the computed phase boundaries agree well with CALPHAD boundaries for Ta-rich alloys. For Ti-rich alloys, the transformation temperatures are overestimated by up to 200 K. In the case of Ti-Nb system, the calculated boundary of the bcc-solid-solution phase decreases rapidly in temperature with increasing Nb concentration compared to CALPHAD boundary, deviating from the latter by up to 600 K at 80% Nb. The difference in the transformation temperatures in Ti-V and Ti-Ta alloys and solubility of V/Nb/Ta in hcp Ti with respect to CALPHAD results are within what one would expect given the numerical approximations made (namely the truncation of the cluster expansion, of the force constants for phonon calculations, and the use of the transferable force constant approximation). The significant difference of transformation temperatures in Ti-Nb system with respect to CALPHAD is likely due to our simplified treatment of mechanical instabilities (namely, the exclusion of structures that

relax too far from the assumed lattice symmetry in the fit of the cluster expansion). For systems where the sensitivity of the results to the exact relaxation cutoff is too large, it would be of interest to explore more formal treatments of mechanical instabilities [63] to see if accuracy improvements result. This work further clearly demonstrates that phonon free energy contributions are essential for predicting qualitatively correct phase boundaries.

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