Computational Thermodynamics and Kinetics of Displacive Transformations in Titanium-Based Alloys

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Abstract

The thermodynamics of Ti-based systems are described for β - α' / α'' martensitic transformation and athermal ω formation at low temperatures. The new descriptions can better represent the relationship between the partitionless equilibrium temperature and the measured martensite-formation/reversion temperatures. The anomalous β -stabilizing effects of Al, Sn, and Zr in ternary Ti-V/Nb-based alloys are well modeled for the first time. The Gibbs energy function of ω -Ti at ambient pressure is assessed. The formation temperature of athermal ω phase is assessed in some binary systems and estimated in some ternary systems based on electrical

resistivity and first-principles calculations. The critical driving force for heterogeneous martensitic nucleation is modeled by solution-hardening interfacial friction using the present thermodynamic descriptions. The competition between martensite and athermal ω phase can be understood based on their transformation thermodynamic and kinetic factors.

Keywords: Titanium alloys; Martensitic transformations; Athermal ω phase; Thermodynamics; Kinetics

1. Introduction

The thermodynamics and kinetics of martensitic transformation are fundamental to the design of alloys exploiting transformation-induced plasticity (TRIP) and toughening, shape memory, and superelasticity. In contrast to the success in steels, TRIP Ti alloys with high strength, ductility, and fracture toughness have been much less investigated[1-4]. In Ti alloys, the body-centered cubic (bcc) β phase transforms martensitically to the hexagonal close-packed (hcp) α' phase or to the α'' phase with an orthorhombically-distorted hcp structure (Figure 1). As revealed by TRIP steel research, the increase in ductility and toughness is fundamentally determined by the parent-phase stability[5], i.e. β -phase stability for Ti alloys. Existing empirical indicators of β -phase stabilities[2, 6, 7] have very limited predictability, and are inadequate for mechanically-induced martensitic transformations because they cannot include the mechanical driving force brought about by external stress. For a mechanistic modeling of the β - α' / α'' transformations, one needs a thermodynamic database which describes the chemical driving force as a function of temperature and composition, as well as a model for the kinetics of

martensitic nucleation.

Existing databases for Ti-based systems are mostly optimized based on bcc/hcp phase-equilibria data at high temperatures. When the parameters are extrapolated to lower temperatures, their accuracy is not well guaranteed. Therefore the thermodynamic databases usually require refinements based on martensitic transformations. Similar to the kMART database for Fe-based alloys[8-10], this work presents a database for low-temperature martensitic transformations in Ti-based alloys, and a kinetic model for martensitic nucleation. Our work is expected to improve the model by Neelakantan et al. [11] which used the TTTI3 database (Ti-DATA version 3) [12]. For the martensitic formation and reversion temperatures in Ti-based alloys, existing literature covers many binary systems and some Ti-Nb-based ternary systems. For Ti-V-based ternary and quaternary systems, we have conducted calorimetric and dilatometric experiments as well as first-principles calculations, in order to supplement the available data for building the database.

The athermal ω phase in Ti-based alloys has been observed in a compositional window very close to mechanically-induced martensitic transformations. It is well known that athermal ω is competitive to martensite, therefore it is difficult to design a TRIP Ti alloy without a quantitative description of athermal ω . In this work we model the thermodynamics of athermal ω phase in some binary and ternary systems. This can also serve as a foundation for future modeling of thermal ω which involves solute partitioning.

2. Experimental

Experimental Ti-V-Al and Ti-V-Al-Fe alloys, denoted as “C_x-y(-z)” or “D_x-y(-z)” roughly for Ti-x at% V-y at% Al(-z at% Fe), were prepared by arc-melting using pure elements (99.98% Ti, 99.7% V, 99.999% Al, 99.7% Fe). Each alloy button was about 3~5g and re-melted for 6 times.

After the re-melting the mass change was less than 0.005%, therefore the nominal compositions were used. The measured oxygen and nitrogen contents were about 580wppm O and 53wppm N as measured by LECO analyzer. For heat treatments, the buttons were encapsulated in quartz tubes evacuated to a pressure lower than 10^{-4} atm. The buttons were solutionized in single β phase region at 1073K for 2h, followed by quenching in iced brine while breaking the quartz tubes. For the convenience of machining, some buttons were cold rolled and recrystallized at 1073K for 1hr followed by quenching in iced brine.

2.1 Differential scanning calorimetry (DSC)

Selected alloys were cut to pieces of about 1mm thick and were analyzed using a Mettler Toledo DSC822e calorimeter. Starting at an almost fully martensitic microstructure with small amounts of retained β phase, the samples were heated in the DSC at 40K/min. The corresponding heat flow curves are shown in Figure 2. On heating, the heat-flow peaks are associated in sequence with (1) martensitic reversion $\alpha'' \rightarrow \beta$; (2) formation of thermal ω $\beta \rightarrow \omega_{th}$; (3) dissolution of thermal ω , $\omega_{th} \rightarrow \beta$; and (4) formation of primary α phase, $\beta \rightarrow \alpha$, consistent with the thermal analysis results by Plejewski et al.[13]. The finish temperature of martensitic reversion A_f have been measured (Table 1). The A_f in some alloys may be underestimated due to an overlapping of opposite $\beta \rightarrow \omega_{th}$ peaks.

In other DSC runs of the same alloys, during cooling from a temperature just above A_f , none of the samples except C13-7 showed the exothermic peak associated with martensitic formation. Similar phenomena were also reported for Ti-Nb based alloys[14]. Plejewski et al. have found by dilatometry that slow cooling allows the formation of thermal ω phase at a higher temperature than M_s which prohibits martensitic transformation, while fast cooling can avoid

thermal ω phase and allow the formation of martensite[13]. In order to measure both M_S (martensite-start temperature) and A_f , we used a dilatometer that can provide fast cooling.

2.2 Dilatometry

We used a dilatometer with induction heating in vacuum and gas quenching. The samples were $\phi 2\text{mm} \times 10.0\text{mm}$ cylinders cut out of the buttons cold rolled and recrystallized. M_S and A_f temperatures were determined from the length change – temperature (Δl - T) curves, where an increment of Δl at about 420~500K on quenching was attributed to the martensitic formation, and a decrement of Δl of a similar magnitude at about 500~650K on heating to the martensitic reversion (Figure 3a). The martensitic formation and reversion were also obvious from a temperature-time (T - t) curve from the thermocouple attached to the sample (Figure 3b). The M_S values obtained by Δl - T and T - t curves were consistent with each other within an experimental uncertainty of 20K. It was found that the Δl - T curves were highly reproducible over solutionizing-quench thermal cycles. This verified that the thermal ω phase was suppressed by high-speed quenching. Table 2 lists the measured M_S and A_f temperatures.

3. First-principles calculations

First-principles density functional theory (DFT)[15, 16] calculations were carried out to obtain total energies of β (bcc), α' (hcp) and ω phases at 0K. For substitutional disordered alloys, we used two methods in this work: virtual crystal approximation (VCA) and the local self-consistent Green's function method based on exact muffin-tin orbitals (EMTO-LSGF)[17-20].

We used Quantum Espresso (QE) [21, 22] with the ultra-soft pseudopotentials (USPP) from Garrity, Bennett, Rabe and Vanderbilt (GBRV)[23, 24]. The calculated bcc-hcp energy

difference was converged within 0.5%. The Murnaghan equation of state was used for finding the equilibrium lattice parameters and bulk modulus. VCA potentials were generated using QE for Ti-V, Ti-Mo and Ti-Nb systems from the GBRV-USPPs of pure elements. For EMTO-LSGF calculations, the slope matrices, shape functions, and $4 \times 4 \times 4$ supercells of bcc, hcp and ω structures were generated with negligible short-range ordering in the nearest 10 neighbor shells. The chemical compositions of the supercells included A_7B_1 , A_6B_2 , A_5B_3 for binary alloys and $A_6B_1C_1$, $A_5B_2C_1$ and $A_4B_3C_1$ for ternary. The electrons in the two outmost shells were considered as valence electrons. The local interaction zone was up to the 3rd nearest neighbors. The bcc-hcp energy difference converged to a similar threshold as the QE calculations. Figure 4 shows the total energy differences of Ti-V and Ti-V-Al as an example. Table 3 lists x_0 , the composition where two phases have equal total energies at 0K. By definition, x_0 should be the endpoint of the T_0 curve at 0K.

4. Thermodynamic modeling

For a disordered solid solution of phase ϕ , we express its molar Gibbs energy (G_m) as a Redlich-Kister-Muggianu polynomial[25]:

$$G_m^\phi = \sum_i x_i G_{m,i}^\phi + RT \sum_i x_i \ln x_i + \sum_{i,j>i} x_i x_j \sum_n^n L_{i,j}^\phi (x_i - x_j)^n + \sum_{i,j>i,k>i,j} x_i x_j x_k^0 L_{i,j,k}^\phi \quad (1)$$

where i, j, k denote the chemical elements in the solution, and x stands for atomic fraction. The G_m functions of pure elements are relative to their molar enthalpy values at standard reference state H_0^{SER} . The polynomial order n usually takes 0, 1, and 2 for binary interactions. For ternary interactions, usually order 0 is sufficient. In this work we do not consider interstitial elements (O,

N, C, etc.) or ordered phases, therefore the complete form of sublattice model is not necessary.

4.1 Unary systems

In the SGTE database for pure elements[26], bcc and hcp descriptions are available for all elements under consideration in this work, while no ω description is assessed except for Zr. In this work we integrate various experimental and first-principles data to describe unary systems. We also extend the descriptions to 0K following the equations and boundary conditions of Vřešťál et al.[27].

4.1.1 ω -Ti

In order to construct the Gibbs free energy of ω -Ti, we consider the pressure-temperature (P - T) phase diagram of pure Ti[28], the rapid quenching experiment [29], and DFT calculations using the quasi-harmonic approximation (QHA) and Debye model [30]. For the β - ω transus, we take 723K from Mirzayev *et al.*[29], which has less uncertainty (15K) than the extrapolation of the high-pressure β - ω phase boundary and the QHA calculation. For the α - ω transus, we prefer DFT calculations (186K) by Mei et al.[30] to the extrapolation of high-pressure α - ω phase boundaries due to its large pressure hysteresis. From the dP/dT slope of the α - ω boundary, one can get the molar entropy difference $\Delta S_m = S_m(\omega) - S_m(\alpha)$ at 186K from the Clausius-Clapeyron relationship. We take the slope $dP/dT = 0.01316 \text{ GPa/K}$, and the volume change $\Delta V_m = -0.24 \text{ \AA}^3/\text{atom} = -1.445 \times 10^{-7} \text{ m}^3/\text{mol}$ from the DFT calculations by Hu et al.[31]. As a result, $\Delta S_m = (dP/dT)\Delta V_m = -1.902 \text{ J/mol/K}$. In addition, the DFT total energy difference $E(\omega) - E(\alpha) = -203 \text{ J/mol}$ is also taken from Mei et al. [30]. The specific heat $C_p(T)$ of ω -Ti and α -Ti calculated by Mei et al. [30] are not adopted, because they are surprisingly close to each other, compared to the experimental curves of ω -Zr and α -Zr[32]. The molar Gibbs function of ω -Ti is shown in Figure 5.

4.1.2 ω -phase, other elements

The energy difference $E(\omega)-E(\beta)$ at 0K can be obtained from the QE-USPP calculations. However, it may not be directly applicable to a CALPHAD database. A systematic comparison of bcc-fcc and bcc-hcp phase stabilities from DFT calculations and the SGTE database has been done by Wang et al.[33], which implies a factor of 0.357 to convert DFT phase stabilities to the CALPHAD values, attributed to dynamical instability. The same factor is used to convert the DFT $E(\omega)-E(\beta)$ to its CALPHAD value for the pure elements except Al, Sn, and V whose $E(\omega)-E(\beta)$ are small. We assume a constant $G_m(\omega)-G_m(\beta)$ independent of temperature, as in the case of the SGTE database for many unstable phases. Table 4 shows the 0K energy differences.

4.2 Binary systems

The objective of the thermodynamic optimization is to provide accurate driving forces for martensitic transformation and athermal ω phase. There are some general rules we follow in this work:

(1) We adopt a unified description for the equilibrium α , the hcp martensite α' , and the orthorhombic martensite α'' . The primary reason is the M_S temperatures for α' and α'' are not discernible within experimental scatter. The α'/α'' orthorhombic distortion is of the same nature with the tetragonal distortion of substitutional bcc ferrous martensite, which is explained by Cahn and Rosenberg with an anisotropy of pair correlations due to short range ordering[34, 35]. The effect of the orthorhombic distortion on thermodynamics is discussed in Section 6.3. Nevertheless, for a general alloy we neglect such an effect on thermodynamics, mainly due to a lack of calorimetric data.

(2) The calculated $T_0(\beta/\alpha)$ must not be systematically lower than the experimental M_S .

(3) We take $T_0(\beta/\alpha)=0.5(M_S+A_S)$ for nonthermoelastic martensite with large hysteresis, and $T_0(\beta/\alpha)=A_f$ for thermoelastic martensite in polycrystals following Salzbrenner and Cohen[36]. When such T_0 data are available, these are given more weight than phase boundary data.

(4) We use the β -phase descriptions from other assessments (mostly from COST507B[37]), and modify the α -phase descriptions if necessary. The ω -phase description is created with reference to the β phase.

(5) Partitionless equilibrium compositions at 0K x_0 from first-principles calculations are taken as a reference, but not taken for optimization unless no experimental data are available.

The formation temperature of athermal ω phase has been measured by electrical resistivity, transmission electron microscopy, and thermal analysis. We take the ω -start temperature ω_s measured by electrical resistivity as $T_0(\beta/\omega)$, because it connects the $T_0(\beta/\omega)$ of pure Ti and first-principles calculations smoothly. This is best seen in the Ti-V system (Figure 6) where the VCA first-principles calculations are most reliable due to the intimate chemical nature of Ti and V.

4.3 Ternary systems

Among all the ternary systems, only Ti-Nb-X has sufficient available quantitative information related to martensitic transformations near room temperature, motivated by research interests primarily on shape memory effect. For Ti-V-Al and Ti-V-Al-Fe alloys, we use the A_f data from DSC and dilatometry for $T_0(\beta/\alpha)$. For the Ti-V-Sn system we use the x_0 data from DFT for the estimation $T_0(\beta/\alpha)$ and $T_0(\beta/\omega)$. In the Ti-Nb-Sn/Zr and Ti-V-Sn systems which are not assessed before, large negative interaction terms are added to the β phase to remove the high-

temperature miscibility gap before optimizing the α -phase parameters. It is noteworthy that T_0 is determined by the inter-phase differences of interaction terms, not their absolute values.

4.4 Results

The new thermodynamic database presented hereby is named “TiGen” for “Titanium Genome” (see Appendix and Online Supplemental Material for the entire database). We hereby discuss its performance on binary and ternary systems.

For the Ti-V/Mo/Nb/Ta/Fe systems (Figures 6-10), the new $T_0(\beta/\alpha)$ curves are better bracketed by experimental M_S and A_f (or A_S), with a similar curvature to the measured points. This new assessment can systematically avoid the unphysical condition $T_0(\beta/\alpha) < M_S$, thus yielding more accurate driving-force values for the kinetics of martensitic nucleation (Section 5). The temperature hysteresis $A_f - M_S$ (or $A_S - M_S$) is small for the Ti-V/Mo/Nb/Ta systems, where we assume thermoelasticity and take $T_0(\beta/\alpha) = A_f$. For Ti-Fe alloys where $A_S - M_S$ is large, we assume nonthermoelastic behavior and take $T_0(\beta/\alpha) = 0.5(M_S + A_S)$. The data from Yamane and Ito [38] are preferred for the high quench speeds used in the work. The $T_0(\beta/\alpha)$ is improved considerably for the Ti-Fe system. All the reassessments make very little difference in the β/α equilibrium phase boundaries.

For the Ti-V/Mo/Nb systems, the ω -phase stabilities have been modeled in previous work based on room-temperature observations[45] or on the thermal ω phase[46, 62], all with considerable uncertainties. In this work we adopt the ω_S temperatures measured by resistivity and treat them as $T_0(\beta/\omega)$. The intersection of $T_0(\beta/\omega)$ and M_S terminate the M_S curve by quenching. This explains in a quantitative fashion the competition between athermal ω and martensite and the premature termination of M_S well above room temperature. It is noteworthy that the intersection of $T_0(\beta/\omega)$ and M_S in the Ti-V and Ti-Mo systems are about 600K, higher

than the counterpart in the Ti-Nb system (about 400K). This may be part of the reason why in the Ti-Nb system it is much easier to get mechanically-induced martensite near room temperature allowing more intensive study as shape-memory and superelastic alloys. The Ti-Ta and Ti-Fe systems do not have experimental ω_s data, and the $T_0(\beta/\omega)$ for the Ti-Fe system is estimated based on the existence of ω diffraction spots even in an as-quenched Ti-20at%Fe alloy[67].

The Ti-Zr system is slightly improved by fitting $T_0(\beta/\omega)$ to $0.5(M_S + A_S)$, while the Ti-Al/Sn systems are not reassessed (Figure 11). Al, Sn, and Zr are α -stabilizing or weakly β -stabilizing in the binary systems. However, in ternary systems such as Ti-Nb-X and Ti-V-X, they may become stronger β stabilizing elements over α'' martensite and ω phase and lower both A_f and ω_s temperatures. Such an anomalous behavior, which cannot be reproduced by previous databases, are correctly reflected in the Ti-Nb-based alloys (Figure 12). Similarly, the effect of Al as a β -stabilizer in Ti-V-Al and Ti-V-Al-Fe systems is well reproduced (Figure 13).

5. Kinetics of martensitic transformations in Ti alloys

The theory of heterogeneous nucleation of martensite has been established by Olson and Cohen[80-83]. According to this theory, the nucleation of martensite does not require an embryo of the same crystal structure, but rather it requires suitable defects as nucleation sites. Provided sufficient driving force, martensite nucleates without an energy barrier and grows spontaneously. The semi-coherent martensitic interface is described by two categories of dislocations, whose motion encounters various kinds of obstacles that exert a frictional work against the martensitic interfacial motion[8, 9]. The critical condition for martensite to nucleate is given by the following equation:

$$\Delta G_{ch} + \Delta G_{\sigma} = -(W_f + G_0)$$

with the left hand side being the total driving force contributed from chemical thermodynamics (ΔG_{ch}) and applied stress (ΔG_{σ}), and the right hand side being the critical driving force (ΔG_{crit}) which consists of a composition-dependent frictional work term W_f and a nucleant potency term G_0 . In the case of martensite formed by quenching, only the chemical driving force contributes. For $\beta \rightarrow \alpha'/\alpha''$ transformation in Ti alloys,

$$\Delta G_{ch} = G_m(\alpha) - G_m(\beta)$$

with fixed composition, which is calculated using the TiGen database. By its definition, the critical driving force should equal the chemical driving force at the M_S temperature:

$$\Delta G_{crit} = \Delta G_{ch} \big|_{T=M_S}$$

For martensite in solid solutions, the frictional work W_f comes solely from solution hardening. We model ΔG_{crit} in binary systems and add their contributions for multicomponent systems. The ΔG_{crit} of Ti-V/Nb/Mo/Ta/Fe/Al/Zr binary systems can be represented by:

$$\Delta G_{crit} = -G_0 - \sum_{i \neq Zr} K_i x_i - K_{Zr}^{(1)} x_{Zr} - K_{Zr}^{(2)} x_{Zr}^2 \quad (5)$$

This is consistent with the linear solution hardening law for slip observed in hcp Ti-based alloys[84-89] and the hardness of hcp Ti-Zr alloys over the entire composition range[90].

Many of the M_S temperatures obtained by Duwez and his coworkers are higher than those from others, in some cases giving negative driving force for martensitic transformation, therefore not used for fitting. For Al, the results from Sato et al.[40] are not used because they suggest frictional works much larger than those from Jepson et al.[56] and Ti-V/Nb-Al alloys. In addition,

the ΔG_{crit} of binary Ti-Sn alloys does not extrapolate to the common intercept G_0 determined by other systems, and it tends to flatten out at about -500J/mol beyond 4at% Sn. This is inconsistent with the case of Ti-Nb-Sn alloys (Figure 12), where the contribution of Sn to ΔG_{crit} is negligible up to 5at% Sn, featured by the small A_f-M_s difference. Therefore, for modeling the M_s of multicomponent Ti alloys, $K(\text{Sn})$ is taken as zero. The physical reason why Sn behaves differently in binary and ternary alloys is not clear.

The parameters for Equation 5 are shown in Figure 14 and Table 5.

The M_s temperatures of the alloys listed in Table 2 are calculated using Equations 3-5, and they are in good agreement with the measured values (Figure 15). This suggests that the ω_s temperatures of these alloys may be much lower than M_s . Otherwise, the athermal ω particles formed prior to martensite may exert extra frictional work against the martensitic interface, which gives a much lower M_s than expected, or no martensite by quenching at all. Such a case can be seen in the Ti-V system beyond 12at% V (Figure 6) or in the Ti-Mo system beyond 6at% Mo (Figure 7).

6. Discussion

6.1 Range of application

The TiGen database in this work focuses on displacive martensitic and athermal ω transformations near room temperature. It is optimized using low-temperature data largely neglected by previous CALPHAD assessments, with a slight compromise to phase equilibria data if necessary. Therefore the high-temperature β - α phase equilibria calculated by TiGen may

not be accurate, and for such purpose TTTI3 may be more appropriate for modeling diffusional transformations.

The martensite formation/reversion temperatures in many ternary alloys remain unmeasured. In this work, only Ti-Nb-Al/Sn/Zr and Ti-V-Al have been assessed based on experimental data. The parameters for Ti-V-Sn/Zr systems are estimated from 0K phase stabilities by first-principles calculations. Future directions include dilatometric measurements of M_s and A_f of Ti-V-Sn/Zr alloys to improve the estimated curves employed in this work.

6.2 Assessment strategies for the anomalous β -stabilizing effects of Al, Sn and Zr

From the experimental data of Ti-Nb/V-Al/Sn/Zr ternary alloys whose martensitic transformation/reversion occurs near room temperature, we can see that Al, Sn and Zr are stronger β stabilizing elements than their effects in Ti-Al/Sn/Zr binary alloys. In this work we use only chemical interaction terms between Nb/V and Al/Sn/Zr to account for this effect. However, there is evidence that such a β -stabilizing effect of Al, Sn and Zr also exists in other systems like Ti-Fe/Cr/Mo-based ternary alloys[91-94]. Simply using fixed chemical interactions will need system-by-system assessments. It may be more efficient and physically significant to attribute the β -stabilizing effect to a temperature effect, and re-assess the low-temperature part of Ti-Al/Sn/Zr binary systems.

6.3 The results of treating α'' as α' : the Ti-Nb system as an example

The current treatment unifies the orthorhombic α'' martensite and the hcp α' phase in terms of thermodynamics. As mentioned, this is supported by the continuity of M_s temperature at the α'/α'' transition composition. However, since α'' martensite has a crystal structure intermediate between bcc and hcp, it is reasonable to describe the β -to- α'' transformation as a

crystallographically incomplete β -to- α' transformation that should have a smaller transformation enthalpy change. This is demonstrated in the Ti-Nb system as follows. We have measured the transformation enthalpy of martensitic reversion α'' -to- β in Ti-(22-24)at%Nb alloys using DSC. The as-quenched microstructure of Ti-24Nb alloy has been confirmed as fully martensitic at nanoscale[95], therefore the measured enthalpy change can be converted to enthalpy change per mole martensite. Another data point of Ti-26Nb comes from Clausius-Clapeyron relations of uniaxial tensile tests [58]. While the measured A_f temperatures agree with calculated $T_0(\beta/\alpha)$ as expected, the experimental α'' - β transformation enthalpy is much smaller than the calculated counterpart of α' - β transformation.

The transformation enthalpy changes for other Ti-based systems are rarely reported, making it difficult to reliably correct the transformation enthalpy change for a general composition. As a result, the transformation entropy change, and subsequently the critical driving force of α'' martensitic nucleation, is likely overestimated. The overestimation is effectively canceled in the fitting procedure in Section 5 for M_S calculation ($\Delta G_{ch} = \Delta G_{crit}$). However, for stress-assisted martensite where mechanical driving force contributes ($\Delta G_{ch} + \Delta G_{\sigma} = \Delta G_{crit}$), a calibration to ΔG_{ch} together with ΔG_{crit} is needed in order to properly account for the orthorhombic α'' structure. This has been carried out in an investigation of the Ti-10V-2Fe-3Al alloy and is proved feasible[96].

6.4 Treatment of $T_0(\beta/\omega)$

In Ti-based systems, the hexagonal perfect ω is a stable phase at high pressure, yet upon cooling from β phase region it may form as dispersed defect-stabilized nanoparticles instead of bulk phase. Moreover at some compositions the ω particles are not of a perfect hexagonal structure but an “incommensurate” trigonal structure ω' . Along the β -to- ω deformation path,

mean-field methods such as VCA predict the stability of β and/or perfect ω , and incommensurate structures are not stable[97]. In the same spirit as the Cahn-Rosenberg distortion, one may hypothesize that short-range ordering may play a role in the stabilization of incommensurate ω' [98], which is beyond the single-site mean-field approximation.

So far, only the binary Ti-V, Ti-Mo, and Ti-Nb systems have sufficient data to allow a satisfactory modeling of $T_0(\beta/\omega)$. Since the binary systems suggest that electrical resistivity measurements give accurate ω_S data, more experiments of the same kind can be done for Ti-Fe, Ti-Ta, and Ti-V/Nb-Al/Sn/Zr alloys to determine ω_S . Moreover, the thermodynamic descriptions based on athermal ω can also lay a foundation for modeling thermal ω .

Many aspects of athermal and thermal ω formation, and their interplay with martensitic formation and reversion, remain unrevealed. One particular interesting phenomenon is the “catalysis” effect: For some as-quenched alloy with β phase partially transformed to martensite, a short heat treatment can make the transformation complete. This has been reported in various metastable- β Ti alloys[75, 91, 99, 100]. For the thermodynamic and kinetic modeling of martensitic transformation in such systems, one has to keep in mind that ω phase or its embryo may conceal the real M_S temperature, and that the kinetics of ω phase may have a time-dependent effect on martensitic kinetics.

7. Conclusions

In this work we present a thermodynamic database for the martensitic transformations and athermal ω formation for some binary and ternary Ti systems. The martensitic formation and reversion temperatures provide useful data for accurate assessments at low temperatures where

phase equilibria are difficult to obtain. The TiGen database in this work can accurately reproduce the partitionless equilibrium temperature T_0 between bcc and hcp phases, $T_0(\beta/\alpha)$, in six binary systems and some Ti-V/Nb-based ternary systems. Al, Sn, and Zr are found to be stronger beta stabilizing elements for low-temperature martensitic transformations, which is accounted for by chemical interaction terms with V and Nb.

The ω -start temperature measured by electrical resistivity is close to the T_0 temperature between bcc and ω phases. The description of ω phase is added based on the resistivity results in binary alloys and estimated from first-principles calculations for ternary alloys. In Ti-V/Mo/Nb systems, M_S is terminated by its intersection with $T_0(\beta/\omega)$, beyond which athermal ω forms at a higher temperature and inhibits the martensitic transformation.

The kinetics of martensitic transformation is modeled by using an interfacial frictional work based on solution hardening. The frictional work is found linear with the atomic fractions of alloying elements, analogous to the solution-hardening laws for slip deformation found in Ti alloys. For a more accurate prediction of martensitic kinetics, it is necessary to include the effect of martensitic orthorhombicity on transformation thermodynamics, and the interplay between ω phase and martensite.

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Appendix. Thermodynamic parameters of the TiGen database

Term	Expression	Temperature range	Reference /Note
BCC_A2			
$G_{\text{Al}}^{\text{BCC}} - H_0^{\text{SER}}$	$5.058\text{E}3 + 3RT\ln(1 - e^{-253.76/T}) - 1.40059\text{E}-2 T^2 - 2.95510\text{E}-11 T^5 + 2.29125\text{E}-5 T^3$	$0 < T < 298.15$	After [27]
	$2106.85 + 132.280038 T - 24.3671976 T \ln(T) - 1.884662\text{E}-3 T^2 - 0.877664\text{E}-6 T^3 + 74092 T^{-1}$	$298.15 < T < 700$	[26]
	$-1193.24 + 218.235446 T - 38.5844296 T \ln(T) + 18.531982\text{E}-3 T^2 - 5.764227\text{E}-6 T^3 + 74092 T^{-1}$	$700 < T < 933.47$	
	$-1195.378 + 183.871153 T - 31.748192 T \ln(T) - 1.231\text{E}28 T^{-9}$	$933.47 < T < 2900$	
$G_{\text{Fe}}^{\text{BCC}} - H_0^{\text{SER}}$	$3.874\text{E}3 + 3RT\ln(1 - e^{-308.77/T}) - 4.81992\text{E}-2 T^2 - 8.76367\text{E}-11 T^5 + 7.68574\text{E}-5 T^3$	$0 < T < 298.15$	[27]
	$1225.7 + 124.134T - 23.5143 T \ln(T) - 4.39752\text{E}-3 T^2 - 0.0589269\text{E}-6 T^3 + 77358.5 T^{-1}$	$298.15 < T < 1811$	[26]
	$-25383.581 + 299.31255 T - 46 T \ln(T) + 2.2960305\text{E}31 T^{-9}$	$1811 < T < 6000$	

$G_{\text{Mo}}^{\text{BCC}} - H_0^{\text{SER}}$	$-4.53966\text{E}3 + 3RT\ln(1 - e^{-346.5/T}) - 2.14188\text{E}-2 T^2$ $- 2.93372\text{E}-11 T^5 + 2.97137\text{E}-5 T^3$	$0 < T < 298.15$	[27]
	$-7746.302 + 131.9197 T - 23.56414 T\ln(T) -$ $3.443396\text{E}-3 T^2 + 0.5662834\text{E}-6 T^3 + 65812.39$ $T^{-1} - 0.1309265\text{E}-9 T^4$	$298.15 < T < 2896$	[26]
	$-30556.41 + 283.559746 T - 42.63829 T\ln(T) -$ $4849.315\text{E}30 T^{-9}$	$2896 < T < 5000$	
$G_{\text{Nb}}^{\text{BCC}} - H_0^{\text{SER}}$	$-5.30319\text{E}3 + 3RT\ln(1 - e^{-211.75/T}) - 9.81739\text{E}-3$ $T^2 - 2.30524\text{E}-11 T^5 + 1.68426\text{E}-5 T^3$	$0 < T < 298.15$	[27]
	$-8519.353 + 142.045475 T - 26.4711 T\ln(T) +$ $0.203475\text{E}-3 T^2 - 0.350119\text{E}-6 T^3 + 93399 T^{-1}$	$298.15 < T < 2750$	[26]
	$-37669.3 + 271.720843 T - 41.77 T\ln(T) +$ $1528.24\text{E}29 T^{-9}$	$2750 < T < 6000$	
$G_{\text{Sn}}^{\text{BCC}} - H_0^{\text{SER}}$	$-2.10719\text{E}3 + 3RT\ln(1 - e^{-118.58/T}) - 1.09254\text{E}-1$ $T^2 - 6.08287\text{E}-09 T^5 + 5.66209\text{E}-4 T^3$	$0 < T < 100$	After [27]
	$-3558.517 + 116.765451 T - 25.858 T\ln(T) +$ $0.51185\text{E}-3 T^2 - 3.192767\text{E}-6 T^3 + 18440 T^{-1}$	$100 < T < 250$	[26]
	$-1455.135 + 59.443315 T - 15.961 T\ln(T) -$ $18.8702\text{E}-3 T^2 + 3.121167\text{E}-6 T^3 - 61960 T^{-1}$	$250 < T < 505.078$	
	$6924.724 - 1.994731 T - 8.2590486 T\ln(T) -$ $16.814429\text{E}-3 T^2 + 2.623131\text{E}-6 T^3 - 1081244$	$505.078 < T < 800$	

	$T^{-1} - 1.2307\text{E}25 T^{-9}$		
	$-3856.959 + 132.99688 T - 28.4512 T \ln(T) - 1.2307\text{E}25 T^{-9}$	$800 < T < 3000$	
$G_{\text{Ta}}^{\text{BCC}} - H_0^{\text{SER}}$	$-5.79696\text{E}3 + 3RT \ln(1 - e^{-184.8/T}) - 1.47751\text{E}-2 T^2 - 1.96608\text{E}-11 T^5 + 2.01945\text{E}-05 T^3$	$0 < T < 298.15$	[27]
	$-7285.889 + 119.139857 T - 23.7592624 T \ln(T) - 2.623033\text{E}-3 T^2 + 0.170109\text{E}-6 T^3 - 3293 T^{-1}$	$298.15 < T < 1300$	[26]
	$-22389.955 + 243.88676 T - 41.137088 T \ln(T) + 6.167572\text{E}-3 T^2 - 0.655136\text{E}-6 T^3 + 2429586 T^{-1}$	$1300 < T < 2500$	
	$+229382.886 - 722.59722 T + 78.5244752 T \ln(T) - 17.983376\text{E}-3 T^2 + 0.195033\text{E}-6 T^3 - 93813648 T^{-1}$	$2500 < T < 3290$	
	$-1042384.014 + 2985.491246 T - 362.1591318 T \ln(T) + 43.117795\text{E}-3 T^2 - 1.055148\text{E}-6 T^3 + 554714342 T^{-1}$	$3290 < T < 6000$	
$G_{\text{Ti}}^{\text{BCC}} - H_0^{\text{SER}}$	$9.46204\text{E}2 + 3RT \ln(1 - e^{-220.22/T}) - 1.05060\text{E}-2 T^2 - 2.83258\text{E}-12 T^5 + 8.61145\text{E}-6 T^3$	$0 < T < 298.15$	[27]
	$-1272.064 + 134.71418 T - 25.5768 T \ln(T) - 0.663845\text{E}-3 T^2 - 0.278803\text{E}-6 T^3 + 7208 T^{-1}$	$298.15 < T < 1155$	[26]
	$6667.385 + 105.366379 T - 22.3771 T \ln(T) +$	$1155 < T < 1941$	

	$1.21707\text{E-}3 T^2 - 0.84534\text{E-}6 T^3 - 2002750 T^{-1}$		
	$26483.26 - 182.426471 T + 19.0900905 T \ln(T) - 22.00832\text{E-}3 T^2 + 1.228863\text{E-}6 T^3 + 1400501 T^{-1}$	$1941 < T < 4000$	
$G_{\text{V}}^{\text{BCC}} - H_0^{\text{SER}}$	$-4.82592\text{E}3 + 3RT \ln(1 - e^{-292.6/T}) - 1.63735\text{E-}2 T^2 - 2.63497\text{E-}11 T^5 + 2.36400\text{E-}5 T^3$	$0 < T < 298.15$	[27]
	$-7930.43 + 133.346053 T - 24.134 T \ln(T) - 3.098\text{E-}3 T^2 + 0.12175\text{E-}6 T^3 + 69460 T^{-1}$	$298.15 < T < 790$	[26]
	$-7967.842 + 143.291093 T - 25.9 T \ln(T) + 0.0625\text{E-}3 T^2 - 0.68\text{E-}6 T^3$	$790 < T < 2183$	
	$-41689.864 + 321.140783 T - 47.43 T \ln(T) + 644.389\text{E}29 T^{-9}$	$2183 < T < 4000$	
$G_{\text{Zr}}^{\text{BCC}} - H_0^{\text{SER}}$	$1.15981\text{E}3 + 3RT \ln(1 - e^{-147.07/T}) - 1.64156\text{E-}2 T^2 - 2.71022\text{E-}11 T^5 + 2.48309\text{E-}5 T^3$	$0 < T < 298.15$	[27]
	$-525.539 + 124.9457 T - 25.607406 T \ln(T) - 3.40084\text{E-}4 T^2 - 9.7289735\text{E-}9 T^3 - 7.6142894\text{E-}11 T^4 + 25233 T^{-1}$	$298.15 < T < 2128$	[26]
	$-30705.955 + 264.284163 T - 42.144 T \ln(T) + 1.276058\text{E}32 T^{-9}$	$2128 < T < 4000$	
${}^0\text{L}_{\text{Al,Fe}}^{\text{BCC}}$	$-122960 + 32 T$	$0 < T < 6000$	[37]

${}^1L_{\text{Al,Fe}}^{\text{BCC}}$	2945		
${}^0L_{\text{Al,Nb}}^{\text{BCC}}$	$-104050 + 30\ T$	$0 < T < 6000$	[37]
${}^1L_{\text{Al,Nb}}^{\text{BCC}}$	$9140 - 4\ T$		
${}^2L_{\text{Al,Nb}}^{\text{BCC}}$	12000		
${}^0L_{\text{Al,Ti}}^{\text{BCC}}$	$-128500 + 39\ T$	$0 < T < 6000$	[37]
${}^1L_{\text{Al,Ti}}^{\text{BCC}}$	6000		
${}^2L_{\text{Al,Ti}}^{\text{BCC}}$	21200		
${}^0L_{\text{Al,Ti,V}}^{\text{BCC}}$	32045.963		
${}^0L_{\text{Al,V}}^{\text{BCC}}$	$-95000 + 20\ T$		
${}^1L_{\text{Al,V}}^{\text{BCC}}$	-6000		
${}^0L_{\text{Fe,Ti}}^{\text{BCC}}$	$-59098 + 11.5\ T$	$0 < T < 6000$	[101]
${}^1L_{\text{Fe,Ti}}^{\text{BCC}}$	$-1796 + T$		
${}^2L_{\text{Fe,Ti}}^{\text{BCC}}$	$5602 + 3.5\ T$		
${}^0L_{\text{Mo,Nb}}^{\text{BCC}}$	$-68202.6 + 29.85596\ T$	$0 < T < 6000$	[102]
${}^1L_{\text{Mo,Nb}}^{\text{BCC}}$	8201.3		
${}^0L_{\text{Mo,Ta}}^{\text{BCC}}$	$-75129.2 + 30\ T$		
${}^1L_{\text{Mo,Ta}}^{\text{BCC}}$	6039.24		
${}^0L_{\text{Mo,Ti}}^{\text{BCC}}$	2000	$0 < T < 6000$	[37]

${}^1L_{\text{Mo,Ti}}^{\text{BCC}}$	-2000		
${}^0L_{\text{Nb,Sn}}^{\text{BCC}}$	-100000	$0 < T < 6000$	¹
${}^1L_{\text{Nb,Sn}}^{\text{BCC}}$	0		
${}^0L_{\text{Nb,Sn,Ti}}^{\text{BCC}}$	-100000		
${}^0L_{\text{Nb,Ta}}^{\text{BCC}}$	1298.03	$0 < T < 6000$	[102]
${}^0L_{\text{Nb,Ti}}^{\text{BCC}}$	14000	$0 < T < 6000$	[37]
${}^1L_{\text{Nb,Ti}}^{\text{BCC}}$	2500		
${}^0L_{\text{Nb,Zr}}^{\text{BCC}}$	$15911 + 3.35 T$	$0 < T < 6000$	[103]
${}^1L_{\text{Nb,Zr}}^{\text{BCC}}$	$3919 - 1.091 T$		
${}^0L_{\text{Sn,Ti}}^{\text{BCC}}$	$-115000 + 6.77583 T$	$0 < T < 6000$	[37]
${}^1L_{\text{Sn,Ti}}^{\text{BCC}}$	$45000 + 1.58018 T$		
${}^0L_{\text{Sn,Ti,V}}^{\text{BCC}}$	-300000	$0 < T < 6000$	²
${}^0L_{\text{Sn,V}}^{\text{BCC}}$	$13379.1 + 23.937 T$	$0 < T < 6000$	[104]
${}^1L_{\text{Sn,V}}^{\text{BCC}}$	$99320.6 + 2.753 T$		
${}^2L_{\text{Sn,V}}^{\text{BCC}}$	$-107163 + 52.026 T$		
${}^0L_{\text{Ta,Ti}}^{\text{BCC}}$	12000	$0 < T < 6000$	[37]
${}^1L_{\text{Ta,Ti}}^{\text{BCC}}$	-2500		

¹ To eliminate the miscibility gap of bcc Ti-Nb-Sn.

² To eliminate the miscibility gap of bcc Ti-V-Sn for $x(\text{Sn}) < 0.1$ and $T > 900\text{K}$.

${}^0L_{\text{Ti,V}}^{\text{BCC}}$	$10500 - 1.5 T$	$0 < T < 6000$	[37]
${}^1L_{\text{Ti,V}}^{\text{BCC}}$	2000		
${}^2L_{\text{Ti,V}}^{\text{BCC}}$	1000		
${}^0L_{\text{Ti,Zr}}^{\text{BCC}}$	$-3460 - 3.3 T$	$0 < T < 6000$	[105]
${}^0L_{\text{V,Zr}}^{\text{BCC}}$	$21876 + 7.76 T$	$0 < T < 6000$	[37]
${}^1L_{\text{V,Zr}}^{\text{BCC}}$	$8995.72 - 0.897 T$		
HCP_A3			
$G_{\text{Al}}^{\text{HCP}}$	$695.876 + 3RT\ln(1 - e^{-253.76/T}) - 5.31731\text{E-}04 T^2 - 4.13142\text{E-}12 T^5 + 3.16167\text{E-}07 T^3$	$0 < T < 298.15$	After [27]
	$G_{\text{Al}}^{\text{BCC}} - 4602 + 3.013 T$	$298.15 < T < 2900$	[26]
$G_{\text{Fe}}^{\text{HCP}}$	$808.209 + 3RT\ln(1 - e^{-308.77/T}) - 2.18394\text{E-}2 T^2 - 3.18388\text{E-}11 T^5 + 2.94128\text{E-}05 T^3$	$0 < T < 298.15$	After [27]
	$G_{\text{Fe}}^{\text{BCC}} - 3705.78 + 12.591 T - 1.15 T\ln(T) + 6.4\text{E-}4 T^2$	$298.15 < T < 1811$	[26]
	$G_{\text{Fe}}^{\text{BCC}} - 3957.199 + 5.24951 T + 0.4925095\text{E}31 T^{-9}$	$1811 < T < 6000$	
$G_{\text{Mo}}^{\text{HCP}}$	$7010.34 + 3RT\ln(1 - e^{-346.5/T}) - 2.14188\text{E-}2 T^2 - 2.93372\text{E-}11 T^5 + 2.97137\text{E-}5 T^3$	$0 < T < 298.15$	After [27]
	$G_{\text{Mo}}^{\text{BCC}} + 11550$	$298.15 < T < 4000$	[26]

$G_{\text{Nb}}^{\text{HCP}}$	$4887.63 + 3RT\ln(1-e^{-211.75/T}) + 9.15462\text{E-}4 T^2 - 2.80445\text{E-}12 T^5 - 1.15648\text{E-}6 T^3$	$0 < T < 298.15$	
	$G_{\text{Nb}}^{\text{BCC}} + 10000 + 2.4 T$	$298.15 < T < 6000$	[26]
$G_{\text{Sn}}^{\text{HCP}}$	$-2564.52 + 3RT\ln(1-e^{-118.58/T}) - 8.79202\text{E-}2 T^2 - 5.01621\text{E-}9 T^5 + 4.59542\text{E-}4 T^3$	$0 < T < 100$	After [27]
	$G_{\text{Sn}}^{\text{BCC}} - 500 + 1.6 T$	$100 < T < 3000$	[26]
$G_{\text{Ta}}^{\text{HCP}}$	$6393.86 + 3RT\ln(1-e^{-184.8/T}) - 4.04228\text{E-}3 T^2 + 5.87157\text{E-}13 T^5 + 2.19543\text{E-}6 T^3$	$0 < T < 298.15$	After [27]
	$G_{\text{Ta}}^{\text{BCC}} + 12000 + 2.4 T$	$298.15 < T < 3000$	[26]
$G_{\text{Ti}}^{\text{HCP}}$	$-4828.47 + 3RT\ln(1-e^{-323.4/T}) - 2.20720\text{E-}2 T^2 - 3.09397\text{E-}11 T^5 + 2.91272\text{E-}5 T^3$	$0 < T < 298.15$	[27]
	$-8059.921 + 133.615208 T - 23.9933 T\ln(T) - 4.777975\text{E-}3 T^2 + 0.106716\text{E-}6 T^3 + 72636 T^{-1}$	$298.15 < T < 900$	[26]
	$-7811.815 + 132.988068 T - 23.9887 T\ln(T) - 4.2033\text{E-}3 T^2 - 0.090876\text{E-}6 T^3 + 42680 T^{-1}$	$900 < T < 1155$	
	$908.837 + 66.976538 T - 14.9466 T\ln(T) - 8.1465\text{E-}3 T^2 + 0.202715\text{E-}6 T^3 - 1477660 T^{-1}$	$1155 < T < 1941$	
	$-124526.786 + 638.806871 T - 87.2182461 T\ln(T) + 8.204849\text{E-}3 T^2 - 0.304747\text{E-}6 T^3 + 36699805 T^{-1}$	$1941 < T < 4000$	

G_V^{HCP}	$-605.053 + 3RT\ln(1-e^{-318.78/T}) - 1.29361E-2 T^2$ $- 1.58176E-11 T^5 + 1.60438E-5 T^3$	$0 < T < 298.15$	After [27]
	$G_V^{\text{BCC}} + 4000 + 2.4 T$	$298.15 < T < 4000$	[26]
G_{Zr}^{HCP}	$-5518.62 + 3RT\ln(1-e^{-224.07/T}) - 4.03105E-2 T^2$ $- 6.56351E-10 T^5 + 1.24814E-4 T^3$	$0 < T < 130$	[27]
	$-7827.595 + 125.64905 T - 24.1618 T\ln(T) -$ $4.37791E-3 T^2 + 34971 T^{-1}$	$130 < T < 2128$	[26]
	$-26085.921 + 262.724183 T - 42.144 T\ln(T) -$ $1.342895E31 T^{-9}$	$2128 < T < 4000$	
${}^0L_{Al,Fe}^{\text{HCP}}$	297616	$0 < T < 6000$	³
${}^0L_{Al,Nb}^{\text{HCP}}$	664	$0 < T < 6000$	⁴
${}^1L_{Al,Nb}^{\text{HCP}}$	5000		[37]
${}^2L_{Al,Nb}^{\text{HCP}}$	10000		
${}^0L_{Al,Ti}^{\text{HCP}}$	$-133500 + 39 T$	$0 < T < 6000$	[37]
${}^1L_{Al,Ti}^{\text{HCP}}$	750		
${}^2L_{Al,Ti}^{\text{HCP}}$	17500		
${}^0L_{Al,V}^{\text{HCP}}$	-14048	$0 < T < 6000$	³
${}^1L_{Al,V}^{\text{HCP}}$	-6000		[37]

³ To fit to the A_f temperatures of Ti-V-Al-Fe alloys (Figure 13).

⁴ To fit to the A_f temperatures of Ti-Nb-Al alloys (Figure 12a)

${}^0L_{\text{Fe,Ti}}^{\text{HCP}}$	$-2958.67 - 34.61 T$	$0 < T < 6000$	Figure 10
${}^1L_{\text{Fe,Ti}}^{\text{HCP}}$	$-61567 + 12.25 T$		
${}^2L_{\text{Fe,Ti}}^{\text{HCP}}$	-10668		
${}^0L_{\text{Mo,Ti}}^{\text{HCP}}$	$46600 - 30 T$	$0 < T < 6000$	Figure 7
${}^0L_{\text{Nb,Sn}}^{\text{HCP}}$	${}^0L_{\text{Nb,Sn}}^{\text{BCC}} + 5.50766 (T-800)^2 + 0.0129648 (T-800)^3 + 8.76177\text{E}-6 (T-800)^4$	$0 < T < 800$	5
	${}^0L_{\text{Nb,Sn}}^{\text{BCC}}$	$800 < T < 6000$	
${}^1L_{\text{Nb,Sn}}^{\text{HCP}}$	${}^1L_{\text{Nb,Sn}}^{\text{BCC}} + 15.726 (T-800)^2 - 0.0394321 (T-800)^3 - 2.72345\text{E}-5 (T-800)^4$	$0 < T < 800$	
	${}^1L_{\text{Nb,Sn}}^{\text{BCC}}$	$800 < T < 6000$	
${}^0L_{\text{Nb,Sn,Ti}}^{\text{HCP}}$	${}^0L_{\text{Nb,Sn,Ti}}^{\text{BCC}}$	$0 < T < 6000$	
${}^0L_{\text{Nb,Ta}}^{\text{HCP}}$	43091	$0 < T < 6000$	6
${}^0L_{\text{Nb,Ti}}^{\text{HCP}}$	$17200 - 4 T$	$0 < T < 6000$	Figure 8
${}^0L_{\text{Nb,Ti,Zr}}^{\text{HCP}}$	114864	$0 < T < 6000$	7
${}^0L_{\text{Nb,Zr}}^{\text{HCP}}$	24411	$0 < T < 6000$	[103]
${}^0L_{\text{Sn,Ti}}^{\text{HCP}}$	$-111502.08 + 1.8068 T$	$0 < T < 6000$	[37]
${}^1L_{\text{Sn,Ti}}^{\text{HCP}}$	$43871.41 + 2.08175 T$		

⁵ To fit to the A_f temperatures of Ti-Nb-Sn alloys (Figure 12, *c* and *d*)

⁶ To fit to $A_f=285\text{K}$ at $x(\text{Nb})=0.22$, $x(\text{Ta})=0.05$ [106].

⁷ To fit to the A_f of Ti-0.2Nb-0.06Zr (Figure 12b).

${}^0L_{\text{Sn,Ti,V}}^{\text{HCP}}$	${}^0L_{\text{Sn,Ti,V}}^{\text{BCC}} + 150000$	$0 < T < 6000$	⁸
${}^0L_{\text{Ta,Ti}}^{\text{HCP}}$	$324.67 + 8.08 T$	$0 < T < 6000$	Figure 9
${}^0L_{\text{Ti,V}}^{\text{HCP}}$	$36037 - 18 T$	$0 < T < 6000$	Figure 6
${}^0L_{\text{Ti,V,Zr}}^{\text{HCP}}$	250000	$0 < T < 6000$	⁹
${}^0L_{\text{Ti,Zr}}^{\text{HCP}}$	$8316.21 - 10.87 T$	$0 < T < 6000$	Figure 11c
${}^0L_{\text{V,Zr}}^{\text{HCP}}$	$29007 - 7.2944 T$	$0 < T < 6000$	[37]
OMEGA			
$G_{\text{Al}}^{\text{OMEGA}}$	$G_{\text{Al}}^{\text{BCC}} + 1606$	$0 < T < 6000$	Table 4
$G_{\text{Fe}}^{\text{OMEGA}}$	$G_{\text{Fe}}^{\text{BCC}} + 9962$	$0 < T < 6000$	
$G_{\text{Mo}}^{\text{OMEGA}}$	$G_{\text{Mo}}^{\text{BCC}} + 13938$	$0 < T < 6000$	
$G_{\text{Nb}}^{\text{OMEGA}}$	$G_{\text{Nb}}^{\text{BCC}} + 6878$	$0 < T < 6000$	
$G_{\text{Sn}}^{\text{OMEGA}}$	$G_{\text{Sn}}^{\text{BCC}} - 74$	$0 < T < 6000$	
$G_{\text{Ta}}^{\text{OMEGA}}$	$G_{\text{Ta}}^{\text{BCC}} + 7795$	$0 < T < 6000$	
$G_{\text{Ti}}^{\text{OMEGA}}$	$-5031.472 + 3RT\ln(1 - e^{-287.50/T}) - 8.82619E-3 T^2 - 4.28689E-11 T^5 + 2.33675E-5 T^3$	$0 < T < 298.15$	Figure 5
	$G_{\text{Ti}}^{\text{HCP}} - 1401.86 + 4.439080 T + 110185.9 T^{-1}$	$298.15 < T < 6000$	
$G_{\text{V}}^{\text{OMEGA}}$	$G_{\text{V}}^{\text{BCC}} + 8965$	$0 < T < 6000$	Table 4

⁸ To fit to $T_0(\text{bcc/hcp})=0$ at $x(\text{V})=0.17$, $x(\text{Sn})=0.125$ (Table 3).

⁹ To let $T_0(\text{bcc/hcp})$ cross 450K between 13wt%V and 14wt%V, with 6wt%Zr[107] .

G_{Zr}^{OMEGA}	$-6037.34 + 3RT\ln(1 - e^{-231.46/T}) - 1.27009E-02 T^2$ $-2.34807E-12 T^5 + 7.51980E-06 T^3$	$0 < T < 298.15$	After [27]
	$G_{Zr}^{HCP} - 1050.487 + 18.783184 T - 2.6938$ $T\ln(T) + 1.5784645E-3 T^2 + 3406 T^{-1}$	$298.15 < T < 2128$	[26]
	$G_{Zr}^{HCP} - 3414.603 + 2.566675 T + 8.517345E31$ T^{-9}	$2128 < T < 4000$	
${}^0L_{Al,Ti,V}^{OMEGA}$	-533686	$0 < T < 6000$	¹⁰
${}^0L_{Fe,Ti}^{OMEGA}$	$-59000 + 30 T$	$0 < T < 6000$	Figure 10
${}^0L_{Mo,Ti}^{OMEGA}$	$25606 - 28.04 T$	$0 < T < 6000$	Figure 7
${}^0L_{Nb,Ti}^{OMEGA}$	$16369 + 5.78 T$	$0 < T < 6000$	Figure 8
${}^0L_{Nb,Zr}^{OMEGA}$	28204	$0 < T < 6000$	¹¹
${}^0L_{Sn,Ti,V}^{OMEGA}$	${}^0L_{Sn,Ti,V}^{BCC} - 510204$	$0 < T < 6000$	¹²
${}^0L_{Ti,V}^{OMEGA}$	$12000 - 10 T$	$0 < T < 6000$	Figure 6

¹⁰ To fit to $T_0(bcc/omega)=0$ at $x(V)=0.253$, $x(Al)=0.125$. (Table 3)

¹¹ To fit to the ω_s temperature of Zr-Nb alloys [108].

¹² To fit to $T_0(bcc/omega)=0$ at $x(V)=0.224$, $x(Sn)=0.125$. (Table 3)

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Table 1. A_f temperatures measured by DSC. The values with asterisks (*) are estimated due to overlapping $\beta \rightarrow \omega_{th}$ peaks.

Sample	at% V	at% Al	at% Fe	A_f (K)
C15-5	14.84	5.32	0	555
C14-6	14.34	5.55	0	548
C13-7	13.38	6.95	0	580
C12-8	11.84	8.62	0	644*
C12-9	11.83	9.48	0	621*
C12-10	11.75	10.24	0	600*
C13-5-0.5	12.68	5.48	0.495	504

Table 2. M_S and A_f measured by dilatometry

Sample	at%V	at%Al	at%Fe	M_S (K)	A_f (K)
D13-6	13.49	5.55	0	493	573
D14-6	14.02	5.53	0	463	533
D15-6	14.47	5.52	0	423	513
D13-7	13.03	7.03	0	493	568
D12-5.5-0.5	12.00	5.50	0.50	453	558
D9-7-1	9.07	6.98	1.03	483	623

Table 3. Calculated partitionless equilibrium compositions at 0K

	QE-VCA		EMTO-LSGF	
	$x_o(\beta/\alpha)$	$x_o(\beta/\omega)$	$x_o(\beta/\alpha)$	$x_o(\beta/\omega)$
$\text{Ti}_{1-x}\text{V}_x$	0.27	0.40	0.21	0.36
$\text{Ti}_{1-x}\text{Mo}_x$	0.17	0.21	0.09	0.14
$\text{Ti}_{1-x}\text{Nb}_x$	0.38	0.42	0.16	0.25
$\text{Ti}_{1-x}\text{Ta}_x$	--		0.19	0.27
$\text{Ti}_{1-x}\text{Fe}_x$			0.08	0.12
$\text{Ti}_{0.875-x}\text{V}_x\text{Al}_{0.125}$			0.19	0.23
$\text{Ti}_{0.875-x}\text{V}_x\text{Sn}_{0.125}$			0.17	0.20
$\text{Ti}_{0.875-x}\text{V}_x\text{Zr}_{0.125}$			-0.08	-0.10

Table 4. $G_m(\omega)-G_m(\beta)$ at 0K, DFT (QE-USPP) and CALPHAD values

Element	DFT (J/mol)	CALPHAD (J/mol)
V	12655	8965
Nb	19267	6878
Ta	21835	7795
Mo	39043	13938
Fe	27904	9962
Al	1606	1606
Sn	-74	-74

Table 5. Parameters for ΔG_{crit} of Ti alloys.

	G_0 (J/mol)	
Pure Ti	71	
Alloying element i	K_i (J/mol)	Composition range
Fe	16714	$0 \leq x_{Fe} \leq 0.05$
Mo	6951	$0 \leq x_{Mo} \leq 0.06$
V	2441	$0 \leq x_V \leq 0.12$
Ta	664	$0 \leq x_{Ta} \leq 0.4$
Nb	533	$0 \leq x_{Nb} \leq 0.26$
Al	472	$0 \leq x_{Al} \leq 0.25$
Zr	721 ($K^{(1)}$)	$0 \leq x_{Zr} \leq 1$
	-620 ($K^{(2)}$)

Figure captions:

Figure 1. Equivalent representation of bcc (red), orthorhombic (blue), and hcp (gray) structures using an orthorhombic cell.

Figure 2. Heat flow curves of some martensitic Ti alloys. A_f temperatures marked in red.

Figure 3. Dilatometric curves: (a) Change of length – temperature; (b) Cooling curve with a thermal arrest.

Figure 4. First-principles 0K total energies, (a) Ti-V, QE-VCA; (b) Ti-V, EMTO-LSGF; (c) Ti-V-Al, EMTO-LSGF.

Figure 5. The molar Gibbs energy of ω -Ti (from this work) together with bcc β -Ti and hcp α -Ti (by Dinsdale [26]).

Figure 6. The Ti-V system [29,39-46].

Figure 7. The Ti-Mo system [40-42, 45-53].

Figure 8. The Ti-Nb system [14, 40-41, 46, 54-62].

Figure 9. The Ti-Ta system [54, 63].

Figure 10. The Ti-Fe system [38, 64-66].

Figure 11. The Ti-Al, Ti-Sn, and Ti-Zr systems [40-41, 56, 68-70].

Figure 12. The Ti-Nb-Al/Sn/Zr systems [59, 71-76].

Figure 13. Calculated $T_o(\beta/\alpha)$ versus measured A_f of Ti-V-Al(-Fe) alloys [77-79].

Figure 14. Modeling ΔG_{crit} of Ti alloys using TiGen.

Figure 15. M_S temperatures of Ti-V-Al(-Fe) alloys, measured versus calculated.

Figure 16. Transformation enthalpy change in the Ti-Nb system [58].

Figure1

Structure	Lattice parameters	Shuffle	Molar volume (N_A =Avogadro's number)
bcc (β)	$b/a = c/a = \sqrt{2}$	$\delta/b = 0$	$V_m^{\text{bcc}} = N_A a^3/2$
orthorhombic(α'')	$\sqrt{2} < b/a < \sqrt{3}$	$0 < \delta/b < 1/6$	$V_m^{\text{ort}} = N_A abc/4$
hcp(α')	$b/a = \sqrt{3}$	$\delta/b = 1/6$	$V_m^{\text{hcp}} = N_A a^2 c(\sqrt{3}/4)$

Figure2

Figure3a

Figure3b

Figure4a

Figure4b

Figure4c

Figure5

Figure6

Figure7

Figure8

Figure9

Figure10

Figure11a

Figure11b

Figure11c

Figure12a

Figure12b

Figure12c

Figure12d

Figure13

Figure14

Figure15

Figure16