Enthalpies of Solution in Ti-X (X = Mo, Nb, V and W) Alloys from First-Principles Calculations

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The effects of solute X (Mo, Nb, V and W) on the phase stability of β -Ti alloys were studied from first-principles calculations. The first-principles calculations yielded solution enthalpies for hexagonal close-packed (hcp)-Ti₃₅X₁ and hcp-X₃₅Ti₁ and body-centered cubic (bcc)-Ti₂₆X₁ and bcc-X₂₆Ti₁ solid solution alloys. The enthalpy curves for the α (hcp)- and β (bcc)-phases of Ti-X alloys were described as a function of the X concentration by using the calculated solution enthalpies and sub-regular solution model. While the enthalpies of the α -phases increased with increasing concentrations of Mo, Nb, V and W, the enthalpies of the β -phases decreased with increasing concentrations. This is consistent with the experimental results, showing that Mo, Nb, V and W are β -stabilizers. The β -stabilizing strength of solute elements in Ti alloys is gauged using the experimental critical concentration. We found a good linear correlation between the experimental critical concentration and the theoretical metastable equilibrium concentration at which the enthalpy of the α -phase is equal to that of the β -phase. The metastable equilibrium concentration decreased with the increasing lattice stability of the bcc structure with reference to hcp structure.

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1. Introduction

Ti and Ti-based alloys have either one or a mixture of α -phase and β -phase, which are hexagonal close-packed (hcp) structures and body-centered cubic (bcc) structures, respectively. The transition temperature, that is, the temperature required for the transition from α - to β -phase, is about 1155 K for pure Ti. Some alloying elements raise the α - β -transition temperature (i.e., α -stabilizers), while others lower it (i.e., β -stabilizers). For example, Al and O are α -stabilizers, while Mo and V are β -stabilizers. It is well known that the elastic and other mechanical properties of Ti-based alloys are determined by the properties of the individual phases in the alloys and their phase fractions. Therefore, α -, $\alpha + \beta$ - and β -Ti alloys exhibiting a wide variety of mechanical properties have been developed by controlling the constituent phase volume fractions, alloy compositions and microstructures. β -Ti alloys have attracted considerable attention in orthopedic implant applications because of the low elastic moduli, good biocompatibility and bio-corrosion resistance of the alloys.¹⁻⁵⁾ Extensive investigations have been carried out to develop β -Ti alloys containing Nb, V, Mo and Ta transition elements, with a low Young's modulus and high strength, for the replacement of human bone.³⁻⁵⁾ It has also been reported that shape-memory effect and superelasticity can be achieved using β -Ti alloys.⁶⁻⁸⁾

The theoretical approach to materials design of β -Ti alloys was pioneered by Morinaga *et al.* based on the molecular orbital calculation of electronic structures (the so-called discrete variational X cluster method, DV-X α method).^{9,10)} Following that, Kuroda *et al.* developed new β -Ti alloys with low elastic moduli for bio-implant applications on the basis of the *d*-electron alloy design method by using the bond order (B_o) and the metal *d*-orbital energy level (M_d) calculated from DV-X α .³⁾ Unique Ti-based "gum metal" alloys with low

elastic moduli and large elastic strains have been developed, and their chemical compositions have been characterized based on three parameters: an average valence electron number (e/a) of 4.24, a B_o of 2.87 and a M_d of 2.45.¹¹⁾ Although these results demonstrate that DV-X α is very powerful for designing Ti-based alloys, it does not provide important quantitative information, such as the critical concentration (the minimum alloy content required to stabilize the β -phase) and the elastic constants.

During the last decade, the quality of first-principles calculations of electronic and structural properties has improved considerably. The total energy of a given crystal structure can be accurately calculated, and the lattice stability of the crystal structure and the formation enthalpy of compounds can be evaluated at 0 K by using only the atomic number and atomic positions as input.¹²⁻²⁴⁾ Changes in the lattice constants and elastic constants of solid solution alloys have been also studied using first-principles calculations.²⁵⁻³⁰⁾ For example, Ikehata *et al.* calculated the elastic constants of β -type Ti-X (X = V, Nb, Ta, Mo and W) alloys from first principles and found that $c_{11}-c_{12}$ becomes nearly zero with an e/a of around 4.20-4.24.²⁶⁾ Wu *et al.* calculated the lattice constants, elastic properties and cohesive energies of β -type Ti-Ta alloys.²⁹⁾ Raabe *et al.* calculated the formation enthalpy of Ti-Mo and Ti-Nb alloys for a total of 48 bcc and 28 hcp configurations and found that the β -phase is energetically more favored than an α -phase for high concentrations of Mo and Nb (>10 and >20 at%, respectively).¹²⁾

The objective of this work is to understand and predict how alloy composition affects the stability of the β -phase. Therefore, the effects of the amount of solute X (X = Mo, Nb, V and W) on the stability between the α - and β -phases were studied from first-principles calculations. Mo, Nb, V and W were chosen because they are the typically used β -stabilizers. The first-principles calculations yielded the solution enthalpies for hcp-Ti₃₅X₁, hcp-X₃₅Ti₁, bcc-Ti₂₆X₁ and bcc-X₂₆Ti₁ solid solution alloys. The enthalpy curves

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Fig. 1 Schematics of supercells modeling (a) hcp-Ti₃₅X₁ or hcp-X₃₅Ti₁ and (b) bcc-Ti₂₆X₁ or bcc-X₂₆Ti₁ solid solutions. Gray spheres represent solute atoms, and white spheres represent solvent atoms. The solid lines indicate the boundary of the supercells.

for the α - and β -phases of the Ti-X alloys were described by using the solution enthalpies and sub-regular solution model.

2. Calculation Procedures

First-principles calculations were performed using the Cambridge Serial Total-Energy Package (CASTEP).³¹⁾ CASTEP is an *ab initio* pseudopotential method code for solving the electronic ground state of periodic systems in which wave functions are expanded in a plane-wave basis that is set using a technique based on the density functional theory (DFT).^{32,33)} The electronic exchange-correlation energy used in the DFT was given by the generalized gradient approximation (GGA) proposed by Perdew *et al.* (PW91).³⁴⁾ Ultra-soft pseudopotentials (USP)³⁵⁾ were used for all the elements. A cut-off energy of 5.61×10^{-17} J (350 eV) was used for the plane-wave basis in all the calculations. A Gaussian smearing³⁶⁾ of 1.60×10^{-20} J (0.1 eV) was applied to the occupation numbers.

The hcp-Ti₃₅X₁, hcp-X₃₅Ti₁, bcc-Ti₂₆X₁ and bcc-X₂₆Ti₁ solid solutions were modeled using supercells, which are periodic in all three directions, containing 36 and 27 atoms (Fig. 1). The hcp-Ti₃₅X₁ and hcp-X₃₅Ti₁ supercells were hexagonal cells with $3 \times 3 \times 2$ primitive unit cells. The bcc-Ti₂₆X₁ and bcc-X₂₆Ti₁ supercells are rhombohedral cells consisting of $3 \times 3 \times 3$ primitive unit cells. The supercells contain only one substitutional solute atom per supercell and correspond to 3.70 and 2.78 at% solid solutions. The energy integration over a Brillouin zone was made using k -points in accordance with the Monkhorst-Pack grid³⁷⁾ with sets of $6 \times 6 \times 5$ k -points for the hcp-Ti₃₅X₁ and hcp-X₃₅Ti₁ supercells and $6 \times 6 \times 6$ k -points for the bcc-Ti₂₆X₁ and bcc-X₂₆Ti₁ supercells.

Let $\Delta H_{X(Ti)}^\Phi$ be the solution enthalpy of a substitutional solute, X, in a matrix of Ti for the solution phase, Φ (Φ = hcp or bcc). Similarly, $\Delta H_{Ti(X)}^\Phi$ is the solution enthalpy of the solute Ti in a matrix of X. The enthalpy of solution is the change in energy produced when replacing a single solvent atom by a solute atom, and it is expressed in units of energy per solute atom. In the supercell approach, $\Delta H_{X(Ti)}^\Phi$ and $\Delta H_{Ti(X)}^\Phi$ are derived from the following relations:^{19,21)}

$$\Delta H_{X(Ti)}^\Phi = E^\Phi[Ti_{n-1}X_1] - (n-1)\mu_{Ti}^\Phi - \mu_X^\Phi \quad \text{and} \quad (1)$$

$$\Delta H_{Ti(X)}^\Phi = E^\Phi[X_{n-1}Ti_1] - (n-1)\mu_X^\Phi - \mu_{Ti}^\Phi, \quad (2)$$

where $E^\Phi[Ti_{n-1}X_1]$ and $E^\Phi[X_{n-1}Ti_1]$ are the total energies of the supercells with $n-1$ solvent atoms and 1 solute atom. μ_{Ti}^Φ and μ_X^Φ are the corresponding chemical potentials (total energies per atom) of pure Ti and X.

Full structural relaxation of the atomic configurations and lattice constants were taken into account for the calculations of $E^\Phi[Ti_{n-1}X_1]$ and $E^\Phi[X_{n-1}Ti_1]$ because introducing the substitutional solute atom leads to a local lattice distortion and to changes in the cell volume. Stable atomic configurations were obtained through relaxation based on the Hellmann-Feynman forces calculated from first principles. The lattice constants at zero pressure were also optimized using a Broyden-Fletcher-Goldfarb-Shanno (BFGS)³⁸⁾ minimization algorithm in conjunction with the stress calculated from first principles. The convergence parameters were as follows: the total energy tolerance was 1.6×10^{-24} J/atom, the maximum force tolerance was 4.8×10^{-12} N, the maximal stress component was 0.05 GPa, and the maximal displacement was 1×10^{-4} nm.

3. Results and Discussion

3.1 Lattice stability

We briefly discuss lattice stability (i.e., promotion energy), which is the difference in the structural enthalpies of the pure elements at 0 K, before discussing the solution enthalpies of the Ti-X solid solution alloys. It is obvious that the relative enthalpies of a pure element in various competing crystal structures, so-called lattice stabilities, are the foundation for understanding the phase stability of the alloys. The total energies were calculated for each of the face-centered cubic (fcc), bcc and hcp structures of Ti, Mo, Nb, V and W. The lattice stability of the bcc structure with reference to hcp structure, ($\Delta H_X^{\text{hcp-bcc}} = \mu_X^{\text{hcp}} - \mu_X^{\text{bcc}}$), and that of the bcc structure with reference to fcc structure, ($\Delta H_X^{\text{fcc-bcc}} = \mu_X^{\text{fcc}} - \mu_X^{\text{bcc}}$), is given in Table 1. Positive values of $\Delta H_X^{\text{hcp-bcc}}$ and $\Delta H_X^{\text{fcc-bcc}}$ mean that the bcc structure is more energetically stable than hcp and fcc structures, respectively ($\Delta H_X^{\text{hcp-bcc}} = -(\mu_X^{\text{bcc}} - \mu_X^{\text{hcp}})$ and $\Delta H_X^{\text{fcc-bcc}} = -(\mu_X^{\text{bcc}} - \mu_X^{\text{fcc}})$). The ground state structures for these elements are also shown in Table 1. In all cases, the observed ground state structure was most energetically favored.

Table 1 also includes the previous first-principles calculation results reported by the following authors: (1) Berne *et al.* using the first-principles full-potential linear muffin-tin orbital (FPLMTO) method within the local-density approximation (LDA),¹³⁾ (2) Wang *et al.* using the projector augmented-wave (PAW) method within the GGA,¹⁴⁾ and

Table 1 The lattice stability of the bcc structure with reference to hcp structure, $\Delta H_X^{\text{hcp-bcc}}$ and that of the bcc structure with reference to fcc structure, $\Delta H_X^{\text{fcc-bcc}}$.

Element	$\Delta H_X^{\text{hcp-bcc}}$ (kJ/mol)	$\Delta H_X^{\text{fcc-bcc}}$ (kJ/mol)	Ground state
Ti	-9.5 ^{*1}	-4.3 ^{*1}	hcp
	-10.3 ^{*3}	-4.8 ^{*3}	
		-4.0 ^{*4}	
	-4.6 ^{*5}	1.4 ^{*5}	
Mo	44.9 ^{*1}	40.1 ^{*1}	bcc
	49 ^{*2}	43 ^{*2}	
	39.9 ^{*3}	38.7 ^{*3}	
		41.3 ^{*4}	
Nb	11.6 ^{*5}	15.4 ^{*5}	bcc
	28.2 ^{*1}	32.0 ^{*1}	
	41 ^{*2}	39 ^{*2}	
	28.1 ^{*3}	31.2 ^{*3}	
V		31.5 ^{*4}	bcc
	10.7 ^{*5}	14.0 ^{*5}	
	30.9 ^{*1}	24.0 ^{*1}	
	24.5 ^{*3}	24.0 ^{*3}	
W		24.9 ^{*4}	bcc
	4.7 ^{*5}	8.0 ^{*5}	
	60.8 ^{*1}	49.1 ^{*1}	
	56 ^{*2}	48 ^{*2}	
W	43.2 ^{*3}	45.0 ^{*3}	bcc
		47.3 ^{*4}	
	14.8 ^{*5}	19.5 ^{*5}	

^{*1}Present work (USP-GGA)

^{*2}FPLMTO-LDA by Berne *et al.*¹³⁾

^{*3}PAW-GGA by Wang *et al.*¹⁴⁾

^{*4}PAW-GGA by Sluiter¹⁵⁾

^{*5}SGTE-CALPHAD at 298.15 K⁴⁵⁾

(3) Sluiter using the PAW-GGA method.¹⁵⁾ The first-principles results in our work were consistent with those in the previous works: the root mean square (RMS) of the differences between the results in this work and those in previous works was 5.6 kJ/mol.

The calculation of phase diagrams (CALPHAD) method is a semi-empirical method used for modeling thermodynamic properties and calculating equilibrium phase diagrams.^{39–42)} The CALPHAD method was pioneered by Kaufman, who systematically introduced the foundational concept of lattice stability.^{43,44)} It is possible to calculate a phase diagram by minimizing the total Gibbs energy when the exact molar Gibbs free energies of all the phases of a given system are known. The Gibbs free energies of the different phases are given by theoretical thermodynamic models. The parameters (e.g., the lattice stabilities and interaction parameters) of the models are then determined by refining a critical set of experimental data, such as calorimetric and phase-equilibrium measurements, by using a least-squares method and are subsequently used for calculating the phase diagrams. The fitting of the parameters is often called the assessment of a system.

The lattice stabilities for pure elements assessed by Scientific Group Thermodata Europe (SGTE) were previously published for various phase structures and have been

Table 2 Solution enthalpies for Ti–Mo, Ti–Nb, Ti–V and Ti–W solid solution alloys.

Alloy	$\Delta H_{X(\text{Ti})}^{\text{hcp}}$ (kJ/mol)	$\Delta H_{\text{Ti}(X)}^{\text{hcp}}$ (kJ/mol)	$\Delta H_{X(\text{Ti})}^{\text{bcc}}$ (kJ/mol)	$\Delta H_{\text{Ti}(X)}^{\text{bcc}}$ (kJ/mol)
Ti–Mo	8.2 ^{*1}	-11.9 ^{*1}	-83.0 ^{*1}	-91.6 ^{*1}
	7.2 ^{*2}		-69.0 ^{*2}	
	22.8–0.0067 ^{*4,*5}	22.8–0.0067 ^{*4,*5}	4.0 ^{*4}	0.0 ^{*4}
Ti–Nb	5.8 ^{*1}	0.2 ^{*1}	-11.5 ^{*1}	-1.6 ^{*1}
	13.2 ^{*4}	13.2 ^{*4}	8.9 ^{*4}	8.9 ^{*4}
Ti–V	16.1 ^{*1}	17.4 ^{*1}	-11.6 ^{*1}	14.4 ^{*1}
	18.3 ^{*3}			
	23.2 ^{*4}	23.2 ^{*4}	15.5 ^{*4}	12.5 ^{*4}
Ti–W	3.1 ^{*1}	-20.2 ^{*1}	-74.5 ^{*1}	-94.7 ^{*1}

^{*1}Present work with 36-atom cell or 27-atom cell

^{*2}Present work with 54-atom cell

^{*3}USP-GGA by Hennig *et al.*: value converted from $\Delta H_{X(\text{Ti})}^{\phi*}$ ²⁰⁾

^{*4}CALPHAD data converted from $L_{\text{Ti,X}}^{\phi}$ ^{46,47)}

^{*5}Temperature (T in Kelvin) dependence is taken into account.

widely used as a basis for thermodynamic modeling of multi-component systems.⁴⁵⁾ However, it was found that the SGTE-CALPHAD data were not very consistent with the first-principles results for most of the transition metals, and this has been an unresolved issue in computational thermodynamics during the last decade.^{14–17)} The primary reason for the discrepancy seems to be the structural instability of transition metals in some crystal structures.^{14–17)} Another possible reason is the fact that the first-principles data were obtained at 0 K while the SGTE-CALPHAD data is restricted at low temperatures to 298.15 K. Table 1 also includes the SGTE-CALPHAD data for lattice stabilities at 298.15 K.⁴⁵⁾ We also found inconsistencies between the first-principles results and the SGTE-CALPHAD data: the RMS of the differences between the results in this work and the SGTE-CALPHAD data is 25.4 kJ/mol. Although this difference is substantial, it is not so surprising given the previous comparison results between SGTE-CALPHAD data and first-principles results.^{14,15)}

3.2 Solution enthalpy

The solution enthalpies of the hcp-Ti₃₅X₁, hcp-X₃₅Ti₁, bcc-Ti₂₆X₁ and bcc-X₂₆Ti₁ solid solution alloys are listed in Table 2. The solution enthalpies of the hcp-Ti₅₃Mo₁ and bcc-Ti₅₃Mo₁ were also calculated from first principles, and the results are compared in Table 2. We see that for the Ti–Mo alloy, the solution enthalpy reasonably converged with the calculations using 36- or 27-atom cells.

Hennig *et al.* reported a solution enthalpy for V in hcp-Ti of 49.2 kJ/mol by first-principles calculations using the USP-GGA method, and this value is inconsistent with the first-principles result in this work, i.e., 16.1 kJ/mol.²⁰⁾ This discrepancy is due to the difference in the definition of solution enthalpy. To the best of our knowledge, Chetty *et al.* pioneered the first-principles calculations of solution enthalpy and estimated it as follows:¹⁹⁾

$$\Delta H_{X(\text{Ti})}^{\phi*} = E^{\phi}[\text{Ti}_{n-1}\text{X}_1] - (n-1)\mu_{\text{Ti}}^{\phi} - \mu_{\text{X}}^{\text{GS}}, \quad (3)$$

where $\mu_{\text{X}}^{\text{GS}}$ is the chemical potential of X in its ground state (GS). In other words, the lattice stability of the solute element

was not taken into account in the definition by Chetty *et al.*¹⁹⁾ Generally, many researchers including Hennig *et al.* have used such a definition.^{18–21)} One can obtain the relationship between $\Delta H_{X(Ti)}^\phi$ and $\Delta H_{X(Ti)}^{\phi*}$ easily as follows:

$$\begin{aligned}\Delta H_{X(Ti)}^\phi &= \Delta H_{X(Ti)}^{\phi*} - (\mu_X^\phi - \mu_X^{GS}) \\ &= \Delta H_{X(Ti)}^{\phi*} - \Delta H_X^{\phi-GS}.\end{aligned}\quad (4)$$

The solution enthalpy, $\Delta H_{V(Ti)}^{\phi*}$, of 49.2 kJ/mol calculated by Hennig *et al.*²⁰⁾ is converted to a $\Delta H_{V(Ti)}^\phi$ of 18.3 kJ/mol by using the lattice stability of V, $\Delta H_V^{hcp-bcc} = 30.9$ kJ/mol, as shown in Table 1. The converted value for the solution enthalpy, 18.3 kJ/mol, is consistent with the result, 16.1 kJ/mol, in this work.

The solution enthalpy can be converted from the interaction parameter in the semi-empirical CALPHAD method.^{21–23)} In the CALPHAD method, the mixing enthalpy, $\Delta H_{mix}^\phi(x)$, i.e., the excess enthalpy of mixing, is fitted to a polynomial (Redlich-Kister formula) of composition x :

$$\Delta H_{mix}^\phi(x) = x(1-x) \sum_{i=0}^m {}^iL_{Ti,X}^\phi (1-2x)^i, \quad (5)$$

where ${}^iL_{Ti,X}^\phi$ is the i th interaction parameter between the elements Ti and X. The accuracy of the mixing enthalpy in the CALPHAD method depends on the order of the polynomial fit. The third-order polynomial fit ($m=1$), with ${}^0L^\phi$ and ${}^1L^\phi$, is conventionally used for various systems.^{21–23,46,47)} The second-order polynomial fit ($m=0$), with only ${}^0L^\phi$, corresponds to the regular solution model, which is a very simple and inaccurate formula.⁴⁸⁾

The solution enthalpy, $\Delta H_{X(Ti)}^\phi$, expressed in units of energy per solute atom, is simply the dilute limit of the mixing enthalpy, ΔH_{mix}^ϕ , expressed in units of energy per atom. Thus, the solution enthalpy is easily obtained from the mixing enthalpy as follows:

$$\Delta H_{X(Ti)}^\phi = \left(\frac{\partial \Delta H_{mix}^\phi}{\partial x} \right)_{x=0}. \quad (6)$$

This equation gives²²⁾

$$\Delta H_{X(Ti)}^\phi = {}^0L_{Ti,X}^\phi + \sum_{i=1}^m {}^iL_{Ti,X}^\phi. \quad (7)$$

Similar to the $\Delta H_{X(Ti)}^\phi$ calculation, one can obtain $\Delta H_{Ti(X)}^\phi$ as follows:²²⁾

$$\Delta H_{Ti(X)}^\phi = {}^0L_{Ti,X}^\phi - \sum_{i=1}^m {}^iL_{Ti,X}^\phi. \quad (8)$$

Conversely, the interaction parameters can be estimated from the solution enthalpies by using the third-order polynomial fit ($m=1$) as follows:

$${}^0L_{Ti,X}^\phi = (\Delta H_{X(Ti)}^\phi + \Delta H_{Ti(X)}^\phi)/2 \quad \text{and} \quad (9)$$

$${}^1L_{Ti,X}^\phi = (\Delta H_{X(Ti)}^\phi - \Delta H_{Ti(X)}^\phi)/2. \quad (10)$$

The interaction parameters reported in the CALPHAD study are shown in Table 3,^{46,47)} with the first-principles results converted using eqs. (9) and (10). The solution enthalpies converted from the interaction parameters in the CALPHAD study are also compared with the first-principles results in Table 2. The differences between the semi-empirical CALPHAD and first-principles results are so great that there is no consistency even among the signs for

Table 3 Interaction parameters reported in CALPHAD study,^{46,47)} with first-principles results converted from solution enthalpies.

Alloy	${}^0L_{Ti,X}^{hcp}$ (kJ/mol)	${}^1L_{Ti,X}^{hcp}$ (kJ/mol)	${}^0L_{Ti,X}^{bcc}$ (kJ/mol)	${}^1L_{Ti,X}^{bcc}$ (kJ/mol)	Method
Ti-Mo	22.8–0.006 T^*	—	2.0	2.0	CALPHAD ⁴⁶⁾
Ti-Nb	13.2	—	8.9	—	CALPHAD ⁴⁷⁾
Ti-V	23.2	—	14.0	1.5	CALPHAD ⁴⁷⁾
Ti-Mo	–1.8	10.1	–87.3	4.3	This work
Ti-Nb	3.0	2.8	–6.6	–4.9	This work
Ti-V	16.7	–0.6	1.4	–13.0	This work
Ti-W	–8.5	11.7	–84.6	10.1	This work

*Temperature (T in Kelvin) dependence is taken into account.

$\Delta H_{Ti(Mo)}^{hcp}$, $\Delta H_{Mo(Ti)}^{bcc}$, $\Delta H_{Ti(Mo)}^{bcc}$, $\Delta H_{Nb(Ti)}^{bcc}$, $\Delta H_{Ti(Nb)}^{bcc}$ and $\Delta H_{V(Ti)}^{bcc}$. The RMS of the differences between the values of solution enthalpies in this work and those in the CALPHAD study was 39.7 kJ/mol.

One possible reason for such inconsistency is the insufficient assessment of the systems in the CALPHAD study; that is, the interaction parameters of the CALPHAD study for hcp Ti-Mo, hcp Ti-Nb, hcp Ti-V and bcc Ti-Nb have lower reliability, corresponding to the regular solution model, because of the second-order polynomial fit ($m=0$).^{46,47)}

The temperature dependence was not taken into account for the CALPHAD data of Table 2 expect for $\Delta H_{Mo(Ti)}^{hcp}$ and $\Delta H_{Ti(Mo)}^{hcp}$; for only ${}^0L_{Ti,Mo}^{hcp}$ CALPHAD study took into account the temperature dependence.^{46,47)} However, the interaction parameters in the CALPHAD study have been usually assessed for the use at more than 298.15 K because the SGTE-CALPHAD lattice stability is restricted at low temperatures to 298.15 K. The fact that the first-principles data were obtained at 0 K while the CALPHAD data is for the exclusive use at higher than 298.15 K is also a possible reason of the inconsistencies in the solution enthalpies.

The inconsistency between the first-principles results and the SGTE-CALPHAD data for the lattice stability, as discussed in the previous section, is also due to the inconsistencies in the solution enthalpies. The assessment of the interaction parameters for the binary system used in the CALPHAD method was based on the lattice stability from the SGTE database, which is inconsistent with first-principles results for most of the transition metals, as shown in Table 1, and this leads to the compound increase in the magnitude of the inconsistency.

Moreover, the fundamental disadvantages of using the semi-empirical CALPHAD method, in thermodynamic fitting, have recently come to light.^{22,23)} Sluiter and Kawazoe calculated the solution enthalpies of Al alloys from first principles and compared the results with those assessed by several other researchers using the CALPHAD method.^{22,23)} Sluiter and Kawazoe found not only a discrepancy between the CALPHAD data and the first-principles results of solution enthalpies but also contradictions among the results obtained by various researchers using the CALPHAD method.^{22,23)} Sluiter and Kawazoe argued that such contradictory results indicate that CALPHAD is a rather unreliable method for calculating solution enthalpies.^{22,23)} The accuracy of the

Fig. 2 Enthalpies of hcp (α) and bcc (β) phases for (a) Ti-Mo, (b) Ti-Nb, (c) Ti-V and (d) Ti-W alloys, as a function of alloy composition. The arrow shows the metastable equilibrium concentration, $^{\circ}c_0$, at which the enthalpy of the hcp phase is equal to that of bcc phase. The first-principles calculated formation enthalpies for hcp-Ti₃₅X₁, hcp-X₃₅Ti₁, bcc-Ti₂₆X₁ and bcc-X₂₆Ti₁ are also shown with the formation enthalpies calculated by Raabe *et al.* for 48 bcc and 28 hcp configurations in total.¹²⁾

CALPHAD data depends on the skill of the researcher because CALPHAD data are semi-empirical values obtained from “fitting” to limited experimental data. The authors expect to efficiently use the present first-principles results for Ti-X alloys as references to assess the CALPHAD method.

3.3 Mixing enthalpy

From the definition of mixing enthalpy $\Delta H_{\text{mix}}^{\Phi}$, the enthalpy of a binary solid solution alloy with the composition Ti_{1-x}X_x and a crystal structure Φ is given by

$$H^{\Phi}(x) = H_{\text{Ti}}^{\Phi}(1-x) + H_{\text{X}}^{\Phi}x + \Delta H_{\text{mix}}^{\Phi}, \quad (11)$$

where H_{Ti}^{Φ} and H_{X}^{Φ} are the enthalpies of the pure elements Ti and X with crystal structure Φ . The enthalpies of the pure elements with stable structures in the ground state were chosen as the references for the system: $H_{\text{Ti}}^{\text{hcp}} = 0$ and $H_{\text{X}}^{\text{bcc}} = 0$ (X = Mo, Nb, V and W). On the basis of the sub-regular solution model, Leach presented the relationship between the mixing enthalpy and solution enthalpies as follows:⁴⁸⁾

$$\Delta H_{\text{mix}}^{\Phi}(x) = \Delta H_{\text{X(Ti)}}^{\Phi}x(1-x)^2 + \Delta H_{\text{Ti(X)}}^{\Phi}x^2(1-x). \quad (12)$$

This equation can also be derived by substituting eqs. (9) and (10) into eq. (5). It is noted that eq. (12) corresponds to the third-order polynomial fit ($m = 1$) of the Redlich-Kister formula.

Figure 2 shows the enthalpy curves for the hcp (α) and bcc (β) phases of Ti-X alloys as a function of alloy composition, calculated based on first-principles and sub-regular solution model. While the enthalpies of the hcp phases increase with the increasing concentration of Mo, Nb, V and W, the enthalpies of the bcc phases decrease with increasing concentration. This is consistent with the experimental results, showing that Mo, Nb, V and W act as β -stabilizers. In Fig. 2, the intersection point of the hcp and bcc enthalpy curves represents the metastable equilibrium concentration $^{\circ}c_0$ at 0 K. The bcc phase is more favored in terms of energy than the hcp phase when the concentration of solute X is more than $^{\circ}c_0$. The values of $^{\circ}c_0$ were 6.8, 19.1, 15.6 and 6.7 at% for Mo, Nb, V and W, respectively. These theoretical values of $^{\circ}c_0$ are very important for understanding and predicting how the alloy composition affects the stability of the β -phase. We will discuss the relationship between the theoretical metastable equilibrium and experimental critical concentrations in the following section.

The supercells of hcp-Ti₃₅X₁, hcp-X₃₅Ti₁, bcc-Ti₂₆X₁ and bcc-X₂₆Ti₁ are assumed to be dilute compounds. The formation enthalpy $H_f^{\Phi}(x)$ of an intermetallic compound with concentration x , expressed in units of energy per atom, can be obtained using the supercell approach directly, without the sub-regular solution model, as follows:^{12,21)}

$$H_f^\Phi(x) = \frac{E^\Phi[\text{Ti}_{1-x}\text{X}_x]}{n} - (1-x)\mu_{\text{Ti}}^{\text{GS}} - x\mu_{\text{X}}^{\text{GS}}, \quad (13)$$

where $E^\Phi[\text{Ti}_{1-x}\text{X}_x]$ is the fully relaxed total energy of the supercell with n atoms of $\text{Ti}_{1-x}\text{X}_x$ in the Φ structure. When the concentration of the $\text{Ti}_{1-x}\text{X}_x$ compound is sufficiently dilute, the formation enthalpy of the compound is approximately equal to the enthalpy of the random solid solution calculated by sub-regular solution model. In a non-interacting system (ideal solution), the formation enthalpy of the compound is equal to the enthalpy of the random solid solution because the local atomic configuration of the solute atoms has no effect on the enthalpy of the alloys. The formation enthalpies of hcp- $\text{Ti}_{135}\text{X}_1$, hcp- X_{35}Ti_1 , bcc- Ti_{26}X_1 and bcc- X_{26}Ti_1 calculated from first principles are also shown in Fig. 2. Raabe *et al.* calculated the formation enthalpies of Ti-Mo and Ti-Nb alloys for a total of 48 bcc and 28 hcp configurations.¹²⁾ The first-principles results of the formation enthalpies calculated by Raabe *et al.* are also shown in Figs. 2(a) and 2(b). The calculated formation enthalpies from first principles are consistent with the enthalpy curves for the solid solutions, with the exception of the Ti-rich Ti-Mo alloys. This indicates that the enthalpy of solid solution for the Ti-alloys depends almost exclusively on concentration and not on the local atomic configuration. However, the difference between the formation enthalpies and the enthalpy of solid solution in the Ti-rich Ti-Mo alloys can be attributed to the local atomic configurations.

3.4 Metastable equilibrium temperature

We need to calculate the contribution of entropy effects to the free energy in order to determine the thermodynamic properties of alloys at finite temperatures. The entropy effects for solids can be decomposed into two, namely, the contribution from the configuration and that from the lattice thermal vibration. All the first-principles results in this work did not take into account the entropy effects and the corresponding change in enthalpies, or free energies, at 0 K. The Gibbs free energy $G^\Phi(T, x)$ of a solid solution alloy with composition x at the temperature T , expressed in units of energy per atom, is calculated using the following equation:

$$G^\Phi(T, x) = G_{\text{Ti}}^\Phi(1-x) + G_{\text{X}}^\Phi x + \Delta G_{\text{mix}}^\Phi - S_{\text{conf}} T, \quad (14)$$

where G_{Ti}^Φ and G_{X}^Φ are Gibbs free energies of pure Ti and X with Φ crystal structures; S_{conf} is the entropy with regard to the local atomic configuration, i.e., the so-called mixing entropy; and $\Delta G_{\text{mix}}^\Phi$ is the excess Gibbs free energy of mixing. The mixing entropy can be calculated from the ideal mixing approximation, which becomes exact for solid solutions, where the enthalpy depends only on the concentration and not on the local atomic configuration. The ideal mixing entropy S_{conf} is given by

$$S_{\text{conf}}(x) = R[x \ln(x) + (1-x) \ln(1-x)], \quad (15)$$

where R is the gas constant. Similar to the mixing enthalpy given by eq. (12), $\Delta G_{\text{mix}}^\Phi$ is given by

$$\Delta G_{\text{mix}}^\Phi(T, x) = \Delta G_{\text{X(Ti)}}^\Phi x(1-x)^2 + \Delta G_{\text{Ti(X)}}^\Phi x^2(1-x), \quad (16)$$

where $\Delta G_{\text{X(Ti)}}^\Phi$ and $\Delta G_{\text{Ti(X)}}^\Phi$ are the Gibbs free energies of solution for X and Ti. Contributions from vibrations to the

Fig. 3 Schematics of (a) binary phase diagram and (b) Gibbs free energy of α - and β -phases, as a function of solute concentration in Ti-X alloy. The M_s line represents the martensite start temperature. c_{cr} is the critical concentration required to completely retain β -phase upon quenching from β -phase region. T_0 line represents the metastable equilibrium temperature between the α - and β -phases, at which $G^{\text{hcp}} = G^{\text{bcc}}$. c_0 and 0c_0 are metastable equilibrium concentrations between the α - and β -phases at room temperature (298 K) and 0 K, respectively.

entropy are included in G_{Ti}^Φ , G_{X}^Φ , $\Delta G_{\text{X(Ti)}}^\Phi$ and $\Delta G_{\text{Ti(X)}}^\Phi$. Recently, contributions from vibrations have been calculated using the phonon approach based on first-principles calculations not only for pure metals but also for solid solution alloys.²⁴⁾ In this study, the entropy effects were not taken into account because vast computational resources are required in order to calculate the contributions from vibrations. We defer the discussion on calculations taking into account these contributions in Ti-based alloys to a future paper. However, the enthalpies calculated without the entropy effects at 0 K corresponded well with the experimental critical concentration, as will be shown below.

Figure 3 shows the schematics of a binary phase diagram for a Ti-X alloy,^{49,50)} and the Gibbs free energy of the α - and β -phases at room temperature (298 K), as a function of alloy composition. The α -transus is the boundary between the single-phase α -region and the $\alpha + \beta$ -region, and the β -transus is the boundary between the β -region and the $\alpha + \beta$ -region, as shown in Fig. 3(a). The α -transus and β -transus can be obtained theoretically by applying the rule of common tangents, for example, c_α and c_β , at room temperature, as shown in Fig. 3(b). The alloys to the left of c_α are classified as α -alloys and those to the right of c_β are classified as stable β -alloys, as shown in Fig. 3(a).

It is to be noted that stable β -alloys are different from metastable β -alloys. β -alloys, including stable and metastable β -alloys, are defined as alloys that retain 100% β -phase upon quenching from temperature above the β -transus.^{49,50)} These alloys contain enough β -stabilizing elements to prevent cooling through the martensite start line (M_s), consequently preventing the formation of martensite, such as hexagonal martensite (α'), at room temperature. The critical concentration c_{cr} is the minimum possible concentration of β -stabilizer at which a binary Ti alloy quenched from the single-phase β -region in water no longer forms martensite. The β -stabilizing strength of an alloying element in binary Ti alloys is defined by the critical concentration. The alloys that lie between c_{cr} and c_β are still within the $\alpha + \beta$ two-phase region, as shown in Fig. 3(a). Thus, although one can quench to retain 100% β -phase in this region, such β -alloys are metastable and will precipitate a second phase, such as an α -phase, during aging below the β -transus temperature.

The critical concentration has been used to gauge the β -stabilizing strength in ternary, quaternary and higher order alloys. In multi-component Ti alloys, the coefficient of β -stabilization, K_β , is determined by⁵⁰⁾

$$K_\beta = \sum_{i=1}^n \frac{x^i}{c_{cr}^i}, \quad (17)$$

where x^i is the concentration of the i th β -stabilizing element in the Ti alloy and c_{cr}^i is its critical concentration. The Mo equivalency $[Mo]_{eq}$ is more commonly used to indicate the β -stability of multi-component Ti alloys and is defined by the following equation:^{49,51)}

$$[Mo]_{eq} = c_{cr}^{Mo} K_\beta, \quad (18)$$

where c_{cr}^{Mo} is the critical concentration of Mo. Although the Mo equivalency is an arbitrary parameter, Ti alloys can be arranged in a sequence in accordance with the stability of the β -phase by using the Mo equivalency, which is very useful and convenient for researchers developing new Ti-based alloys.^{49,52)} Thus, the critical concentration is of significant scientific and engineering value as a basis for determining Mo equivalency.

Several reviews have already dealt with the thermodynamics of martensitic transformation mainly in Fe alloys.^{53,54)} Kaufman especially has discussed the martensitic transformation of Ti alloys and has estimated its driving force.⁴³⁾ Martensitic transformation is defined as a diffusionless transformation. In view of the diffusionless nature of martensitic reactions, martensitic transformation must occur without a change in the alloy composition. This leads to the concept of so-called “metastable equilibrium temperature” (T_0) at which the Gibbs free energies of the parent (β) phase and product (α) phase at the same composition are equal.⁵⁵⁾ The c_0 is the metastable equilibrium concentration at room temperature, where the Gibbs free energy of the α -phase is equal to that of the β -phase, as shown in Fig. 3(b). The 0c_0 is the metastable equilibrium concentration at 0 K and is determined using the first-principles calculations as described in the previous section.

The driving force for martensitic transformation is defined as the difference in the free energies of the α - and β -phases and is expressed as $\Delta G^{\beta-\alpha} = G^\beta - G^\alpha$. The value of $\Delta G^{\beta-\alpha}$

Fig. 4 Comparison of theoretical values for metastable equilibrium concentration at 0 K from the first-principles data with experimental values for critical concentration.^{50,51)} The dashed line represents the linear least-squares fitting, $c_{cr} = 0.98 {}^0c_0$.

is positive when the martensite is more stable than the β -phase and is otherwise negative, as shown in Fig. 3(b). Because of the energy-barrier condition, the martensitic reaction does not necessarily start when the martensite becomes more stable than the β -phase.⁵⁵⁾ As a result, M_s lies below T_0 while quenching from above the β -transus, and c_{cr} is to the left of c_0 , as shown in Fig. 3(a). In case of Fe alloys, the critical driving force for the martensitic transformation at M_s is about 0.9–1.3 kJ/mol, and the supercooling between T_0 and M_s is about 200 K.⁵³⁾ However, the critical driving force and the supercooling of nonferrous alloys is much lower than those of Fe alloys.⁵³⁾ In Ti-based alloys, the supercooling between T_0 and M_s is about 50 K, and the critical driving force at M_s is about 0.2 kJ/mol.^{43,56)} Thus, the difference between c_{cr} and c_0 is negligible ($c_{cr} \approx c_0$) for Ti-based alloys. For example, this difference was calculated as only 0.1 at% for Ti–Mo alloys, from the enthalpy curves shown in Fig. 2(a). Because T_0 decreases monotonically with increasing solute concentration, c_0 is approximately proportional to 0c_0 . A linear approximation of T_0 gives the following relationship:

$$c_0 \approx \frac{1155 - 298}{1155} {}^0c_0 = 0.75 {}^0c_0. \quad (19)$$

This equation gives a rough approximation of $c_{cr} \approx 0.75 {}^0c_0$.

Figure 4 shows a comparison of the theoretical metastable equilibrium concentration at 0 K from the first-principles data, 0c_0 , with the experimental critical concentration, c_{cr} .^{50,51)} We found a good linear correlation between the experimental critical concentration and the theoretical metastable equilibrium concentration. In Fig. 4, the dashed line represents the linear least-squares fitting, $c_{cr} = 0.98 {}^0c_0$. This good linear correlation is explained by the T_0 concept as discussed above. We can predict how the alloy composition will affect the stability of the β -phase on the basis of the first-principles calculations of the metastable equilibrium concentration. In future work, we will study the metastable equilibrium concentration for elements other than Mo, Nb, V and W.

Additionally, metastable equilibrium concentration at 298 K were calculated by using the SGTE-CALPHAD lattice

Fig. 5 Comparison of theoretical values for metastable equilibrium concentration at 298 K from the CALPHAD data with experimental values for critical concentration.^{50,51)} The dashed line indicates the relation $c_{cr} = c_0$.

stability shown in Table 1 and CALPHAD data of solution enthalpies shown in Table 2. Figure 5 shows a comparison of the theoretical metastable equilibrium concentration at 298 K from the CALPHAD data, c_0 , with the experimental critical concentration, c_{cr} .^{50,51)} In the case of Ti-based alloys, the difference between c_{cr} and c_0 is negligible ($c_{cr} \approx c_0$) as discussed above. However, we found a poor agreement between the experimental critical concentration and the theoretical metastable equilibrium concentration at 298 K from CALPHAD data. The first-principles data can provide superior prediction of the critical concentration compared with CALPHAD data while the first-principles data was evaluated at 0 K.

A question that remains unanswered is, what property of an alloying element determines the metastable equilibrium concentration? The metastable equilibrium concentration, 0c_0 , is derived from eq. (11) with the condition $H^{hcp} = H^{bcc}$ as follows:

$${}^0c_0 = \frac{(\Delta H_{mix}^{bcc} - \Delta H_{mix}^{hcp}) - \Delta H_{Ti}^{hcp-bcc}}{\Delta H_X^{hcp-bcc} - \Delta H_{Ti}^{hcp-bcc}}, \quad (20)$$

where $\Delta H_{Ti}^{hcp-bcc}$ and $\Delta H_X^{hcp-bcc}$ are the lattice stabilities of the elements Ti and X. $\Delta H_{Ti}^{hcp-bcc}$ is constant of -9.5 kJ/mol, as calculated from first principles. If $\Delta H_{mix}^{bcc} - \Delta H_{mix}^{hcp}$ is independent of the alloying element, 0c_0 will be inversely proportional to $\Delta H_X^{hcp-bcc} + 9.5$ kJ/mol; that is, ${}^0c_0 \propto 1/(\Delta H_X^{hcp-bcc} + 9.5 \text{ kJ/mol})$. Figure 6 shows metastable equilibrium concentration as a function of lattice stability, $\Delta H_X^{hcp-bcc}$. The metastable equilibrium concentration is roughly inversely proportional to the lattice stability; that is, the metastable equilibrium concentration decreases with increasing lattice stability. This leads to an obvious conclusion that an alloying element whose bcc structure is more stable in the pure element is a stronger β -stabilizer for the alloy. We will also study the relationship between 0c_0 and $\Delta H_X^{hcp-bcc}$ for other elements, such as Ni and Cu, in future work.

4. Conclusions

The effects of solute X (Mo, Nb, V and W) content on the

Fig. 6 Metastable equilibrium concentration as a function of lattice stability of the bcc structure with reference to hcp structure. The dashed line is a guide for the eye.

phase stability of β -Ti alloys were studied from first-principles calculations. The results were as follows:

- (1) The lattice stabilities of Ti, Mo, Nb, V and W and the solution enthalpies of hcp Ti-X and bcc Ti-X solid solution alloys were calculated from first principles. The results were consistent with previous first-principles results.
- (2) The enthalpy curves for the α - and β -phases of the Ti-X alloys were described as a function of the alloy composition by using the solution enthalpies and sub-regular solution model. While the enthalpies of the α -phases increased with increasing concentrations of Mo, Nb, V and W, the enthalpies of the β -phases decreased with increasing concentrations. This is consistent with the experimental results, showing that Mo, Nb, V and W are β -stabilizers. The β -phase is more favored in terms of energy than the α -phase when the concentration of solute X is more than the metastable equilibrium concentration 0c_0 . The values of 0c_0 were 6.8, 19.1, 15.6 and 6.7 at% for Mo, Nb, V and W, respectively.
- (3) We found a good linear correlation between the experimental critical concentration and the theoretical metastable equilibrium concentration. This good correlation is explained using the T_0 concept. We could predict how the alloy composition would affect the stability of the β -phase on the basis of first-principles calculations of the metastable equilibrium concentration.
- (4) The metastable equilibrium concentration decreased with the increasing lattice stability of the bcc structure with reference to hcp structure. This suggests that an alloying element whose bcc structure is more stable in the pure element acts as a stronger β -stabilizer for the alloy.

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