

Thermodynamic Evaluation of the Phase Equilibria and Glass-Forming Ability of the Ti-Be System

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(Submitted December 28, 2004; in revised form March 17, 2005)

The glass-forming ability of Ti-Be alloys is of great interest. Experimental and theoretical evaluations of the glass-forming ability of this binary alloy show that the formation of a metastable TiBe phase with a CsCl-type B2 structure controls the glass-forming ability in this system. However, there is no information on the thermochemical properties of metastable TiBe for the quantitative evaluation of the glass-forming ability using Davies-Uhlmann kinetic formulations. We have carried out a thermodynamic analysis using experimental phase diagram data and the energy of formation of the stoichiometric compounds from *ab initio* calculations. Furthermore, the Gibbs energy of formation for the body-centered cubic (bcc) phase was evaluated over the entire composition range by applying the cluster expansion method (CEM) to the total energy of some bcc-based ordered structures obtained from *ab initio* calculations. For the bcc phase, the two-sublattice formalism, $(\text{Ti}, \text{Be})_{0.5}(\text{Ti}, \text{Be})_{0.5}$, was adopted to describe the A2/B2 transformation. A good agreement between the calculated values and experimental phase equilibria was obtained. Evaluation of the glass-forming ability was also attempted utilizing the thermodynamic quantities obtained from the phase diagram assessment. The calculated glass-forming ability agrees well with the experimental results.

Keywords *ab initio* calculations, CALPHAD, entropy of fusion, glass-forming ability, metastable, phase equilibria, titanium-beryllium

1. Introduction

There is interest in the glass-forming ability of Ti-rich Ti-Be alloys [1979Tan], and Be_{12}Ti is a candidate material for neutron multipliers in thermo-nuclear fusion blankets because of its excellent properties compared with beryllium [2004Kaw].

In elucidating the glass-forming ability of this binary system, experimental work has been carried out by Tanner and Ray [1979Tan]. According to their results, alloys produced by splat-quenching in the composition range 37-41 mol% Be exhibit a fully glass state, and the critical cooling rate for glass-formation was estimated to be 10^7 - 10^8 K/s. Furthermore, Tanner et al. found a metastable TiBe phase with a CsCl-type B2 structure in quenched alloys in the composition range 7.5-50 mol% Be [1978Tan, 1979Tan].

This paper was presented at the International Symposium on User Aspects of Phase Diagrams, Materials Solutions Conference and Exposition, Columbus, Ohio, 18-20 October, 2004.

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Saunders et al. [1985Sau, 1988Sau] evaluated the glass-forming ability of this system theoretically and showed that the metastable TiBe phase controlled the glass-forming ability of this alloy. The thermodynamic quantities were derived using phase diagram calculations [1973Kau], which were then input into the Davies-Uhlmann kinetic equations. However, the thermodynamic quantities for the metastable TiBe phase that were required to be input into the Davies-Uhlmann kinetic equations could not be evaluated precisely in the previous calculations [1985Sau, 1988Sau], where the phase stability of the TiBe phase was assessed to avoid the appearance as an equilibrium phase, assuming that the TiBe phase had an entropy of fusion comparable to that of similar B2 compounds [1967Rob]. Therefore, more precise information on the thermochemical properties of TiBe is required for a quantitative evaluation of the glass-forming ability of this binary system.

In the current study, a thermodynamic analysis of the Ti-Be binary system was carried out using thermochemical properties obtained from *ab initio* energetic calculations to take into account the metastable TiBe phase. Furthermore, the glass-forming ability of this binary alloy system was evaluated utilizing the thermodynamic quantities obtained from the phase diagram assessment.

2. Calculation Procedures

2.1 *Ab initio* Calculations

Although the metastable TiBe phase controls the glass-forming ability of this alloy system, the thermodynamic properties of this phase cannot be obtained experimentally. Thus, in the current study, the energy of formation for some body-centered cubic (bcc)-based ordered structures was

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Table 1 Crystallographic data of bcc-based and compound phases used in our calculations

Phase	Strukturbericht designation	Space group	Prototype	Lattice parameters, nm		
				<i>a</i>	<i>b</i>	<i>c</i>
Bcc-based ordered phase						
Ti ₃ Be	<i>D0₃</i>	<i>Fm</i> $\bar{3}$ <i>m</i>	BiF ₃
TiBe	<i>B2</i>	<i>Pm</i> $\bar{3}$ <i>m</i>	CsCl	0.2940
	<i>B32</i>	<i>Fd</i> $\bar{3}$ <i>m</i>	NaTl
TiBe ₃	<i>D0₃</i>	<i>Fm</i> $\bar{3}$ <i>m</i>	BiF ₃
Other compound phase						
TiBe ₂	<i>C15</i>	<i>Fd</i> $\bar{3}$ <i>m</i>	MgCu ₂	0.6427
TiBe ₃	...	<i>R</i> $\bar{3}$ <i>m</i>	NbBe ₃	0.449	...	2.132
α Ti ₂ Be ₁₇	...	<i>R</i> $\bar{3}$ <i>m</i>	Nb ₂ Be ₁₇	0.734	...	1.073
β Ti ₂ Be ₁₇	...	<i>P6₃/mmc</i>	Th ₂ Ni ₁₇	0.735	...	0.726
TiBe ₁₂	<i>D20_b</i>	<i>I4/mmm</i>	Mn ₁₂ Th	0.735	...	0.419

calculated using the full potential linearized augmented plane wave (FLAPW) method [1990Bla] with a general gradient approximation (GGA) [1996Per]. The energy of formation for some of the intermetallic compound phases appearing in the Ti-Be binary system was also derived in the same way.

To derive the Gibbs energy of the bcc-based ordered phases, the authors initially calculated the change in the total energy of the bcc-based superstructures, Ti (*A2*), Ti₃Be(*D0₃*), TiBe(*B2*), TiBe(*B32*), TiBe₃(*D0₃*), and Be(*A2*), with volume using the WIEN2k software code [2003Sch]. The calculation of the total energy for each phase was based on the structural data compiled by Villars [1997Vil], and the crystallographic data involved in our calculations are shown in Table 1. In Villars's compilation of the intermetallic compounds in the Ti-Be binary system, information on the atomic positions was available only for the TiBe₂ phase, and therefore, the remaining phases referenced the atomic positions of their prototype structures. With the total energies obtained in such a way, the energy of formation $\Delta E_{\text{form}}^{\phi}$ for the ϕ phase was defined from the total energy E_{tot}^{ϕ} by subtracting the concentration weighted averages of the pure elements:

$$\Delta E_{\text{form}}^{\phi}(V) = E_{\text{tot}}^{\phi}(V) - (1 - x_{\text{Be}}^{\phi})E_{\text{tot}}^{\text{bcc-Ti}} - x_{\text{Ti}}(V_{\text{Ti}}) - x_{\text{Be}}^{\phi}E_{\text{tot}}^{\text{bcc-Be}} - x_{\text{Be}}(V_{\text{Be}}) \quad (\text{Eq 1})$$

where x_{Be}^{ϕ} denotes the mole fraction of Be in the ϕ structure, and V is the volume. We assumed muffin-tin radii (R_{mt}) of 2.0 a.u. for the Ti atom and 1.8 a.u. for the Be atom. The plane wave basis set with $R_{\text{mt}}K_{\text{max}} = 8.05$ for Be atom was used, which almost corresponds to the cut-off energy of 20 Ry. The term K_{max} denotes the maximum radius of a sphere centered at the origin of reciprocal space, in which all the reciprocal lattice vectors taken into the basis set are present. The energy of formation for some bcc-based ordered phases and other compound phases is summarized in Table 2. The equilibrium lattice constant corresponding to the minimum total energy is also listed in Table 2. The values of the

Table 2 Calculated results of the energy of formation and equilibrium lattice parameters for various phases in the Ti-Be system. (Reference states: bcc Ti and bcc Be)

Phase	Energy of formation, kJ/g-atom		Lattice parameter, nm			Ref
	Ab initio	Assessed	<i>a</i>	<i>b</i>	<i>c</i>	
Bcc-based ordered phase						
Ti ₃ Be(<i>D0₃</i>)	3.6	...	0.6220	Present work
TiBe(<i>B2</i>)	-23.6	-27.0	0.2934	Present work
		-19.1	[1979Kau]
TiBe(<i>B32</i>)	28.3	...	0.5953	Present work
TiBe ₃ (<i>D0₃</i>)	-12.8	...	0.5469	Present work
Other compound phase						
TiBe ₂	-25.7	-29.7	0.6420	Present work
		-26.5	[1973Kau]
		-24.9	[1979Kau]
TiBe ₃	-27.9	-28.0	0.4476	...	2.1253	Present work
		-29.7	[1973Kau]
		-26.0	[1979Kau]
α Ti ₂ Be ₁₇	-21.4	-24.3	0.7386	...	1.0798	Present work
		-31.3	[1973Kau]
		-26.4	[1979Kau]
β Ti ₂ Be ₁₇	-22.0	...	0.7353	...	0.7263	Present work
TiBe ₁₂	-22.2	-22.8	0.7326	...	0.4154	Present work
		-28.5	[1973Kau]
		-23.8	[1979Kau]

formation energies listed in Table 2 are referred to as bcc Ti and bcc Be.

Then, the effective cluster interaction energies $\{v_i(V)\}$ can be extracted from the calculated energies of formation using the cluster expansion method (CEM) developed by Connolly and Williams [1983Con, 1996Slu]:

$$\Delta E_{\text{form}}^{\phi}(V) = \sum_{i=0}^{\gamma} v_i(V) \cdot \xi_i^{\phi} \quad (\text{Eq 2})$$

where $v_i(V)$ is the effective interaction energy of the i th order cluster, and ξ_i^{ϕ} is the multisite correlation function defined for the i th order cluster. The value of ξ_i^{ϕ} can be obtained for the bcc-based ordered structures. In the calculations, based on the results listed in Table 2, $\{\xi_i^{\phi}\}$ forms a 6×6 matrix, and the matrix inversion of Eq 2 yields the effective interaction energies as:

$$v_i(V) = \sum_{i=0}^5 (\xi_i^{\phi})^{-1} \Delta E_{\text{form}}^{\phi}(V) \quad (\text{Eq 3})$$

Equation 3 indicates that the authors take into account geometries up to the tetrahedron cluster.

At a finite temperature, the Gibbs energy of formation consists of both enthalpy and entropy terms, and by using

the effective interaction energy v_i and the correlation function ξ_i^ϕ the enthalpy term can be written:

$$\Delta E = \sum_{i=0}^5 v_i \xi_i \quad (\text{Eq 4})$$

In regard to the entropy term required to obtain the free energy of formation, the authors calculated the configurational entropy using the cluster variation method (CVM) [1951Kik] with a tetrahedron approximation. For the bcc phase, the formula for the entropy is:

$$\Delta S = k \ln \frac{\left\{ \prod_{i,j,k} (N z_{ijk})! \right\}^{12} \left\{ \prod_i (N x_i)! \right\}}{\left\{ \prod_{i,j,k,l} (N w_{ijkl})! \right\}^6 \left\{ \prod_{i,j} (N y_{ij}^{(1)})! \right\}^4 \left\{ \prod_{i,j} (N y_{ij}^{(2)})! \right\}^3} \quad (\text{Eq 5})$$

where x_i , $y_{ij}^{(1)}$, $y_{ij}^{(2)}$, z_{ijk} , and w_{ijkl} are the cluster probabilities of finding the atomic configurations specified by the subscript(s) at a point, the nearest neighbor pair, the second-nearest neighbor pair, a triangle, and a tetrahedron cluster, respectively. The term k is the Boltzmann constant, and N is the number of lattice points.

By minimizing the grand potential with respect to all the correlation functions, the Gibbs energy of formation can be obtained as a function of composition at a constant temperature.

2.2 Thermodynamic Modeling

The Gibbs energies of the liquid, αTi (hcp), and αBe (hcp) phases were described using the conventional regular solution model:

$$G_m^\phi = x_{\text{Be}} \circ G_{\text{Be}}^\phi + x_{\text{Ti}} \circ G_{\text{Ti}}^\phi + RT(x_{\text{Be}} \ln x_{\text{Be}} + x_{\text{Ti}} \ln x_{\text{Ti}}) + x_{\text{Be}} x_{\text{Ti}} L_{\text{Be,Ti}}^\phi \quad (\text{Eq 6})$$

where $\circ G_i^\phi$ denotes the Gibbs energy of element i in the ϕ phase, and is called the lattice stability. The descriptions of the lattice stability parameters were taken from the Scientific Group Thermodata Europe (SGTE) data file [1991Din]. The term R is the universal gas constant, and x_{Be} and x_{Ti} are the mole fractions of Be and Ti, respectively. The interaction energy between Be and Ti is denoted by $L_{\text{Be,Ti}}^\phi$, and has a compositional dependency following the Redlich-Kister polynomial [1949Red]:

$$L_{\text{Be,Ti}} = {}^0L_{\text{Be,Ti}} + (x_{\text{Be}} - x_{\text{Ti}}) \cdot {}^1L_{\text{Be,Ti}} \quad (\text{Eq 7})$$

To describe the A2/B2 transformation in the thermodynamic modeling, the Gibbs energy of the bcc phase was represented using a two-sublattice model [1970Hil] with the formula, $(\text{Ti,Be})_{0.5}(\text{Ti,Be})_{0.5}$. The Gibbs energy of the bcc phase is described:

$$G^{\text{bcc}} = y_{\text{Ti}}^1 y_{\text{Ti}}^2 \circ G_{\text{Ti:Ti}}^{\text{bcc}} + y_{\text{Ti}}^1 y_{\text{Be}}^2 \circ G_{\text{Ti:Be}}^{\text{bcc}} + y_{\text{Be}}^1 y_{\text{Ti}}^2 \circ G_{\text{Be:Ti}}^{\text{bcc}} + y_{\text{Be}}^1 y_{\text{Be}}^2 \circ G_{\text{Be:Be}}^{\text{bcc}} + 0.5RT(y_{\text{Ti}}^1 \ln y_{\text{Ti}}^1 + y_{\text{Be}}^1 \ln y_{\text{Be}}^1) + 0.5RT(y_{\text{Ti}}^2 \ln y_{\text{Ti}}^2 + y_{\text{Be}}^2 \ln y_{\text{Be}}^2) + {}^{\text{ex}}G^{\text{bcc}} \quad (\text{Eq 8})$$

The term y_i^s denotes the site fraction of element i on the s th sublattice, $\circ G_{i,j}$ denotes the Gibbs energy of a hypothetical compound ij , and ${}^{\text{ex}}G^{\text{bcc}}$ is the excess Gibbs energy term containing the interaction energy between unlike atoms, and is expressed:

$${}^{\text{ex}}G^{\text{bcc}} = y_{\text{Ti}}^1 y_{\text{Be}}^1 y_{\text{Ti}}^2 L_{\text{Be,Ti:Ti}} + y_{\text{Ti}}^1 y_{\text{Be}}^1 y_{\text{Be}}^2 L_{\text{Be,Ti:Be}} + y_{\text{Ti}}^2 y_{\text{Be}}^2 y_{\text{Ti}}^1 L_{\text{Ti:Be,Ti}} + y_{\text{Ti}}^2 y_{\text{Be}}^2 y_{\text{Be}}^1 L_{\text{Be:Be,Ti}} \quad (\text{Eq 9})$$

where $L_{i,j:k}$ (or $L_{i,j,k}$) is the interaction parameter between unlike atoms on the same sublattice.

In regard to the stoichiometric compound phases Ti_mBe_n , the Gibbs energy was described:

$$G_m^{\text{Ti}_m\text{Be}_n} = m \cdot \circ G_{\text{Ti}}^{\text{hcp}} + n \cdot \circ G_{\text{Be}}^{\text{hcp}} + \Delta G_{\text{Ti}_m\text{Be}_n}^{\text{f}} \quad (\text{Eq 10})$$

where $\Delta G_{\text{Ti}_m\text{Be}_n}^{\text{f}}$ is the Gibbs energy of formation per mole of formula unit of the compound, and is expressed:

$$\Delta G_{\text{Ti}_m\text{Be}_n}^{\text{f}} = A + B \cdot T \quad (\text{Eq 11})$$

3. Kinetic Formulation

In this study, the authors obtained the critical cooling rate for glass-formation from the time-temperature-transformation (TTT) curves based on the Davies-Uhlmann formulations [1976Dav] for steady-state homogeneous nucleation, although the critical cooling rate can be determined accurately by constructing the continuous-cooling-transformation (CCT) curves. In the Davies-Uhlmann treatment, the time t necessary for the formation of crystalline phase of volume fraction X is given:

$$t \approx \frac{9.3\eta}{kT} \left\{ \frac{a_0^3 X \exp(G^*/kT)}{f^3 N_v [1 - \exp(-G_m/RT)]^3} \right\}^{1/4} \quad (\text{Eq 12})$$

where η is the viscosity of the melt, k is the Boltzmann constant, T is the transformation temperature, a_0 is the mean atomic diameter, N_v is the number of atoms per unit volume, and R is the universal gas constant. The fraction of sites on the interface where atoms may preferentially be added and moved is denoted by f , and is given as [1972Uhl]:

$$f \approx 0.2(T_m - T)/T_m \quad (\text{Eq 13})$$

where T_m is the liquidus temperature and G_m is the molar free energy driving force for liquid to crystallize. G^* is the free energy barrier for nucleation of a spherical nucleus given by the expression:

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$$G^* = \frac{16\pi}{3N} (\sigma_m^3 / G_m^2) \quad (\text{Eq 14})$$

where N is Avogadro's number and σ_m is the liquid/crystal interfacial energy per molar surface area. According to Turnbull [1950Tur], the term σ_m is related to the molar heat of fusion H_m^f based on the relationship between bond energy values across the interface, and can be expressed:

$$\sigma_m = \alpha H_m^f \quad (\text{Eq 15})$$

The constant α was empirically evaluated by Saunders and Miodownik [1988Sau] to be $\alpha \sim 0.41$.

To calculate Eq 12, it is necessary to derive (or estimate) the quantities η , G^* , and G_m .

The Vogel-Fulcher-Tammann (VFT) equation is generally used to describe the viscosity of the supercooled liquid:

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \quad (\text{Eq 16})$$

where η_0 , B , and T_0 are empirical parameters, and T_0 is the ideal glass transition temperature and lies near, but slightly below, the glass transition temperature T_g . The parameters in Eq 16 can be obtained if experimental data on the viscosity of the melt are available. However, there are no experimental data on the viscosity of Ti-Be melts, and in this study, the viscosity was approximated using the Doolittle expression based on the relative free volume f_T given by the expression [1977Ram]:

$$\eta = A \exp(B/f_T) \quad (\text{Eq 17})$$

where

$$f_T = C \exp(-E_H/RT) \quad (\text{Eq 18})$$

The terms A , B , and C are constants, and E_H is the hole formation energy. Due to the lack of experimental data, in this study, E_H was calculated based on the linear relationship between E_H and T_g [1977Ram]. Then, assuming that $f_T = 0.03$ and $\eta = 10^{12}$ Pa s at T_g , and assigning a value of $B = 1$ [1977Ram], the values of the other constants, A and C , can be evaluated. However, glass transition has not been detected in Ti-Be amorphous alloys using differential scanning calorimetry (DSC) [1979Tan], where the DSC traces on heating a Ti-37mol%Be amorphous alloy showed crystallization at $T \sim 673$ K, although a glass transition was observed at $T \sim 673$ K in the ternary $\text{Ti}_{58}\text{Be}_{40}\text{Zr}_2$ alloy [1980Tan]. Thus, we assumed the glass transition temperature required for the estimation of the viscosity to be $T \sim 673$ K, and that T_g was independent of composition based on the experimental evidence.

The molar free energy driving force for the liquid to crystallize G_m can be obtained from the thermodynamic phase diagram calculations. Figure 1 shows the calculated Gibbs energies of the liquid, and the bcc, hexagonal close-packed (hcp), and Ti_4Be_5 phases at $T = 673$ K, representing relative stability of Ti_4Be_5 and the method for deriving the

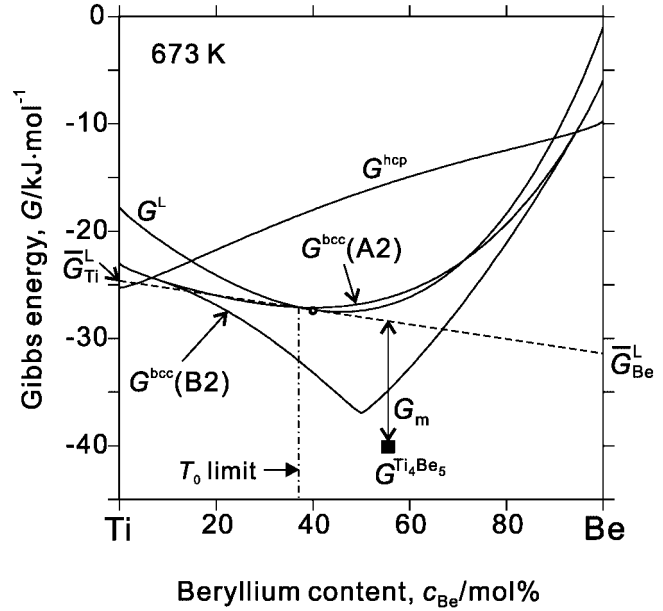


Fig. 1 Construction used in calculating the driving force G_m for the crystallization of compound Ti_4Be_5 from a liquid of composition $x_{\text{Be}} = 0.4$ at $T = 673$ K.

driving force for crystallization of Ti_4Be_5 from a supercooled liquid of composition $x_{\text{Be}} = 0.4$, where G^L , G^{bcc} , G^{hcp} , and $G^{\text{Ti}_4\text{Be}_5}$ denote the Gibbs energy of the liquid, bcc, hcp, and Ti_4Be_5 phases, respectively. The partial molar Gibbs energy of Ti and Be in the liquid phase are denoted by \bar{G}_{Ti}^L and \bar{G}_{Be}^L , respectively, and these represent the chemical potential. In Fig. 1, the driving force for the crystallization of the Ti_4Be_5 phase is given by G_m , where G_m represents the Gibbs energy required to form one mole of Ti_4Be_5 from a liquid of composition $x_{\text{Be}} = 0.4$. Therefore, G_m is expressed:

$$G_m = x_{\text{Ti}}^{\text{Ti}_4\text{Be}_5} \bar{G}_{\text{Ti}}^L + x_{\text{Be}}^{\text{Ti}_4\text{Be}_5} \bar{G}_{\text{Be}}^L - G^{\text{Ti}_4\text{Be}_5} \quad (\text{Eq 19})$$

where $x_{\text{Ti}}^{\text{Ti}_4\text{Be}_5}$ and $x_{\text{Be}}^{\text{Ti}_4\text{Be}_5}$ are the mole fractions of Ti and Be atoms in the Ti_4Be_5 phase. It is noteworthy that, although various models for amorphous phases have been proposed [1999Zho, 2000Tol, 2000Sha, 2001Liu], in this study, the supercooled liquid phase was described by extrapolation of its high-temperature properties.

In Fig. 1, the T_0 limit is also shown, where T_0 denotes the temperature at which the liquid and the disordered bcc phase of the same composition have the same Gibbs energy. For a Be content below the T_0 limit, the liquid phase becomes unstable with respect to the disordered bcc phase of the same composition. Thus, the transformation from the liquid to the disordered solid solution phase occurs because no long range diffusion is necessary for a liquid \rightarrow solid transformation, and the kinetics are governed by atomic movements less than the diameter of one atom. This forms the basis of the T_0 criteria for the glass-forming ability [1981Mas].

In this study, the temperature dependence of G_m was approximated as being linear:

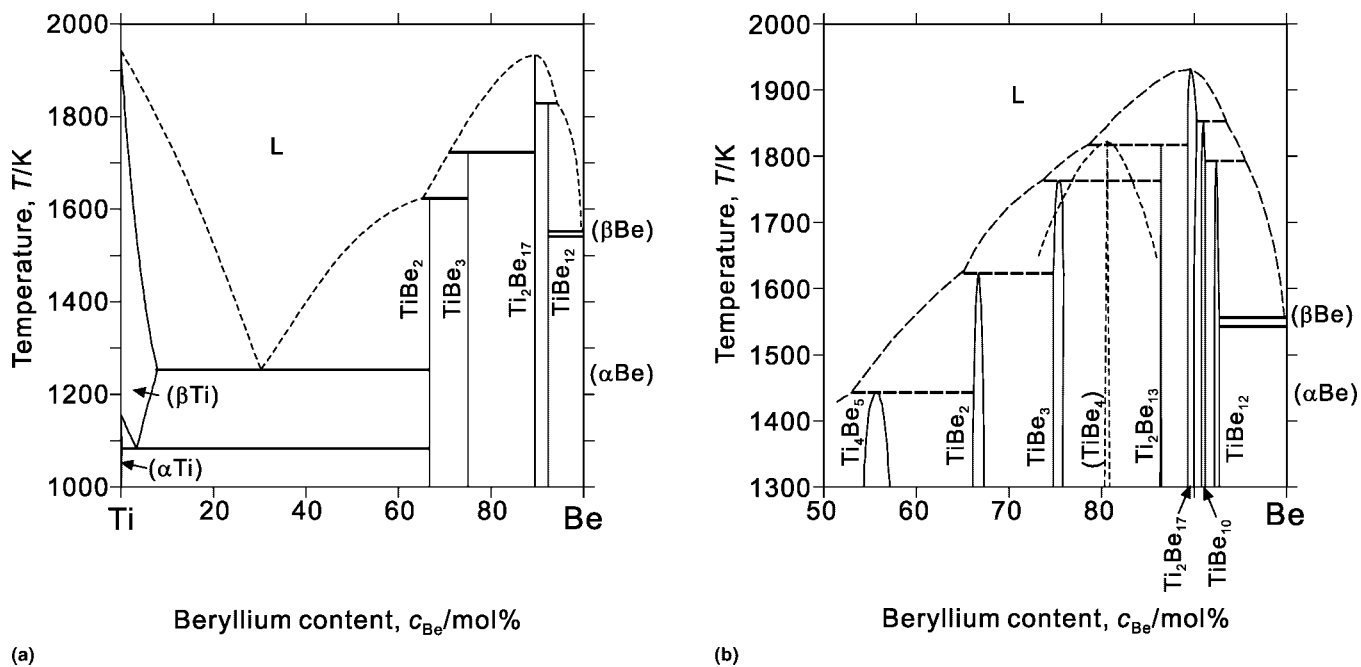


Fig. 2 (a) Ti-Be binary phase diagram over the entire range assessed by [1987Mur], and (b) Be-rich region assessed by [2003Ohn]

$$G_m = H_m^f(T_m - T)/T_m \quad (\text{Eq 20})$$

The value of G^* can be derived by inserting the value of H_m^f into Eq 15 and then using the calculated value of σ_m in Eq 14.

The TTT curves were calculated for the Ti-Be alloys using the values of η , G^* , and G_m derived from the procedures described above. In our calculations, the constants in Eq 12 were taken to be $a_0 = 0.28 \times 10^{-9}$ m, $X = 10^{-6}$, and $N_v = 5 \times 10^{28}$ atoms/m³. The critical cooling rates were calculated:

$$R_c = \frac{T_m - T_n}{t_n} \quad (\text{Eq 21})$$

where T_n and t_n are the temperature and time, respectively, at the nose of the TTT curves.

4. Optimization of Thermodynamic Parameters and Calculation of Phase Diagram

A critical assessment of the phase diagram in the Ti-Be binary system has been carried out by Murray [1987Mur] based on limited experimental work, and the evaluated phase diagram is shown in Fig. 2(a). According to Murray's evaluation, the Ti-Be system consists of the hcp (α Ti, α Be), bcc (β Ti, β Be), TiBe_2 , TiBe_3 , $\text{Ti}_2\text{Be}_{17}$, and TiBe_{12} phases, along with the liquid phase. For the $\text{Ti}_2\text{Be}_{17}$ phase, two allotropic forms, $\alpha\text{Ti}_2\text{Be}_{17}$ [1960Pai, 1961Zal, 1961Gla] and $\beta\text{Ti}_2\text{Be}_{17}$ [1961Zal, 1964Gil], were found. However, in Murray's assessment, the two allotropic forms were not

distinguished in the phase diagram due to the lack of experimental data on the temperature ranges of stability for both $\alpha\text{Ti}_2\text{Be}_{17}$ and $\beta\text{Ti}_2\text{Be}_{17}$. In addition, Tanner and Ray [1979Tan] reported the existence of the metastable TiBe phase with a CsCl-type B2 structure.

The assessment of the phase diagram of this binary system was mainly based on the experimental works of Bedford [1960Bed], Obinata et al. [1962Obi], and Hunter [1966Hun]. Bedford [1960Bed] examined several alloys having the composition range 60-100 mol% Be using thermal analysis, and determined the invariant temperatures for the reactions: $L \leftrightarrow \text{TiBe}_3 + \text{TiBe}_2$, $L + \text{Ti}_2\text{Be}_{17} \leftrightarrow \text{TiBe}_3$, $L + \text{Ti}_2\text{Be}_{17} \leftrightarrow \text{TiBe}_{12}$, and $L \leftrightarrow \text{Ti}_2\text{Be}_{17}$ with uncertainties of $T = 50$ to 60 K. Obinata et al. [1962Obi] investigated the phase equilibria in the composition range 0-60 mol% Be at $T = 1048$ to 1273 K using optical microscopy, thermal analysis, x-ray diffraction, and electrical resistivity measurements. From on microscopy data, Obinata et al. found the eutectic composition at 28.6 mol% Be for $L \leftrightarrow (\beta\text{Ti}) + \text{TiBe}_2$ and the eutectoid composition at about 3 mol% Be for $(\beta\text{Ti}) \leftrightarrow (\alpha\text{Ti}) + \text{TiBe}_2$, at eutectic and eutectoid temperatures of 1253 and 1088 K, respectively. They also found the maximum solubility of Be in (β Ti) and (α Ti) to be 9.8 and ~1 mol%, respectively. Hunter [1966Hun] studied Ti-rich alloys with up to 22 mol% Be using optical microscopy, and placed the eutectoid composition at 2.6 mol% Be with the maximum solubility of Be in (β Ti) at 5 mol%.

Recently, Ohnuma et al. [2003Ohn] reported a new version of experimental phase diagram in the Be-rich region based on results of backscattered electron images of microstructures and data obtained using a diffusion couple technique. The detailed features of this phase diagram are shown in Fig. 2(b). They identified a eutectic and six peritectic reactions from the as-cast microstructures and found out

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new TiBe_{10} , $\text{Ti}_2\text{Be}_{13}$, TiBe_4 , and Ti_4Be_5 compound phases using electron probe microanalysis (EPMA) measurements. The TiBe_4 phase was concluded to be metastable.

In regard to the thermodynamic properties, there is no experimental data on this binary system. A thermodynamic analysis on this binary system has been carried out by Kaufman and Nesor [1973Kau], Kaufman and Tanner [1979Kau], and Murray [1987Mur] on the basis of experimental data on phase boundaries. In the former two analyses, the composition of the eutectic reaction $L \leftrightarrow (\beta\text{Ti}) + \text{TiBe}_2$ at 37.5 mol% Be [1965Ell], was adopted, whereas the latter analysis used about 28 mol% Be. All the calculated phase diagrams reasonably reproduced the characteristic features of this binary system.

In our analysis, the seven binary compound phases, Ti_4Be_5 , TiBe_2 , TiBe_3 , $\text{Ti}_2\text{Be}_{13}$, $\text{Ti}_2\text{Be}_{17}$, TiBe_{10} , and TiBe_{12}

were taken into account as stoichiometric phases. The two allotropic forms of the $\text{Ti}_2\text{Be}_{17}$ phase were not differentiated. The thermodynamic parameters in the Ti-Be system were optimized based mainly on experimental data [1962Obi, 1987Mur, 2003Ohn] together with the thermochemical properties obtained from ab initio calculations. The evaluated parameters of the Ti-Be binary system are listed in Table 3. The calculated Gibbs energy of formation for both the ordered and disordered bcc states at $T = 500$ and 1000 K are shown in Fig. 3, along with the results obtained from ab initio calculations. The decrease in the Gibbs energy of the bcc phase in the vicinity of the equiatomic composition corresponds to a B2 ordering, and hence, this ordered bcc phase is the metastable TiBe phase found by Tanner and Ray [1979Tan]. The calculated phase diagram of the Ti-Be system is shown in Fig. 4, together with the

Table 3 Evaluated thermodynamic parameters in the Ti-Be system

Phase	Symbol	Thermodynamic parameter, J/mol
L	${}^0L_{\text{Be,Ti}}$	$-65,086.12 + 12.07518T$
	${}^1L_{\text{Be,Ti}}$	$-23,038.84$
hcp	${}^0L_{\text{Be,Ti}}^{\text{hcp}}$	20,000
bcc	$G_{\text{Be,Ti}}^{\text{bcc}} (= G_{\text{Ti,Be}}^{\text{bcc}})$	$-26,975.75 + 6.63472T + 0.5^\circ G_{\text{Be}}^{\text{bcc}} + 0.5^\circ G_{\text{Ti}}^{\text{bcc}}$
	${}^0L_{\text{Be,Ti;Be}}^{\text{bcc}} (= {}^0L_{\text{Be;Be,Ti}}^{\text{bcc}})$	$-1000 - 4T$
	${}^0L_{\text{Be,Ti;Ti}}^{\text{bcc}} (= {}^0L_{\text{Ti;Be,Ti}}^{\text{bcc}})$	15,000
Ti_4Be_5	$G_{\text{Ti,Be}}^{\text{Ti}_4\text{Be}_5}$	$-241,192.35 + 44.63426T + 5^\circ G_{\text{Be}}^{\text{hcp}} + 4^\circ G_{\text{Ti}}^{\text{hcp}}$
TiBe_2	$G_{\text{Ti,Be}}^{\text{TiBe}_2}$	$-71,410.16 + 5.74848T + 2^\circ G_{\text{Be}}^{\text{hcp}} + {}^\circ G_{\text{Ti}}^{\text{hcp}}$
TiBe_3	$G_{\text{Ti,Be}}^{\text{TiBe}_3}$	$-88,071.56 + 5.04869T + 3^\circ G_{\text{Be}}^{\text{hcp}} + {}^\circ G_{\text{Ti}}^{\text{hcp}}$
$\text{Ti}_2\text{Be}_{13}$	$G_{\text{Ti,Be}}^{\text{Ti}_2\text{Be}_{13}}$	$-300,774.29 + 33.62421T + 13^\circ G_{\text{Be}}^{\text{hcp}} + 2^\circ G_{\text{Ti}}^{\text{hcp}}$
$\text{Ti}_2\text{Be}_{17}$	$G_{\text{Ti,Be}}^{\text{Ti}_2\text{Be}_{17}}$	$-347,203.54 + 37.43699T + 17^\circ G_{\text{Be}}^{\text{hcp}} + 2^\circ G_{\text{Ti}}^{\text{hcp}}$
TiBe_{10}	$G_{\text{Ti,Be}}^{\text{TiBe}_{10}}$	$-192,214.22 + 25.12979T + 10^\circ G_{\text{Be}}^{\text{hcp}} + {}^\circ G_{\text{Ti}}^{\text{hcp}}$
TiBe_{12}	$G_{\text{Ti,Be}}^{\text{TiBe}_{12}}$	$-217,142.84 + 35.07137T + 12^\circ G_{\text{Be}}^{\text{hcp}} + {}^\circ G_{\text{Ti}}^{\text{hcp}}$

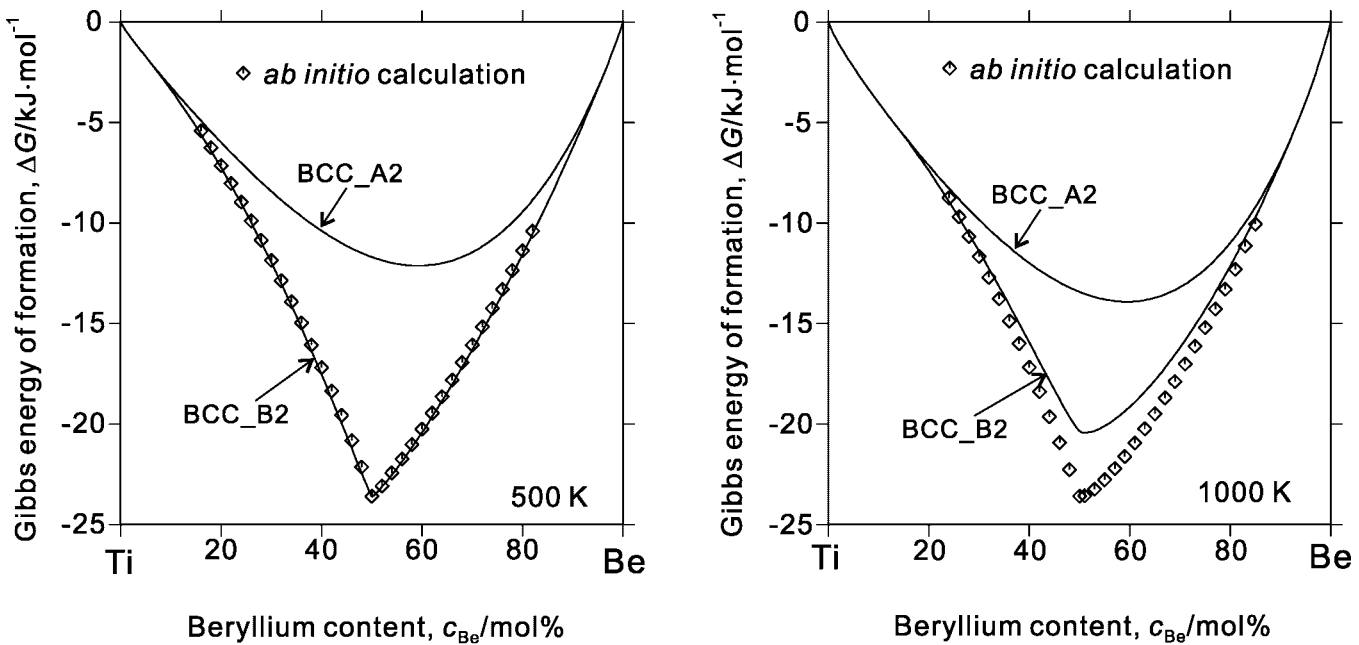


Fig. 3 Gibbs energy of formation for both the ordered and disordered bcc phases at $T = 500$ and 1000 K based on ab initio calculations

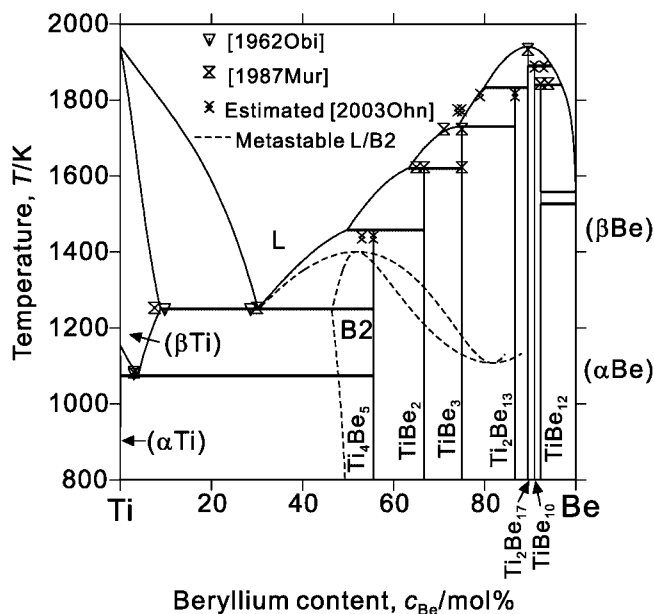


Fig. 4 Calculated Ti-Be phase diagram, together with the experimental invariant points evaluated in [1962Obi, 1987Mur, 2003Ohn]. The broken lines represent the metastable phase equilibria between the liquid and the B2_bcc phase.

experimental data and assessed results [1962Obi, 1987Mur, 2003Ohn]. As mentioned previously, the metastable TiBe phase forms from the melt by rapid-quenching, and the metastable phase equilibrium between the liquid and the B2_bcc phase is also shown by the broken lines in Fig. 4.

The enthalpies of formation for the various compounds in the Ti-Be system are shown in Table 2, together with the assessed values [1973Kau, 1979Kau]. The values listed in Table 2 are referred to as bcc Ti and bcc Be, although the stable state of both Ti and Be at $T = 298.15$ K is the hcp phase.

5. Evaluation of the Glass-Forming Ability

In regard to the glass-forming ability of Ti-Be alloys, Tanner and Ray [1979Tan] investigated alloys in the composition range 2.5-67 mol% Be by rapid-quenching. As mentioned above, they obtained fully glass structures in the composition range 37-40 mol% Be and revealed the existence of the metastable TiBe phase with a CsCl-type B2 structure. Furthermore, they computed the critical cooling rate for glass formation using the Davies-Uhlmann kinetic formulations [1976Dav] and estimated the value to be 10^7 - 10^8 K/s, where the explicit thermodynamic quantities required were not taken into account in their calculations.

Saunders et al. [1985Sau, 1988Sau] evaluated the glass-forming ability of Ti-Be alloys using the Davies-Uhlmann approach, where the thermodynamic quantities were derived employing thermodynamic phase diagram calculations [1973Kau]. The evaluated compositional glass-forming range [1988Sau] showed a discrepancy with the

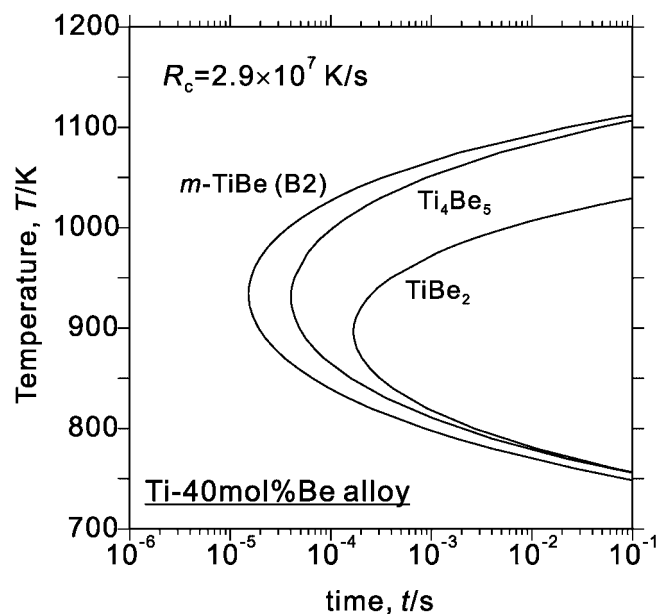


Fig. 5 Calculated TTT curves for the crystallization of B2_bcc phase, Ti_4Be_5 , and $TiBe_2$ from Ti-40 mol% Be liquid alloy

experimental results [1979Tan] and was attributed to the formation of the metastable TiBe phase, for which the thermodynamic properties were not evaluated quantitatively.

In this study, the evaluation of the glass-forming ability of Ti-Be alloys was carried out using the Davies-Uhlmann kinetic approach, which used the thermodynamic quantities obtained from the present phase diagram assessment, where, in particular, the phase stability of the metastable TiBe phase was quantitatively evaluated by incorporating ab initio calculations.

The calculated TTT curves for crystallization from the liquid phase of a Ti-40 mol% Be alloy are shown in Fig. 5. According to our calculations, the metastable TiBe phase controls glass formation in this alloy composition because the nose of the TTT curve occurs at shorter times than those of other crystalline phases. By using Eq 21, the critical cooling rate for glass formation was calculated to be 2.9×10^7 K/s. Figure 6 shows the variation in critical cooling rate for glass formation with Be content, together with the experimental glass-forming range (GFR) [1979Tan]. The calculated GFR shown in Fig. 6 was obtained by setting the cooling rate for rapid quenching at $10^{7.5}$ K/s, as estimated by Tanner and Ray [1979Tan], and by considering the T_0 limit criterion. There is good agreement between the predicted and observed glass-forming ranges.

As shown in Fig. 5, and also as reported by Saunders and Miodownik [1988Sau], the glass-forming ability is controlled by the formation of the metastable TiBe phase, although the primary crystalline phase is Ti_4Be_5 in the Ti-40 mol% Be alloy. The glass-forming ability, which is generally indicated by the minimum cooling rate that avoids the nucleation and growth of crystals, has been estimated using the following three parameters [1998Ino]: (a) a reduced glass transition temperature (T_g/T_m), (b) a supercooled liquid region $\Delta T_x (= T_x - T_g)$, and (3) a critical cooling rate R_c for the

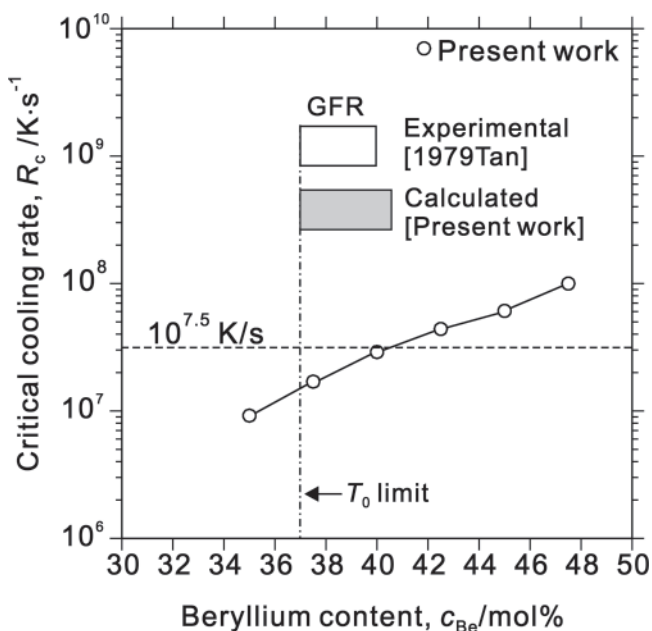


Fig. 6 Calculated critical cooling rates for glass-formation together with the experimentally observed and calculated glass-forming range for a cooling rate of $10^{7.5}$ K/s

formation of the glassy phase. However, Sprusil and Bergmann [1985Spr] empirically, and Saunders and Miodownik [1988Sau] theoretically, reported that another important factor in determining the glass-forming ability was the entropy of fusion. The authors will discuss the effect of the entropy of fusion on glass formation to explain the present results following the approach used by Saunders and Miodownik [1988Sau].

In the calculations, the variation in G_m is approximated as having a linear temperature dependence using Eq 20. Substituting Eqs 15 and 20 into Eq 14 gives:

$$G^* = \frac{16\pi}{3N} \frac{(\alpha H_m^f)^3}{(\Delta T_r H_m^f)^2} \quad (\text{Eq 22})$$

where $\Delta T_r (= T_m - T)/T_m$. Dividing Eq 22 by kT , and because $H_m^f = S_m^f T_m$, where S_m^f is the molar entropy of fusion, Eq 22 becomes:

$$\frac{G^*}{kT} = \frac{16\pi\alpha^3}{3Nk} \frac{S_m^f}{\Delta T_r^2 T_r} \quad (\text{Eq 23})$$

where $T_r = T/T_m$. Equation 23 indicates that G^*/kT is proportional to S_m^f , and implies that at any given supercooling, even if the driving force for crystallization is less for a phase than it is for other possible phases, the crystallization of the phase with a lower value of the entropy of fusion would occur.

According to the calculations using the thermodynamic function formulated in this work, the value of entropy of fusion for the TiBe phase is $13.2 \text{ J mol}^{-1} \text{ K}^{-1}$ for the Ti-40 mol% Be alloy; in contrast, the value of entropy of fusion

for the Ti_4Be_5 phase is $16.6 \text{ J mol}^{-1} \text{ K}^{-1}$. Although there is no crystallographic information available on the Ti_4Be_5 phase, which was first identified by Ohnuma et al. [2003Ohn], it seems that the crystal structure of the TiBe phase with a CsCl-type B2 structure is simpler than that of the Ti_4Be_5 phase. Tanner and Ray [1979Tan] did not detect the Ti_4Be_5 phase in rapidly quenched alloys nor heated samples up to 1276 K. The reason for this is considered to be caused by the lack of information on the appearance of this phase.

Quantitatively considering the crystallization of phases from the supercooled liquid, in which atoms are distributed almost randomly, the crystallization of a phase with a simpler ordered structure than other phases would arise, even if the driving force for the crystallization of that phase was less than that of other phases.

6. Conclusions

A thermodynamic analysis of the Ti-Be binary system has been carried out by combining the thermodynamic properties obtained from ab initio energetic calculations with the reported experimental data on phase boundaries. The glass-forming ability of this alloy system was evaluated by introducing the thermodynamic quantities obtained from the phase diagram calculations involving the metastable phase equilibria into the Davies-Uhlmann kinetic formulation. The results obtained can be summarized as follows.

The calculated phase diagram of the Ti-Be binary system reproduced the experimental phase diagrams. In particular, the phase stability of the metastable TiBe phase, which controls the glass-forming ability of this binary alloy, was quantitatively evaluated by incorporating ab initio energetic calculations into the conventional CALPHAD method.

The calculated glass-forming ability of Ti-Be binary alloys was in good agreement with the experimental compositional amorphization range. Here, the entropy of fusion for the metastable TiBe phase, which plays a key role in evaluation of the glass-forming ability, could be calculated quantitatively.

Acknowledgments

The authors are grateful to Dr. Ohnuma of Tohoku University for providing the experimental data. The authors also acknowledge use of the Thermo-Calc software program in the phase diagram calculations. One of authors (T.T.) acknowledges the financial support from the Inoue Foundation for Science.

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