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Thermodynamic Calculation of Phase Equilibria in the Nb-Ni-Ti-Zr Quaternary System

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The phase equilibria in the Nb-Ni-Ti-Zr quaternary system have been studied using the CALPHAD method. Among the four ternary systems present in the quaternary phase diagram, the Nb-Ti-Zr ternary system was described using a simple ternary extrapolation of the constituent binary systems with no additional ternary parameters. The thermodynamic parameters of the Ni-Ti-Zr ternary system were evaluated using data from first-principles calculations on the ternary NiTi, NiZr, and NiTiZr compound phases as well as available experimental data on the phase boundaries. The calculated isothermal and vertical section diagrams of both the Nb-Ti-Zr and Ni-Ti-Zr ternary systems reproduced the experimental results satisfactorily. The thermodynamic parameters of the Nb-Ni-Ti and Nb-Ni-Zr ternary systems were adopted from previous studies. The liquidus surface in the Nb-Ni-Ti-Zr quaternary system was calculated based on the thermodynamic description of the ternary systems. According to the calculated liquidus surface of $Nb_{40-x-y}Ni_{60}Ti_xZr_y$ alloys, in which a metallic glass was formed over a wide composition range, the liquidus temperature decreased with increasing Zr content up to 20 mol%Zr. [doi:10.2320/matertrans.48.89]

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1. Introduction

Glassy or amorphous alloys form over a wide composition range in the Nb-Ni-Ti and Nb-Ni-Zr systems.[1,2] These amorphous alloys are expected to act as a membrane material for hydrogen purification due to their high hydrogen permeability.[3] In contrast, recent studies indicate that quaternary Nb-Ni-Ti-Zr glassy alloys exhibit high hydrogen impermeability, corrosion resistance, and formability for use in fuel cells as bipolar plates.[4,5] Apart from the formation of glassy or amorphous alloys, the hydrogen permeation characteristics of ternary Nb-Ni-Ti alloys have been investigated, and new hydrogen permeation alloys consisting of NiTi and bcc (Nb,Ti) duplex phases have been developed.[6] Therefore, information on the phase equilibria in the Nb-Ni-Ti-Zr quaternary system is required for further development of these hydrogen energy-related materials. The Calculation of Phase Diagrams (CALPHAD) approach,[7] where phase diagrams are constructed using experimental data and thermodynamic analysis, provides a powerful tool for obtaining information about phase equilibria and the thermodynamic properties of alloy systems.

In this study, a thermodynamic analysis of the constituent ternary systems making up the Nb-Ni-Ti-Zr quaternary system has been carried out, and the phase equilibria in this quaternary system have been calculated based on the thermodynamic descriptions of the constituent ternary systems using the CALPHAD method.

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2. Calculation Procedures

2.1 Thermodynamic descriptions

The Gibbs energy of the liquid and the terminal solid solution phases was described using the conventional regular solution model as follows:

$$\begin{aligned} G_m^\phi = {} & x_{Nb}{}^\circ G_{Nb}^\phi + x_{Ni}{}^\circ G_{Ni}^\phi + x_{Ti}{}^\circ G_{Ti}^\phi + x_{Zr}{}^\circ G_{Zr}^\phi \\ & + RT(x_{Nb}\ln x_{Nb} + x_{Ni}\ln x_{Ni} + x_{Ti}\ln x_{Ti} + x_{Zr}\ln x_{Zr}) \\ & + x_{Nb}x_{Ni}L_{Nb,Ni}^\phi + x_{Nb}x_{Ti}L_{Nb,Ti}^\phi + x_{Nb}x_{Zr}L_{Nb,Zr}^\phi \\ & + x_{Ni}x_{Ti}L_{Ni,Ti}^\phi + x_{Ni}x_{Zr}L_{Ni,Zr}^\phi + x_{Ti}x_{Zr}L_{Ti,Zr}^\phi \\ & + x_{Nb}x_{Ni}x_{Ti}L_{Nb,Ni,Ti}^\phi + x_{Nb}x_{Ni}x_{Zr}L_{Nb,Ni,Zr}^\phi \\ & + x_{Nb}x_{Ti}x_{Zr}L_{Nb,Ti,Zr}^\phi + x_{Ni}x_{Ti}x_{Zr}L_{Ni,Ti,Zr}^\phi \end{aligned} \quad (1)$$

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.[8] The term R is the universal gas constant, and x_{Nb}, x_{Ni}, x_{Ti} and x_{Zr} are the mole fractions of Nb, Ni, Ti, and Zr, respectively. The parameter $L_{i,j}^\phi$ denotes the interaction energy between i and j in the ϕ phase. $L_{i,j,k}^\phi$ is ternary interaction parameter between elements i, j, and k, respectively. The compositional dependency of the interaction parameters $L_{i,j}^\phi$ and $L_{i,j,k}^\phi$ is expressed using an nth degree Redlich-Kister[9] and Redlich-Kister-Muggianu[10] polynomials, respectively.

$$\begin{aligned} L_{i,j}^\phi = {} & {}^0L_{i,j}^\phi + {}^1L_{i,j}^\phi(x_i - x_j)^1 + {}^2L_{i,j}^\phi(x_i - x_j)^2 \\ & + \cdots + {}^nL_{i,j}^\phi(x_i - x_j)^n \end{aligned} \quad (2)$$

$$L_{i,j,k}^\phi = x_i{}^0L_{i,j,k}^\phi + x_j{}^1L_{i,j,k}^\phi + x_k{}^2L_{i,j,k}^\phi \quad (3)$$

The interaction parameters for the quaternary system were not taken into account in our modelling.

The Gibbs energy contributions due to ferromagnetic ordering of the Ni-rich fcc solid solution phase were described using the model of Hillert and Jarl:[11]

Table 1 The sublattice model formulae of the phases in the Nb-Ni-Ti-Zr quaternary system.

Phase	Formula
$NbNi_3$	$(Nb,Ni)_{0.25}(Nb,Ni)_{0.75}$
Nb_6Ni_7	$(Nb,Ni)_{0.4615}(Nb,Ni)_{0.5385}$
Ni_3Ti	$(Ni,Ti)_{0.75}(Ni,Ti)_{0.25}$
NiTi	$(Nb,Ni,Va,Zr)_{0.5}(Nb,Ni,Ti,Zr)_{0.5}$
$NiTi_2$	$(Ni)_{0.333}(Ti,Zr)_{0.667}$
Ni_5Zr	$(Ni,Zr)_{0.833}(Va,Zr)_{0.167}$
Ni_3Zr	$(Ni,Zr)_{0.75}(Va,Zr)_{0.25}$
$Ni_{10}Zr_7$	$(Ni,Zr)_{0.575}(Va,Zr)_{0.425}$
NiZr	$(Ni)_{0.5}(Ti,Zr)_{0.5}$
$NiZr_2$	$(Ni)_{0.333}(Ti,Zr)_{0.667}$
$NiTiZr(\lambda)$	$(Ti,Zr)_{0.333}(Ni,Ti)_{0.667}$

$$^{\mathrm{mag}}G_{\mathrm{m}}^{\phi} = RT\ln(\beta^{\phi}+1)f(\tau), \tag{4}$$

where $^{\mathrm{mag}}G_{\mathrm{m}}^{\phi}$ is the Gibbs energy of the magnetic ordering, β^{ϕ} is the average magnetic moment per atom in the ϕ phase (expressed in Bohr magnetons), and $f(\tau)$ is a polynomial function of τ. The term τ is defined as T/T_{C}^{ϕ}, where T_{C}^{ϕ} is the critical temperature of the magnetic transition in the ϕ phase. Both β^{ϕ} and T_{C}^{ϕ} can be concentration-dependent, and are represented by an equation similar to eq. (2).

The Gibbs energy of compound phases with some homogeneity range was described using the sublattice model.[12] For the simple case of a phase with the formula $(A,B)_m(C,D)_n$, the Gibbs energy per mole of atoms of the compound is given by:

$$\begin{aligned} G_{\mathrm{m}} = {} & y_{\mathrm{A}}^1 y_{\mathrm{C}}^2 {}^{\circ}G_{\mathrm{A:C}} + y_{\mathrm{B}}^1 y_{\mathrm{C}}^2 {}^{\circ}G_{\mathrm{B:C}} + y_{\mathrm{A}}^1 y_{\mathrm{D}}^2 {}^{\circ}G_{\mathrm{A:D}} \\ & + y_{\mathrm{B}}^1 y_{\mathrm{D}}^2 {}^{\circ}G_{\mathrm{B:D}} + mRT(y_{\mathrm{A}}^1 \ln y_{\mathrm{A}}^1 + y_{\mathrm{B}}^1 \ln y_{\mathrm{B}}^1) \\ & + nRT(y_{\mathrm{C}}^2 \ln y_{\mathrm{C}}^2 + y_{\mathrm{D}}^2 \ln y_{\mathrm{D}}^2) + {}^{\mathrm{ex}}G \end{aligned} \tag{5}$$

where ${}^{\circ}G_{\mathrm{A:C}}$ denotes the Gibbs energy of a hypothetical compound A_mC_n, in which all the sites in Sublattice 1 are occupied by element A, and all the sites in Sublattice 2 are occupied by element C, respectively. The colon separates the constituent elements in the sublattice. The site fraction of the elements on the sth sublattice is denoted by y_i^s. The term ${}^{\mathrm{ex}}G$ is the excess Gibbs energy term containing the interaction energy between unlike atoms, and is expressed by the following equation:

$$\begin{aligned} {}^{\mathrm{ex}}G = {} & y_{\mathrm{A}}^1 y_{\mathrm{B}}^1 y_{\mathrm{C}}^2 L_{\mathrm{A,B:C}} + y_{\mathrm{A}}^1 y_{\mathrm{B}}^1 y_{\mathrm{D}}^2 L_{\mathrm{A,B:D}} \\ & + y_{\mathrm{C}}^2 y_{\mathrm{D}}^2 y_{\mathrm{A}}^1 L_{\mathrm{A:C,D}} + y_{\mathrm{C}}^2 y_{\mathrm{D}}^2 y_{\mathrm{B}}^1 L_{\mathrm{B:C,D}}, \end{aligned} \tag{6}$$

where $L_{i,j:k}$ (or $L_{i:j,k}$) is the interaction parameter between unlike atoms on the same sublattice, and is described by an equation similar to eq. (2).

The phases described by the sublattice model in this study and their formulae are listed in Table 1.

The binary compounds, Ni_7Zr_2, $Ni_{21}Zr_8$, and $Ni_{11}Zr_9$, and the five ternary compounds, *i.e.*, $Nb_{15}Ni_{56}Ti_{29}$, $Nb_8Ni_9Ti_3$, $Nb_5Ni_{75}Ti_{20}$, $Nb_{13}Ni_{75}Ti_{12}$, and $Nb_{15}Ni_{80}Ti_5$, were treated as being stoichiometric compounds. For example, the Gibbs energy of the Ni_7Zr_2 phase was described as follows:

$$G_{\mathrm{m}}^{\mathrm{Ni_7Zr_2}} = 0.78 \cdot {}^{\circ}G_{\mathrm{Ni}}^{\gamma} + 0.22 \cdot {}^{\circ}G_{\mathrm{Zr}}^{\beta} + \Delta G_{\mathrm{Ni_7Zr_2}}^{f}, \tag{7}$$

where $\Delta G_{\mathrm{Ni_7Zr_2}}^{f}$ is the Gibbs energy of formation per mole of formula unit of the compound, and is expressed by the following equation:

$$\Delta G_{\mathrm{Ni_7Zr_2}}^{f} = A + B \cdot T. \tag{8}$$

The terms A and B correspond the enthalpy and entropy terms, respectively, and were evaluated in this study.

2.2 First-principles calculations

In this analysis, the solubility of the third element in the NiTi, $NiTi_2$, NiZr, and $NiZr_2$ binary compound phases in the Ni-Ti-Zr ternary system was taken into account based on experimental data. In addition, the ternary compound phase, NiTiZr (λ), with some range in homogeneity, is formed in this ternary system. In treating these phases using the sublattice model, the evaluation of the Gibbs energy parameters for metastable and/or unstable phases, as well as the stable phase, which are called 'end member' compounds, is required, as shown in eq. (5). However, there is little information available for the precise evaluation of the thermodynamic parameters of the metastable phases. Therefore, in this study, the energy of formation for some stable and metastable compound phases in the Ni-Ti-Zr system was obtained using first-principles calculations. The calculations were carried out using the WIEN2k software programme,[13] based on the Full Potential Linearized Augmented Plane Wave (FLAPW) method with a General Gradient Approximation (GGA).[14] Muffin-tin radii of 2.0 au (0.106 nm) for Ni, Ti, and Zr were assumed, and the value of $RK_{\max}$ was fixed at $RK_{\max} = 9.0$, which corresponds to the cut-off energy of almost 20 Ry (270 eV).

3. Results and Discussion

3.1 Nb-Ni-Ti ternary system

In this ternary system, a liquid phase (L), a bcc phase ((Nb,βTi)), an fcc phase ((Ni)), an hcp phase ((αTi)), five binary compounds, and five ternary compounds are known. The thermodynamic analysis of this ternary system has been carried out by the authors' group,[15] based on previous studies of the Nb-Ni,[16] Nb-Ti,[17] and Ni-Ti[18] binary systems, where all the ternary compounds with some range of homogeneity were treated as being stoichiometric phases. In this study, the assessed parameters were adopted, and are listed in Table 2.

3.2 Nb-Ni-Zr ternary system

This ternary system is composed of a liquid phase (L), a bcc phase ((Nb,βZr)), an fcc phase ((Ni)), an hcp phase ((αTi,αZr)), and ten binary compounds. No data on the ternary compound is available in the literature. The thermodynamic parameters of our previous assessment,[19] based on the thermodynamic descriptions of the Nb-Ni,[16] Nb-Zr,[20] and Ni-Zr[21] binary systems, were used in this study. The thermodynamic parameters of the Nb-Ni-Zr system are listed in Table 2.

3.3 Nb-Ti-Zr ternary system

Isothermal sections of the Nb-Ti-Zr ternary system have been reported by several authors[22–27] in the temperature range of 843 to 1373 K over the entire composition range. In

Table 2 The evaluated thermodynamic parameters in the Nb-Ni-Ti-Zr quaternary system.

System	Phase	Thermodynamic parameters (J/mol)	Reference
Nb-Ni	β	$L^{\beta}_{Nb,Ni} = -33500 + 10T$	15)
	γ	$L^{\gamma}_{Nb,Ni} = -70007.4 - 7.39665T + (x_{Nb} - x_{Ni}) \cdot (+96115 - 23.07497T)$ $T^{\gamma}_{C(Nb,Ni)} = -1200 + (x_{Nb} - x_{Ni}) \cdot (+760)$	
	$NbNi_3$	${}^{\circ}G^{NbNi_3}_{Nb:Nb} - {}^{\circ}G^{\beta}_{Nb} = +5000$ ${}^{\circ}G^{NbNi_3}_{Ni:Ni} - {}^{\circ}G^{\gamma}_{Ni} = +5000$ ${}^{\circ}G^{NbNi_3}_{Nb:Ni} - 0.25{}^{\circ}G^{\beta}_{Nb} - 0.75{}^{\circ}G^{\gamma}_{Ni} = -35300.6 + 4.83322T$ ${}^{\circ}G^{NbNi_3}_{Ni:Nb} - 0.25{}^{\circ}G^{\gamma}_{Ni} - 0.75{}^{\circ}G^{\beta}_{Nb} = +45300.575 - 4.83322T$ $L^{NbNi_3}_{Nb,Ni:Nb} = L^{NbNi_3}_{Nb,Ni:Ni} = -3079.625$ $L^{NbNi_3}_{Nb:Nb,Ni} = L^{NbNi_3}_{Ni:Nb,Ni} = +13505.625$	16)
	Nb_6Ni_7	${}^{\circ}G^{Nb_6Ni_7}_{Nb:Nb} - {}^{\circ}G^{\beta}_{Nb} = +9840$ ${}^{\circ}G^{Nb_6Ni_7}_{Nb:Ni} - 0.4615{}^{\circ}G^{\beta}_{Nb} - 0.5385{}^{\circ}G^{\gamma}_{Ni} = -22770 + 0.305T$ $L^{Nb_6Ni_7}_{Nb:Nb,Ni} = +6850 + (y^{1}_{Nb} - y^{1}_{Ni}) \cdot (+26460)$	15)
	L	$L^{L}_{Nb,Ni} = -80037.3 - 6.31498T + (x_{Nb} - x_{Ni}) \cdot (+97884.9 - 19.01069T) + (x_{Nb} - x_{Ni})^2 \cdot (+10000)$	16)
Nb-Ti	α	$L^{\alpha}_{Nb,Ti} = +13150$	17)
	β	$L^{\beta}_{Nb,Ti} = +8900$	
	L	$L^{L}_{Nb,Ti} = +3000$	
Nb-Zr	β	$L^{\beta}_{Nb,Zr} = +15911 + 3.35T + (x_{Nb} - x_{Zr}) \cdot (+3919 - 1.091T)$	20)
	αZr	$L^{\alpha Zr}_{Nb,Zr} = +24411$	
	L	$L^{L}_{Nb,Zr} = +10311 + (x_{Nb} - x_{Zr}) \cdot (+6709)$	
Ni-Ti	αTi	$L^{\alpha}_{Ni,Ti} = -20000$	18)
	β	$L^{\beta}_{Ni,Ti} = -97427.4 + 12.112T + (x_{Ni} - x_{Ti}) \cdot (-32315.3)$	
	γ	$L^{\gamma}_{Ni,Ti} = -130333.64 + 20.22423T + (x_{Ni} - x_{Ti}) \cdot (-46714.31)$ $T^{\gamma}_{C(Ni,Ti)} = -4670$	
	NiTi	${}^{\circ}G^{NiTi}_{Ni:Ni} - {}^{\circ}G^{\gamma}_{Ni} = {}^{\circ}G^{\beta}_{Ni} - {}^{\circ}G^{\gamma}_{Ni}$ ${}^{\circ}G^{NiTi}_{Va:Ni} - 0.5{}^{\circ}G^{\beta}_{Ni} = +81198.65 - 13.702875T$ ${}^{\circ}G^{NiTi}_{Va:Ti} - 0.5{}^{\circ}G^{\beta}_{Ti} = +39351.22 - 8.296145T$ ${}^{\circ}G^{NiTi}_{Ni:Ti} - 0.5{}^{\circ}G^{\beta}_{Ni} - 0.5{}^{\circ}G^{\beta}_{Ti} = -41847.43 + 5.40673T$ $L^{NiTi}_{Ni,Va:Ni} = L^{NiTi}_{Ni,Va:Ti} = -32012.19 + 13.247095T$ $L^{NiTi}_{Ni:Ni,Ti} = L^{NiTi}_{Va:Ni,Ti} = -72295.24 + 23.47071T + (y^{2}_{Ni} - y^{2}_{Ti}) \cdot (-24442.75)$	
	Ni_3Ti	${}^{\circ}G^{Ni_3Ti}_{Ni:Ni} - {}^{\circ}G^{\gamma}_{Ni} = {}^{\circ}G^{\alpha}_{Ni} - {}^{\circ}G^{\gamma}_{Ni}$ ${}^{\circ}G^{Ni_3Ti}_{Ti:Ti} - {}^{\circ}G^{\alpha Ti}_{Ti} = 0$ ${}^{\circ}G^{Ni_3Ti}_{Ni:Ti} - 0.75{}^{\circ}G^{\gamma}_{Ni} - 0.25{}^{\circ}G^{\alpha Ti}_{Ti} = -41421.96 + 7.35868T$ ${}^{\circ}G^{Ni_3Ti}_{Ti:Ni} - 0.25{}^{\circ}G^{\gamma}_{Ni} - 0.75{}^{\circ}G^{\alpha Ti}_{Ti} = -5688.27$ $L^{Ni_3Ti}_{Ni:Ni,Ti} = L^{Ni_3Ti}_{Ti:Ni,Ti} = +18274.75 - 16.21288T$ $L^{Ni_3Ti}_{Ni,Ti:Ni} = L^{Ni_3Ti}_{Ni,Ti:Ti} = +50000$	
	$NiTi_2$	${}^{\circ}G^{NiTi_2}_{Ni:Ti} - 0.333{}^{\circ}G^{\gamma}_{Ni} - 0.667{}^{\circ}G^{\alpha Ti}_{Ti} = -27514.2 + 2.85345T$	
	L	$L^{L}_{Ni,Ti} = -153707 + 34.8594T + (x_{Ni} - x_{Ti}) \cdot (-81824.8 + 25.8099T) + (x_{Ni} - x_{Ti})^2 \cdot (-10.0779T)$	
Ni-Zr	β	$L^{\beta}_{Ni,Zr} = -147500 + 2.3T + (x_{Ni} - x_{Zr}) \cdot (-43500 - 11.6T)$	21)
	γ	$L^{\gamma}_{Ni,Zr} = -130000 + 2T + (x_{Ni} - x_{Zr}) \cdot (-25000 + 2.5T)$	
	αZr	$L^{\alpha Zr}_{Ni,Zr} = -68350 + 3.5T + (x_{Ni} - x_{Zr}) \cdot (+10000 - 6.6T)$	
	NiZr	${}^{\circ}G^{NiZr}_{Ni:Zr} - 0.5{}^{\circ}G^{\gamma}_{Ni} - 0.5{}^{\circ}G^{\beta}_{Zr} = -52275 + 0.6T$	
	$NiZr_2$	${}^{\circ}G^{NiZr_2}_{Ni:Zr} - 0.333{}^{\circ}G^{\gamma}_{Ni} - 0.667{}^{\circ}G^{\beta}_{Zr} = -40650 + 0.15T$	
	Ni_3Zr	${}^{\circ}G^{Ni_3Zr}_{Ni:Va} - 0.75{}^{\circ}G^{\gamma}_{Ni} = +10000 + 1.25T$ ${}^{\circ}G^{Ni_3Zr}_{Zr:Zr} - {}^{\circ}G^{\alpha}_{Zr} = 0$ ${}^{\circ}G^{Ni_3Zr}_{Zr:Va} - 0.5{}^{\circ}G^{\beta}_{Zr} = +47425 + 5.68T$ ${}^{\circ}G^{Ni_3Zr}_{Ni:Zr} - 0.75{}^{\circ}G^{\gamma}_{Ni} - 0.25{}^{\circ}G^{\beta}_{Zr} = -43410 + 0.88T$ $L^{Ni_3Zr}_{Ni:Va,Zr} = -25000 + 4.5T$ $L^{Ni_3Zr}_{Ni,Zr:Va} = +75500$ $L^{Ni_3Zr}_{Ni,Zr:Zr} = +7555$	19)
	Ni_5Zr	${}^{\circ}G^{Ni_5Zr}_{Ni:Va} - 0.833{}^{\circ}G^{\gamma}_{Ni} = +29566 - 8.428T$ ${}^{\circ}G^{Ni_5Zr}_{Zr:Zr} - {}^{\circ}G^{\alpha Zr}_{Zr} = +7600 - 0.9T$ ${}^{\circ}G^{Ni_5Zr}_{Zr:Va} - 0.833{}^{\circ}G^{\beta}_{Zr} = +32493 - 8.22T$ ${}^{\circ}G^{Ni_5Zr}_{Ni:Zr} - 0.833{}^{\circ}G^{\gamma}_{Ni} - 0.167{}^{\circ}G^{\beta}_{Zr} = -33205 + 0.95T$ $L^{Ni_5Zr}_{Ni:Va,Zr} = -19475 + 1.25T$ $L^{Ni_5Zr}_{Ni,Zr:Va} = +76500$ $L^{Ni_5Zr}_{Ni,Zr:Zr} = +7850$	21)

continued on the next page

System	Phase	Thermodynamic parameters (J/mol)	Reference
	Ni_7Zr_2	${}^{\circ}G^{Ni_7Zr_2}_{Ni:Zr} - 0.78{}^{\circ}G^{\gamma}_{Ni} - 0.22{}^{\circ}G^{\beta}_{Zr} = -40775 + 0.3T$	
	$Ni_{10}Zr_7$	${}^{\circ}G^{Ni_{10}Zr_7}_{Ni:Va} - 0.575{}^{\circ}G^{\gamma}_{Ni} = +20051 - 5.8167T$ ${}^{\circ}G^{Ni_{10}Zr_7}_{Ni:Zr} - 0.575{}^{\circ}G^{\gamma}_{Ni} - 0.425{}^{\circ}G^{\beta}_{Zr} = -53000 + 1.75T$ ${}^{\circ}G^{Ni_{10}Zr_7}_{Zr:Va} - 0.575{}^{\circ}G^{\beta}_{Zr} = +22075 - 5.674T$	21)
		${}^{\circ}G^{Ni_{10}Zr_7}_{Zr:Zr} - {}^{\circ}G^{\beta}_{Zr} = +8750 - 2.556T$	19)
		$L^{Ni_{10}Zr_7}_{Ni:Va,Zr} = -19250$ $L^{Ni_{10}Zr_7}_{Ni,Zr:Va} = +56000$ $L^{Ni_{10}Zr_7}_{Ni,Zr:Zr} = +8500$	21)
	$Ni_{11}Zr_9$	${}^{\circ}G^{Ni_{11}Zr_9}_{Ni:Zr} - 0.55{}^{\circ}G^{\gamma}_{Ni} - 0.45{}^{\circ}G^{\beta}_{Zr} = -52000 + 0.74T$	19)
	$Ni_{21}Zr_8$	${}^{\circ}G^{Ni_{21}Zr_8}_{Ni:Zr} - 0.725{}^{\circ}G^{\gamma}_{Ni} - 0.275{}^{\circ}G^{\beta}_{Zr} = -44625 + 0.5T$	21)
	L	$L^{L}_{Ni,Zr} = -200450 + 10.35T + (x_{Ni} - x_{Zr}) \cdot (-42925 + 3.58T) + (x_{Ni} - x_{Zr})^2 \cdot (-34000 + 32.37T)$	
Ti-Zr	β	$L^{\beta}_{Ti,Zr} = -4346 + 5.489T$	
	αZr	$L^{\alpha Zr}_{Ti,Zr} = +5133$	29)
	L	$L^{L}_{Ti,Zr} = -968$	
Nb-Ni-Ti	β	$L^{\beta}_{Nb,Ni,Ti} = x_{Ti} \cdot (+100000)$	
	γ	$L^{\gamma}_{Nb,Ni,Ti} = x_{Nb} \cdot (+60000) + x_{Ni} \cdot (+60000) + x_{Ti} \cdot (+80000)$	
	NiTi	${}^{\circ}G^{NiTi}_{Nb:Ni} - 0.5{}^{\circ}G^{\beta}_{Nb} - 0.5{}^{\circ}G^{\beta}_{Ni} = {}^{\circ}G^{NiTi}_{Ni:Nb} - 0.5{}^{\circ}G^{\beta}_{Ni} - 0.5{}^{\circ}G^{\beta}_{Nb} = 0$ ${}^{\circ}G^{NiTi}_{Nb:Ti} - 0.5{}^{\circ}G^{\beta}_{Nb} - 0.5{}^{\circ}G^{\beta}_{Ti} = +10000$ ${}^{\circ}G^{NiTi}_{Nb:Nb} - {}^{\circ}G^{\beta}_{Nb} = +100000$ ${}^{\circ}G^{NiTi}_{Va:Nb} - 0.5{}^{\circ}G^{\beta}_{Nb} = 0$ $L^{NiTi}_{Ni:Nb,Ti} = -124750 + 85T$ $L^{NiTi}_{Ni:Nb,Ni,Ti} = -41350 - 50T$	15)
	$Nb_{15}Ni_{56}Ti_{29}$	${}^{\circ}G^{Nb_{15}Ni_{56}Ti_{29}}_{Nb:Ni:Ti} - 0.15{}^{\circ}G^{\beta}_{Nb} - 0.56{}^{\circ}G^{\gamma}_{Ni} - 0.29{}^{\circ}G^{\alpha Ti}_{Ti} = -40500 + 3.6T$	
	$Nb_8Ni_9Ti_3$	${}^{\circ}G^{Nb_8Ni_9Ti_3}_{Nb:Ni:Ti} - 0.4{}^{\circ}G^{\beta}_{Nb} - 0.45{}^{\circ}G^{\gamma}_{Ni} - 0.15{}^{\circ}G^{\alpha Ti}_{Ti} = -32000 + 2T$	
	$Nb_5Ni_{75}Ti_{20}$	${}^{\circ}G^{Nb_5Ni_{75}Ti_{20}}_{Nb:Ni:Ti} - 0.05{}^{\circ}G^{\beta}_{Nb} - 0.75{}^{\circ}G^{\gamma}_{Ni} - 0.2{}^{\circ}G^{\alpha Ti}_{Ti} = -43600 + 8.1T$	
	$Nb_{13}Ni_{75}Ti_{12}$	${}^{\circ}G^{Nb_{13}Ni_{75}Ti_{12}}_{Nb:Ni:Ti} - 0.13{}^{\circ}G^{\beta}_{Nb} - 0.75{}^{\circ}G^{\gamma}_{Ni} - 0.12{}^{\circ}G^{\alpha Ti}_{Ti} = -40900 + 5.4T$	
	$Nb_{15}Ni_{80}Ti_5$	${}^{\circ}G^{Nb_{15}Ni_{80}Ti_5}_{Nb:Ni:Ti} - 0.15{}^{\circ}G^{\beta}_{Nb} - 0.80{}^{\circ}G^{\gamma}_{Ni} - 0.05{}^{\circ}G^{\alpha Ti}_{Ti} = -35865 + 5T$	
	L	$L^{L}_{Nb,Ni,Ti} = x_{Ni} \cdot (-45000) + x_{Ti} \cdot (+160000)$	
Nb-Ni-Zr	L	$L^{L}_{Nb,Ni,Zr} = x_{Ni} \cdot (+240000)$	19)
Ni-Ti-Zr	NiTi	${}^{\circ}G^{NiTi}_{Zr:Zr} - {}^{\circ}G^{\beta}_{Zr} = +80$ ${}^{\circ}G^{NiTi}_{Va:Zr} - 0.5{}^{\circ}G^{\alpha}_{Zr} = +41400$ ${}^{\circ}G^{NiTi}_{Ni:Zr} - 0.5{}^{\circ}G^{\gamma}_{Ni} - 0.5{}^{\circ}G^{\alpha Zr}_{Zr} = -33770$ ${}^{\circ}G^{NiTi}_{Zr:Ni} - 0.5{}^{\circ}G^{\alpha Zr}_{Zr} - 0.5{}^{\circ}G^{\gamma}_{Ni} = -33770$ ${}^{\circ}G^{NiTi}_{Zr:Ti} - 0.5{}^{\circ}G^{\alpha Ti}_{Ti} - 0.5{}^{\circ}G^{\alpha Zr}_{Zr} = +10430$ $L^{NiTi}_{Ni:Ti,Zr} = -27000 + 5T + (y^2_{Ti} - y^2_{Zr}) \cdot (-16000 + 5T)$	
	$NiTi_2$	${}^{\circ}G^{NiTi_2}_{Ni:Zr} - 0.333{}^{\circ}G^{\gamma}_{Ni} - 0.667{}^{\circ}G^{\alpha Zr}_{Zr} = -21000$ $L^{NiTi_2}_{Ni:Ti,Zr} = -26000$	
	NiZr	${}^{\circ}G^{NiZr}_{Ni:Ti} - 0.5{}^{\circ}G^{\gamma}_{Ni} - 0.5{}^{\circ}G^{\alpha Ti}_{Ti} = -38700 + 10T$ $L^{NiZr}_{Ni:Ti,Zr} = +12500$	
	$NiZr_2$	${}^{\circ}G^{NiZr_2}_{Ni:Ti} - 0.333{}^{\circ}G^{\gamma}_{Ni} - 0.667{}^{\circ}G^{\alpha Ti}_{Ti} = -26120 + 5T$ $L^{NiZr_2}_{Ni:Ti,Zr} = -2000$	Present Work
	λ	${}^{\circ}G^{\lambda}_{Ti:Ni} - 0.333{}^{\circ}G^{\alpha Ti}_{Ti} - 0.667{}^{\circ}G^{\gamma}_{Ni} = -27700$ ${}^{\circ}G^{\lambda}_{Zr:Ti} - 0.333{}^{\circ}G^{\alpha Zr}_{Zr} - 0.667{}^{\circ}G^{\alpha Ti}_{Ti} = +17000$ ${}^{\circ}G^{\lambda}_{Zr:Ni} - 0.333{}^{\circ}G^{\alpha Ti}_{Zr} - 0.667{}^{\circ}G^{\gamma}_{Ni} = -38100$ ${}^{\circ}G^{\lambda}_{Ti:Ti} - {}^{\circ}G^{\alpha Ti}_{Ti} = +44000$ $L^{\lambda}_{Ti:Ni,Ti} = +60000$ $L^{\lambda}_{Ti,Zr:Ti} = -15000$ $L^{\lambda}_{Ti,Zr:Ni} = +10000$ $L^{\lambda}_{Zr:Ni,Ti} = -132000 + 35T + (y^2_{Ni} - y^2_{Ti}) \cdot (+66000 - 30T)$ $L^{\lambda}_{Ti,Zr:Ni,Ti} = -200000 + 20T$	
	L	$L^{L}_{Ni,Ti,Zr} = x_{Ni} \cdot (-50000) + x_{Ti} \cdot (+40000) + x_{Zr} \cdot (+40000)$	

addition, the liquidus surface[27] and the solidus surface[28] projections have been investigated over the entire composition range. Previous studies indicated that the bcc miscibility gap (β#1 + β#2) in the Nb-Zr binary system extended into the ternary system, and that no ternary compound formed. Hence, this ternary system is composed of solution phases only: the liquid phase, the bcc phase ((Nb,βTi,βZr)), and the hcp phase ((αTi,αZr)). Although the compositions of the constituent phases in both the (β#1 + β#2) two phase region and the tie triangle between the β#1, β#2, and (αTi,αZr)

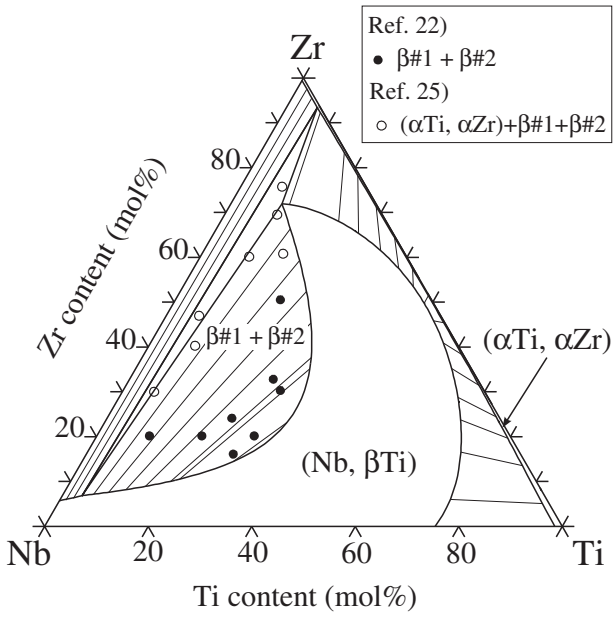

Fig. 1 (a) Calculated and (b) experimental isothermal section diagrams of the Nb-Ti-Zr system at 843 K.

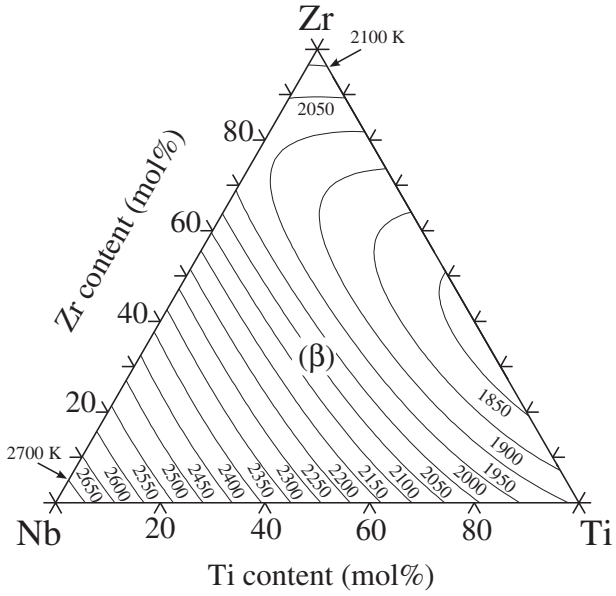

Fig. 2 Calculated liquidus surface projection in the Nb-Ti-Zr system.

phases were not in agreement in the reported data, the phase relationships were well determined.

Thermodynamic modelling of this ternary system has been carried out using a simple ternary extrapolation,[29] based on the Nb-Ti,[17] Nb-Zr,[20] and Ti-Zr[29] binary systems. In this modelling, the same parameters as those used in previous modelling were used. The thermodynamic parameters are listed in Table 2.

The calculated isothermal section diagram of the Nb-Ti-Zr ternary system at 843 K is shown in Fig. 1, together with the experimental data.[22,25] Figure 2 shows the calculated liquidus surface projection of the Nb-Ti-Zr system.

3.4 Ni-Ti-Zr ternary system

An isothermal section of this ternary system has been investigated in the composition region below 50 mol%Ni at 973 K.[30,31] The phase equilibria in the $NiTi_2$-$NiZr_2$[31,32] and NiTi-NiZr[33] sections have been studied using X-ray diffraction (XRD), electron probe microanalysis (EPMA), and differential thermal analysis (DTA). Investigations into the Ni_3Ti-Ni_3Zr section have also been carried out.[34,35] These experimental data on the Ni-Ti-Zr ternary system has been critically reviewed by Gupta.[36] According to the experimental results, the solubility of Ti in both the $NiZr_2$ and NiZr phases reaches about 5 mol% at 973 K. The $NiTi_2$ and NiTi phases dissolve about 9 mol%Zr and 30 mol%Zr at 973 K, respectively. The extensions of the Ni_3Ti and Ni_3Zr phases into the ternary system were found to be about 3 mol%Zr and 2 mol%Ti at 1173 K, respectively. With regard to the ternary compound phase, a $MgZn_2$-type Laves phase, NiTiZr(λ), and $Ni_3(Ti_{0.67}Zr_{0.33})$ with a $BaPb_3$-type structure, were found to form. The reported homogeneity ranges for NiTiZr (λ) were found to be in good agreement in the experimental investigations, whereas whether the NiTiZr (λ) melts congruently was not clarified, and a discrepancy in temperature range of stability of $Ni_3(Ti_{0.67}Zr_{0.33})$ was found.

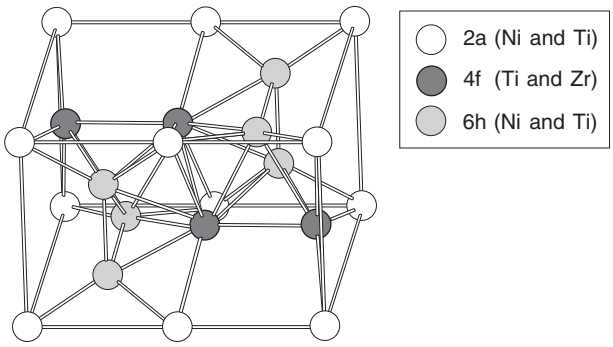

Fig. 3 Crystal structure for NiTiZr(λ) with a $MgZn_2$-type structure.

In our analysis, the solid solubility of the third element in NiTi, NiZr, $NiTi_2$, and $NiZr_2$ was taken into account, and the Gibbs energy was described using sublattices with the formulae $(Ni,Va,Zr)_{0.5}(Ni,Ti,Zr)_{0.5}$, $(Ni)_{0.5}(Ti,Zr)_{0.5}$, $(Ni)_{0.333}(Ti,Zr)_{0.667}$, and $(Ni)_{0.333}(Ti,Zr)_{0.667}$, respectively. The other binary compounds were treated as being pure binary phases due to either negligible solubility of the third element or due to a lack of experimental information. In regard to the ternary NiTiZr(λ) phase, a detailed structural investigation using neutron diffraction has revealed that the 2a and 6h sites were occupied by both Ni and Ti atoms, whereas 4f site was occupied by Ti and Zr atoms in the unit cell shown in Fig. 3, and hence, the formula $(Ti,Zr)_{0.333}(Ni,Ti)_{0.167}(Ni,Ti)_{0.5}$ for the sublattice model was proposed.[37] However, in our modelling, the formula $(Ti,Zr)_{0.333}(Ni,Ti)_{0.667}$ was applied to reduce the thermodynamic parameters to be evaluated and to maintain consistency with other thermodynamic modelling of the Laves phases. The another ternary compound, $Ni_3(Ti_{0.67}Zr_{0.33})$, was not considered in our work, because both the temperature range of stability and the phase equilibria with the other phases have not been clarified. The thermodynamic analysis was carried out based on the experimental data of Eremenko *et al.*[30,31,33] and our first-principles calculations. The calculated energy of formation for the various compounds in the

Table 3 The calculated energy of formation for various compounds in the Ni-Ti-Zr ternary system.

Phase	Compound	Energy of formation (kJ/mol)
NiTi	$(Va)_{0.5}Zr_{0.5}$	+82.8
	$Ti_{0.5}Zr_{0.5}$	+10.4
	$Ni_{0.5}Zr_{0.5}$	−33.8
NiZr	$Ni_{0.5}Ti_{0.5}$	−38.7
$NiZr_2$	$Ni_{0.333}Ti_{0.667}$	−26.1
NiTiZr(λ)	$Ni_{0.333}Ti_{0.667}$	+31.8
	$Ti_{0.333}Ni_{0.667}$	−27.2
	$Zr_{0.333}Ni_{0.667}$	−38.1
	$Zr_{0.333}Ti_{0.667}$	+17.0
	$Ti_{0.333}Ti_{0.667}$	+44.0

Ni-Ti-Zr ternary system is listed in Table 3. Each value is referred to as fcc Ni, hcp Ti, and hcp Zr, and thus the term A in eq. (8) corresponds to the calculated energy of formation listed in Table 3. The thermodynamic parameters evaluated in this study are listed in Table 2.

The calculated isothermal section diagram at 973 K is shown in Fig. 4, together with the experimental diagram.[31] A comparison of the calculated and experimental results shows that the calculated diagram reproduces the experimental phase relationships. However, the composition ranges for NiTi and NiTiZr(λ) are narrower than those determined experimentally. Although a larger solid solubility of Zr in NiTi could be attained by introducing a more negative interaction parameter, the NiTiZr(λ) phase would disappear from the phase diagram due to the increased phase stability of NiTi. However, the phase stability of NiTiZr(λ) was well determined based on the energy of formation of $ZrNi_2$, $Zr(Ni_{2/8}Ti_{6/8})_2$, and $ZrTi_2$, listed in Table 3. Thus, further experimental study is required to determine the solid solubility of Zr in NiTi. With regard to the composition range of NiTiZr(λ), an extension of NiTiZr(λ) towards $NiTi_2$ has been observed experimentally. On the other hand, although the formula for the Laves phase used in our modelling could not be used to describe its behaviour, the energy of formation of the hypothetical Laves phase $NiTi_2$ was calculated to be 31.8 kJ/mol, and thus this parameter is unlikely to allow the NiTiZr(λ) phase to extend towards the composition range of $NiTi_2$. Figure 5 shows the calculated isopleths at the 33.3 mol%Ni and 50 mol%Ni sections, along with the experimental data obtained from DTA experiments. Such a comparison shows that the calculated liquidus temperatures at the 33.3 mol%Ni section agree well with the experimental data,[31,32] whereas the calculated results at the 50 mol%Ni section are lower than the experimental values.[33] The reason for this discrepancy is not clear, and the thermodynamic parameters used could not reproduce both the experimental isothermal section and the isopleth at 50 mol%Ni. The calculated liquidus surface projection of the Ni-Ti-Zr system is shown in Fig. 6. The liquidus surface was composed of 14 ternary invariant reactions, and these points are summarized in the data shown in Table 4. Except for Points E1, U1, and U7, the invariant reactions occurred at relatively low temperature when compared with the melting points of the constituent elements.

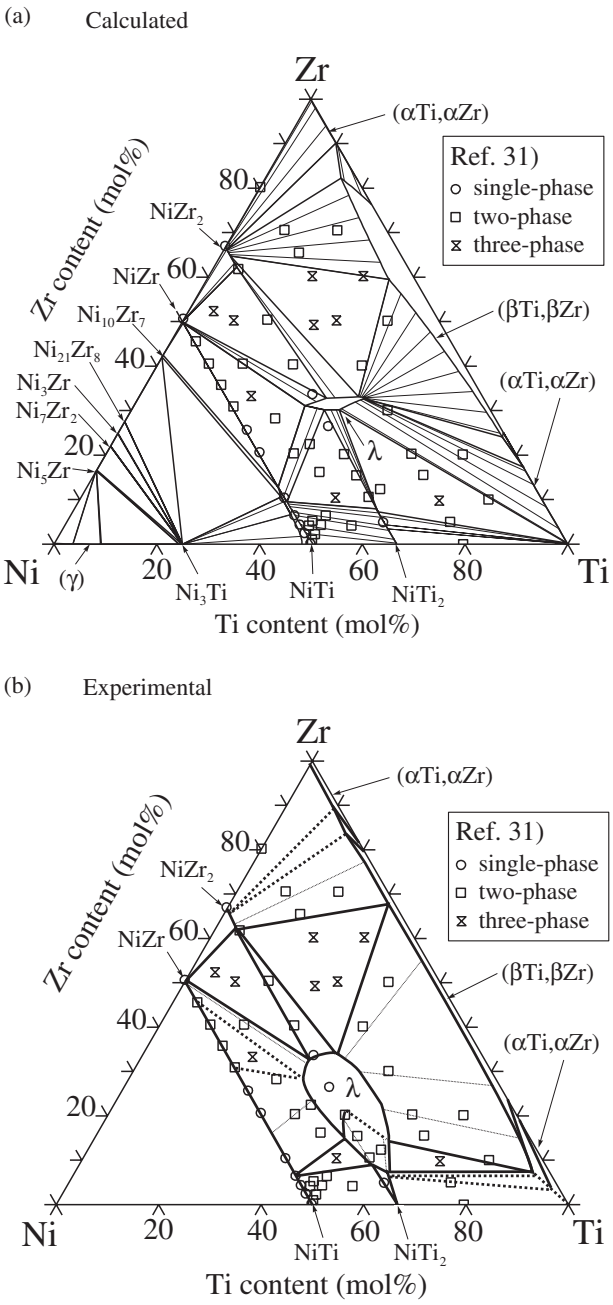

Fig. 4 (a) Calculated and (b) experimental isothermal section diagrams of the Ni-Ti-Zr system at 973 K.

3.5 Nb-Ni-Ti-Zr quaternary system

There is no experimental information on the phase equilibria in the Nb-Ni-Ti-Zr quaternary system. However, the prediction of this quaternary phase diagram is of interest for the development of hydrogen energy-related alloys, as described in the introduction to this paper. In general, the glass-forming ability of alloys is related to the liquidus temperature, and amorphous or glassy alloys are formed in the composition ranges that have relatively low liquidus temperature. Thus, information on the phase equilibria involving the liquid phase is useful.

Figure 7 shows the liquidus surface projection in the alloy composition range $Nb_{40-x-y}Ni_{60}Ti_xZr_y$, in which a metallic glass is formed over a wide composition range.[38] According

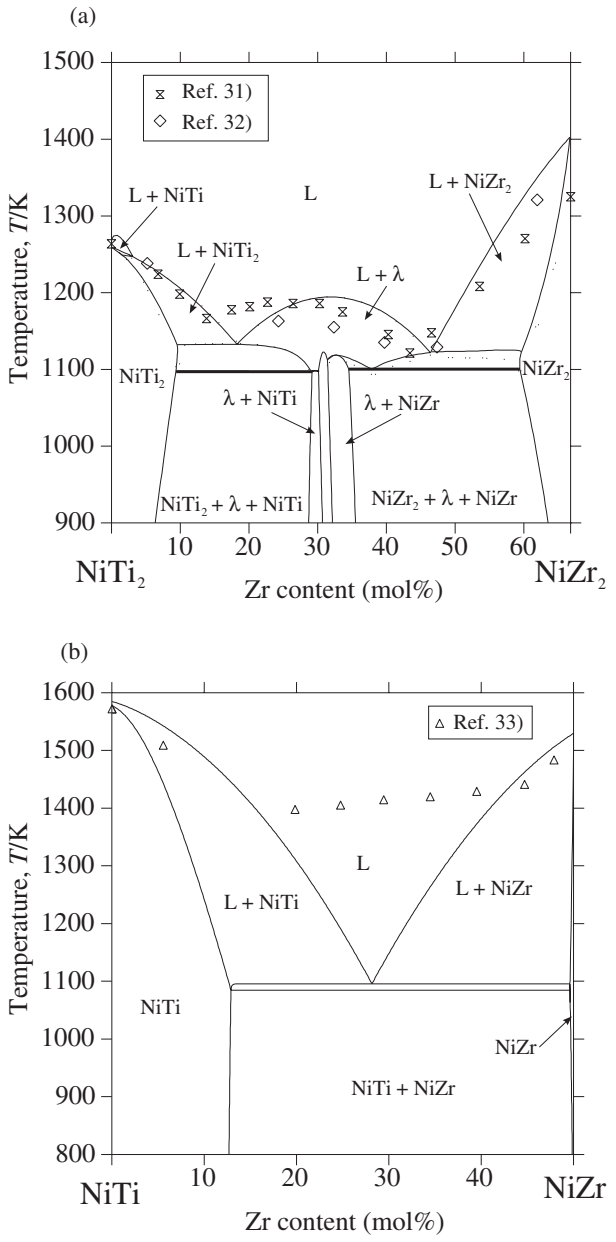

Fig. 5 Calculated isopleths of the Ni-Ti-Zr system at the: (a) 33.3 mol%Ni and (b) 50 mol%Ni sections.

Table 4 The invariant reaction points of the calculated liquidus surface projection in the Ni-Ti-Zr system.

Type	Reaction	Temperature (K)	Composition of liquid phase (mol%)	
			Ti	Zr
E_1	$L \Leftrightarrow (\gamma) + Ni_3Ti + Ni_5Zr$	1335	9.4	7.7
E_2	$L \Leftrightarrow NiTi + Ni_3Ti + Ni_{10}Zr_7$	973	18.9	20.1
E_3	$L \Leftrightarrow NiTi + NiZr + Ni_{10}Zr_7$	1085	20.1	27.4
E_4	$L \Leftrightarrow NiTi + NiZr + \lambda$	1055	26.1	29.0
E_5	$L \Leftrightarrow NiZr + NiZr_2 + \lambda$	1100	18.5	45.1
E_6	$L \Leftrightarrow (\beta) + NiZr_2 + \lambda$	1098	21.8	53.0
E_7	$L \Leftrightarrow NiTi + NiTi_2 + \lambda$	1098	40.2	20.6
U_1	$L + Ni_7Zr_2 \Leftrightarrow Ni_3Ti + Ni_5Zr$	1339	9.6	8.1
U_2	$L + Ni_7Zr_2 \Leftrightarrow Ni_3Ti + Ni_3Zr$	1132	15.7	19.0
U_3	$L + Ni_7Zr_2 + Ni_{21}Zr_8 \Leftrightarrow Ni_3Zr$	1136	13.6	20.8
U_4	$L + Ni_3Zr \Leftrightarrow Ni_3Ti + Ni_{21}Zr_8$	1118	15.8	19.2
U_5	$L + Ni_{21}Zr_8 \Leftrightarrow Ni_3Ti + Ni_{10}Zr_7$	986	18.0	20.4
U_6	$L + (\beta) \Leftrightarrow NiTi_2 + \lambda$	1134	50.3	17.5
U_7	$L + Ni_{11}Zr_9 \Leftrightarrow NiZr + Ni_{10}Zr_7$	1267	11.4	33.9

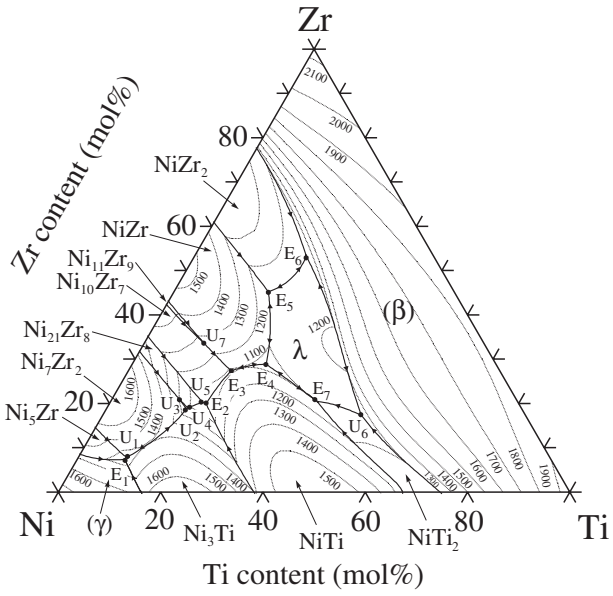

Fig. 6 Calculated liquidus surface projection in the Ni-Ti-Zr system.

to our calculations, the liquidus temperature decreases with increasing Zr content up to 20 mol%Zr. Although there is no comparative information, it is interesting that the compositional range corresponding to a low liquidus temperature is consistent with the experimental region showing a high glass-forming ability.[38)]

The glass-forming ability of various alloys has been evaluated by coupling the Davies-Uhlmann kinetic formulations[39,40)] with the CALPHAD approach.[41)] In the computations, time-temperature-transformation (TTT) curves were obtained utilizing the driving force for crystallization derived from the thermodynamic calculations, and the critical cooling rates could be calculated from the TTT curves. Therefore, the Gibbs energy functions formulated in this study enable us to evaluate the glass-forming ability of Nb-Ni-Ti-Zr alloys quantitatively.

4. Conclusions

A thermodynamic analysis of the constituent ternary systems constructing the Nb-Ni-Ti-Zr quaternary system has been carried out, and the phase equilibria in the Nb-Ni-Ti-Zr quaternary system were studied using the thermodynamic descriptions of four ternary systems. The parameters used in our previous evaluations were adopted for the thermodynamic descriptions of the Nb-Ni-Ti and Nb-Ni-Zr ternary systems. The results are summarized as follows:

(1) The phase equilibria in the Nb-Ti-Zr ternary system could be calculated using a simple extrapolation of the constituent binary systems with no additional ternary parameters.

(2) The thermodynamic parameters for NiTi, $NiTi_2$, NiZr,

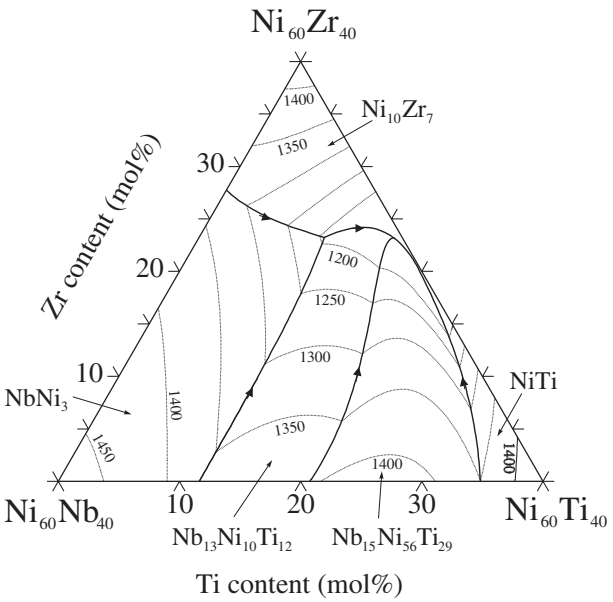

Fig. 7 Calculated liquidus surface projection in the composition range of $Nb_{40-x-y}Ni_{60}Ti_xZr_y$ alloys.

$NiZr_2$, and NiTiZr(λ) were evaluated using first-principles calculations as well as the experimental data on the phase boundaries. The calculated phase diagrams of the Ni-Ti-Zr ternary system agree well with the available experimental data.

(3) The calculated liquidus surface of the Nb-Ni-Ti-Zr quaternary system in the composition range $Nb_{40-x-y}Ni_{60}Ti_xZr_y$ showed that the liquidus temperature decreases with Zr content up to about 20 mol%Zr.

Acknowledgement

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