Experimental Investigation of Isothermal Sections (1000, 1200 °C) in the Ni-Ti-Zr System

X.J. Liu, L. Huang, S.Y. Yang, Y.X. Huang, J.B. Zhang, J. Li, J.H. Zhu, H.X. Jiang, and C.P. Wang

(Submitted November 17, 2014; in revised form April 6, 2015; published online July 25, 2015)

The phase equilibria of the Ni-Ti-Zr ternary system at 1000 and 1200 °C have been experimentally investigated by back-scattered electron, electron probe microanalyzer and x-ray diffraction. In the present study, the established isothermal sections were characterized by a series of binary phases, ternary compounds and solid solutions. The results show that nine three-phase regions and one liquid region at 1000 °C, whereas, four three-phase regions and one liquid region at 1200 °C were experimentally confirmed.

Keywords electron microprobe, microstructure, phase diagrams, ternary alloy systems

1. Introduction

The Ni-Ti alloys are widely used as corrosion-resisting and high-temperature materials. As shape memory alloys (SMAs), Ni-Ti alloys are the most feasible from the view point of the best combination of material properties, e.g. the maximum recoverable strain, excellent corrosion resistance and the best biocompatibility.^[1] These materials have been widely used in robotic, automotive, aerospace, etc., industries. However, due to the fact that the shape memory effect (SME) of unalloyed TiNi occurs in narrow temperature range from 40 to 60 °C, some applications of these alloys have been greatly limited.^[2] Therefore, control of transformation temperatures of NiTi-based shape memory alloys is an important research subject to enhance the reliability and applicability of these functional materials.^[3–7] For this reason, materials scientists have managed to develop NiTi-based alloys with higher martensitic transformation temperature.^[8] Furthermore, experiments have shown that with a small addition of Zr, the martensitic transformation temperature decreases. However, when the concentration of the alloying element Zr exceeds 10 at.%, the martensitic transformation temperature increases to as high as 170 °C for 20.2 at.% Zr.^[9–11] However, similar to all other HTSMAs, the Ni-Ti-Zr alloys suffer from poor mechanical properties, which makes the practical application of these alloys difficult.^[12]

When dealing with the Ni-Ti-Zr alloys as potential structural or functional materials, its accurate phase equilibrium information is especially required in order to design and optimize alloy composition. In previous investigations, Eremenko studied the part of the isothermal section of the Ni-Ti-Zr system at 700 °C.^[13] Gupta published a review paper for this system.^[14] The isothermal section at 800 °C had been constructed by Yeh.^[15] However, there is still lack of the isothermal section data at high temperature. In the present work, the phase equilibria of the Ni-Ti-Zr system at 1000 and 1200 °C were experimentally determined using a combined method of electron probe microanalyzer (EPMA), x-ray diffraction (XRD) and differential scanning calorimetry (DSC). The obtained results are expected to get a better understanding of microstructures in the Ni-Ti-Zr alloys.

In this study, three binary systems Ni-Zr, Ni-Ti and Ti-Zr were adopted and shown in Fig. 1. The Ni-Zr binary system is based primarily on the work of Okamoto^[16], which consisted of eight intermediate phases, Ni₅Zr, Ni₇Zr₂, Ni₃Zr, Ni₂₁Zr₈, Ni₁₀Zr₇, Ni₁₁Zr₉, NiZr and NiZr₂. The Ni-Ti binary phase diagram was edited by Bellen.^[17] Three intermediate phases exist: Ti₂Ni, TiNi and TiNi₃. The Ti-Zr binary phase diagram provided by Kumar is an isomorphous system^[18], with a solidus and liquidus minimum of 1540 °C with ~40 at.% Zr and solid transformation minimum of 605 °C with ~52 at.% Zr. The stable solid phases and their crystal structures in the three binary systems in Ni-Ti-Zr ternary system are listed in Table 1.

2. Experimental Procedure

The alloys were produced using pure metals of nickel (99.8 wt.%), titanium (99.9 wt.%) and zirconium (99.9 wt.%) as the raw materials. Bulk alloy buttons were prepared from pure elements by arc melting under a high purity argon atmosphere using a non-consumable tungsten electrode. The buttons were turned over and remelted no less than four times to achieve homogeneity.

Afterwards, each ingot was cut into small pieces by wire-cutting machine for heat treatment and further observations.

X.J. Liu, S.Y. Yang, Y.X. Huang, J.B. Zhang, and C.P. Wang, Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, P.R. China and Research Center of Materials Design and Applications, Xiamen University, Xiamen 361005, P.R. China; and L. Huang, J. Li, J.H. Zhu, and H.X. Jiang, Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, P.R. China. Contact e-mail: wangcp@xmu.edu.cn.

Fig. 1 Binary phase diagrams constituting the Ni-Ti-Zr ternary system [16-18]

Table 1 The stable solid phases in three binary systems

System	Phase	Pearson's symbol	Prototype	Space group	Strukturbericht	References
Ni-Ti	$\beta(\text{Ti})$	<i>Ci2</i>	W	<i>Im-3m</i>	<i>A2</i>	[17]
	$\alpha(\text{Ti})$	<i>Hp2</i>	Mg	<i>P6₃/mmc</i>	<i>A3</i>	[17]
	Ti_2Ni	<i>CF96</i>	CFe_3W_3	<i>Fd-3m</i>	...	[17]
	TiNi	<i>cP2</i>	CsCl	<i>Pm-3m</i>	<i>B2</i>	[17]
	TiNi_3	<i>hP16</i>	Ni_3Ti	<i>P6₃/mmc</i>	<i>DO₂₄</i>	[17]
Ni-Zr	(Ni)	<i>CF4</i>	Cu	<i>Fd-3m</i>	<i>A1</i>	[17]
	(Ni)	<i>CF4</i>	Cu	<i>Fm-3m</i>	<i>A1</i>	[16]
	Ni_5Zr	<i>CF24</i>	AuBe_5	<i>F3m</i>	<i>C15_b</i>	[16]
	Ni_7Zr_2	<i>Mc36</i>	Ni_7Zr_2	<i>C2/m</i>	...	[16]
	Ni_3Zr	<i>Hp8</i>	Ni_3Sn	<i>P6₃/mmc</i>	<i>DO₁₉</i>	[16]
	$\text{Ni}_{21}\text{Zr}_8$	<i>ap29</i>	$\text{Hf}_8\text{Ni}_{21}$	...	...	[16]
	$\text{Ni}_{10}\text{Zr}_7$	<i>Oc68</i>	$\text{Ni}_{10}\text{Zr}_7$	<i>Aba2</i>	<i>C2ca</i>	[16]
	$\text{Ni}_{11}\text{Zr}_9$	<i>tI40</i>	$\text{Pt}_{11}\text{Zr}_9$	<i>I4/m</i>	...	[16]
	NiZr	<i>Oc8</i>	CrB	<i>Cmcm</i>	<i>B_f</i>	[16]
	NiZr_2	<i>tI12</i>	Al_2Cu	<i>I4/mcm</i>	<i>C16</i>	[16]
Ti-Zr	$\beta(\text{Zr})$	<i>Ci2</i>	W	<i>Im-3 m</i>	<i>A2</i>	[16]
	$\alpha(\text{Ti, Zr})$	<i>Hp2</i>	Mg	<i>P6₃/mmc</i>	<i>A3</i>	[18]
	$\beta(\text{Ti, Zr})$	<i>Ci2</i>	W	<i>Im-3 m</i>	<i>A2</i>	[18]

All samples were sealed in quartz capsules that are evacuated and backfilled with argon gas. The specimens were annealed at 1000 and 1200 °C, respectively. On the basis of the temperature and composition of the specimen, time of the heat treatment varied from several hours to several days. At the end of the heat treatment, the specimens were quenched into ice water.

Compositions of the phases were determined using EPMA (JXA-8100, JEOL, Japan). Pure elements were used

as standards and the measurements were carried out at a voltage of 20 kV and a current of 20 nA. Microprobe measurements for each equilibrium phase were taken on seven points to get high accuracy. The constituent phases of the alloys were further determined by analyzing XRD patterns generated by a Philips PANalytical X-pert diffractometer, operating at 40.0 kV and 30 mA with Cu K α radiation. The data were collected in the range of 2 θ from 20° to 90° at a step size of 0.0167°. The phase

Fig. 2 Typical ternary BSE images obtained from: (a) $\text{Ni}_{10}\text{Ti}_{88}\text{Zr}_2$ (at.%) alloy annealed at 1000 °C for 12 h; (b) $\text{Ni}_{73}\text{Ti}_9\text{Zr}_{18}$ (at.%) alloy annealed at 1000 °C for 188 h; (c) $\text{Ni}_{46}\text{Ti}_{12}\text{Zr}_{42}$ (at.%) alloy annealed at 1200 °C for 24 h; (d) $\text{Ni}_{77}\text{Ti}_5\text{Zr}_{18}$ (at.%) alloy annealed at 1000 °C for 188 h; (e) $\text{Ni}_{91}\text{Ti}_3\text{Zr}_6$ (at.%) alloy annealed at 1200 °C for 12 h; (f) $\text{Ni}_{80}\text{Ti}_4\text{Zr}_{16}$ (at.%) alloy annealed at 1200 °C for 188 h

Fig. 3 X-ray diffraction patterns obtained from: (a) $\text{Ni}_{91}\text{Ti}_3\text{Zr}_6$ (at.%) alloy annealed at 1000 °C for 188 h; (b) $\text{Ni}_{80}\text{Ti}_4\text{Zr}_{16}$ (at.%) alloy annealed at 1000 °C for 188 h

transformation temperature was determined using DSC (DSC-404C, NETZSCH, Germany) test. And the measurements were conducted using small pieces of specimens ranging from 18 to 44 mg with a heating and cooling rate of 20 °C/min in a flowing argon atmosphere with sintered Al_2O_3 as reference.

3. Results and Discussion

3.1 Microstructure

Back-scattered electron (BSE) images of typical ternary Ni-Ti-Zr alloys are shown in Fig. 2(a-f). Phase identification is based on the equilibrium composition measured by EPMA and crystal structure determined by XRD analysis. In this study, liquid phase is denoted as L.

The BSE micrograph of the $\text{Ni}_{10}\text{Ti}_{88}\text{Zr}_2$ (at.%) alloy annealed at 1000 °C for 12 h is showed in Fig. 2(a), where two different phases are distinguished. The result of EPMA suggests that the grey phase is $\beta(\text{Ti}, \text{Zr})$ and the white one is liquid. In addition, the microstructure of $\text{Ni}_{73}\text{Ti}_9\text{Zr}_{18}$ (at.%)

alloy annealed at 1000 °C for 188 h is shown in Fig. 2(b), where there exists a two-phase equilibrium ($\text{TiNi}_3 + \text{Ni}_{21}\text{Zr}_8$). For the $\text{Ni}_{46}\text{Ti}_{12}\text{Zr}_{42}$ (at.%) alloy quenched from 1000 °C, three-phase microstructure is observed, as showed in Fig. 2(c). EPMA result indicates that the grey phase is TiNi, the white one is NiZr, while the other one is liquid. Figure 2(d) shows two-phase microstructure of the $\text{Ni}_{77}\text{Ti}_5\text{Zr}_{18}$ (at.%) alloy, in which the dark phase is TiNi_3 and the pale one is Ni_7Zr_2 . BSE image of the $\text{Ni}_{91}\text{Ti}_3\text{Zr}_6$ (at.%) alloy annealed at 1200 °C for 12 h is presented in Fig. 2(e), showing coexistence of two phases consisted of (Ni) + liquid. Three-phase microstructure of the $\text{TiNi}_3 + \text{Ni}_5\text{Zr} + \text{Ni}_7\text{Zr}_2$ of the $\text{Ni}_{80}\text{Ti}_4\text{Zr}_{16}$ (at.%) alloy annealed at 1200 °C for 188 h is shown in Fig. 2(f).

Figure 3(a) shows the XRD result of $\text{Ni}_{91}\text{Ti}_3\text{Zr}_6$ alloy annealed at 1000 °C for 188 h, a two-phase microstructure of ((Ni) + Ni_5Zr) is substantiated. The XRD result of $\text{Ni}_{80}\text{Ti}_4\text{Zr}_{16}$ alloy annealed at 1000 °C for 188 h is provided in Fig. 3(b), in which the characteristic peaks of the TiNi_3 , Ni_5Zr and Ni_7Zr_2 phases are observed. These results are consistent with their BSE images.

3.2 Isothermal Sections

The equilibrium compositions of the Ni-Ti-Zr ternary system at 1000 and 1200 °C determined by EPMA are summarized in Tables 2 and 3. Based on the experimental data mentioned above, two isothermal sections at 1000 and 1200 °C have been constructed as presented in Fig. 4(a) and (b), respectively. Undetermined three-phase equilibria in Fig. 4(a-b) are labeled in the dashed lines. The phase transformations are examined by the method of DSC and the results are shown in Fig. 5.

From Fig. 4(a), it can be seen that nine three-phase regions and one liquid region at 1000 °C were experimentally confirmed. According to this study, the liquid region at 1000 °C are similar to liquidus surface containing up to 50% Ni reported from Eremenko.^[19] Figure 5 shows the DSC heating curves of the $\text{Ni}_{24}\text{Ti}_{50}\text{Zr}_{26}$ (at.%), $\text{Ni}_{24}\text{Ti}_{45}\text{Zr}_{31}$ (at.%) and $\text{Ni}_{30}\text{Ti}_{20}\text{Zr}_{50}$ (at.%) alloy. The DSC results are used to determine solid $\leftrightarrow$ liquid transition temperatures. For (a) $\text{Ni}_{24}\text{Ti}_{50}\text{Zr}_{26}$ (at.%) and (b) $\text{Ni}_{24}\text{Ti}_{45}\text{Zr}_{31}$ (at.%) alloy in Fig. 5, endothermic peaks appearing at 847 and 826 °C respectively identified to be associated with the transition of the ternary phase $\text{Ni}(\text{Ti}, \text{Zr})_2 \leftrightarrow \text{liquid} + \text{Ni}(\text{Ti}, \text{Zr})_2$, the inconspicuous transition which correspond to $\text{Ni}(\text{Ti}, \text{Zr})_2 \leftrightarrow \text{liquid}$, is measured to start at 888 and 887 °C respectively during the heating process. From Fig. 5, it is clear that three transformation peaks appear at 795, 826 and 864 °C in the heating curve of (c) $\text{Ni}_{30}\text{Ti}_{20}\text{Zr}_{50}$ (at.%) alloy. The three peaks correspond to the follow transitions, respectively, $\text{Ni}(\text{Ti}, \text{Zr})_2 + \text{NiZr} \leftrightarrow \text{liquid} + \text{Ni}(\text{Ti}, \text{Zr})_2 + \text{NiZr}$, $\text{liquid} + \text{Ni}(\text{Ti}, \text{Zr})_2 + \text{NiZr} \leftrightarrow \text{liquid} + \text{NiZr}$ and $\text{liquid} + \text{NiZr} \leftrightarrow \text{liquid}$. Therefore, the liquid region <50 at.% Ni is given in

Table 2 All phase equilibria and related equilibrium compositions of the Ni-Ti-Zr ternary system at 1000 °C determined in the present work

T, (°C)	Alloy, at. %	Annealed time, h	Phase equilibria	Composition, at. %								
				Phase 1			Phase 2			Phase 3		
				Ti	Zr		Ti	Zr		Ti	Zr	
1000	Ni ₁₆ Ti ₄₀ Zr ₄₄	24	β(Ti,Zr)/L	48.5	49.8		36.5	42.1		...	...	
	Ni ₆₀ Ti ₃₅ Zr ₅	188	NiTi/TiNi ₃	39.0	7.2		23.6	1.3		...	...	
	Ni ₁₂ Ti ₅₀ Zr ₃₈	24	β(Ti,Zr)/L	59.4	39.2		43.2	32.8		...	...	
	Ni ₉₁ Ti ₃ Zr ₆	188	(Ni)/Ni ₅ Zr	5.0	0.2		0.6	16.0		...	...	
	Ni ₈₀ Ti ₄ Zr ₁₆	188	TiNi ₃ /Ni ₅ Zr/Ni ₇ Zr ₂	22.5	3.4		0.6	16.3		1.5	20.3	
	Ni ₇₇ Ti ₅ Zr ₁₈	188	TiNi ₃ /Ni ₇ Zr ₂	3.3	21.7		2.5	21.2		...	...	
	Ni ₄₅ Ti ₃₈ Zr ₂₇	24	L/NiTi	33.6	31.7		23.6	26.4		...	...	
	Ni ₃₃ Ti ₂ Zr ₆₅	24	NiZr/L/NiZr ₂	1.6	48.3		3.0	67.8		0.7	66.4	
	Ni ₁₆ Ti ₆ Zr ₇₈	24	L/β(Ti,Zr)	4.8	72.3		7.1	91.1		...	...	
	Ni ₁₆ Ti ₂₀ Zr ₆₄	24	L/β(Ti,Zr)	18.1	58.4		24.4	73.6		...	...	
	Ni ₁₀ Ti ₈₀ Zr ₁₀	24	L/β(Ti,Zr)	62.6	14.4		91.0	7.2		...	...	
	Ni ₁₈ Ti ₁₁ Zr ₇₁	24	L/β(Ti,Zr)	10.7	65.8		12.3	85.1		...	...	
	Ni ₂₀ Ti ₃₉ Zr ₅₁	24	L/β(Ti,Zr)	28.8	48.7		33.3	63.8		...	...	
	Ni ₄₂ Ti ₅₄ Zr ₄	24	TiNi/L	38.2	4.3		60.2	5.1		...	...	
	Ni ₂₀ Ti ₁₅ Zr ₆₅	24	L/β(Ti,Zr)	18.2	56.9		20.4	78.1		...	...	
	Ni ₁₀ Ti ₈₈ Zr ₂	24	L/β(Ti,Zr)	71.7	4.8		92.5	2.5		...	...	
	Ni ₄₀ Ti ₅ Zr ₅₅	24	NiZr/L	2.3	47.3		6.8	62.2		...	...	
	Ni ₄₄ Ti ₃₀ Zr ₂₆	24	NiTi/L	25.0	25.1		38.6	29.7		...	...	
	Ni ₅₃ Ti ₁₂ Zr ₃₅	188	NiTi/Ni ₁₀ Zr ₇	17.3	32.6		10.4	34.3		...	...	
	Ni ₆₂ Ti ₃₃ Zr ₁₅	188	NiTi/Ni ₁₀ Zr ₇ /TiNi ₃	35.9	12.3		20.4	21.1		22.6	2.2	
	Ni ₇₃ Ti ₉ Zr ₁₈	188	Ni ₂ Zr ₈ /TiNi ₃	4.8	23.1		10.5	15.3		...	...	
	Ni ₄₆ Ti ₁₂ Zr ₄₂	24	TiNi/NiZr/L	12.5	38.2		3.5	46.5		26.6	38.3	
	Ni ₅₂ Ti ₈ Zr ₄₀	188	TiNi/NiZr/Ni ₁₀ Zr ₇	13.6	37.4		3.6	46.3		5.2	39.8	
	Ni ₆₅ Ti ₅ Zr ₃₀	188	Ni ₂ Zr ₈ /Ni ₁₀ Zr ₇	2.6	25.0		7.3	34.3		...	...	
	Ni ₈₀ Ti ₁₆ Zr ₄	168	(Ni)/Ni ₅ Zr/TiNi ₃	10.1	0.1		0.2	15.3		24.5	0.5	
	Ni ₇₅ Ti ₅ Zr ₂₀	168	Ni ₂ Zr ₈ /Ni ₇ Zr ₂ /TiNi ₃	3.2	24.7		0.2	22.1		10.0	14.6	
	Ni ₇₀ Ti ₁₂ Zr ₁₈	168	Ni ₂ Zr ₈ /TiNi ₃ /Ni ₁₀ Zr ₇	8.7	19.8		11.9	14.2		18.4	24.2	
	Ni ₂₄ Ti ₅₀ Zr ₂₆	24	Liquid	...	...		...	...		...	...	
	Ni ₂₄ Ti ₄₅ Zr ₃₁	24	Liquid	...	...		...	...		...	...	
	Ni ₃₀ Ti ₂₀ Zr ₅₀	24	Liquid	...	...		...	...		...	...	

Table 3 All phase equilibria and related equilibrium compositions of the Ni-Ti-Zr ternary system at 1200 °C determined in the present work

T, °C	Alloy, at. %	Annealed time, h	Phase equilibria						Composition, at. %					
			Phase 1/phase 2/phase 3	Phase 1			Phase 2			Phase 3			Ti	Zr
				Ti	Zr		Ti	Zr		Ti	Zr			
1200	Ni ₁₀ Ti ₈₈ Zr ₂	12	L/ β (Ti,Zr)	79.2	2.6		92.0	1.9		...	...		...	...
	Ni ₁₈ Ti ₇₁ Zr ₇₁	12	L/ β (Ti,Zr)	15.6	63.4		11.7	88.8		...	...		...	...
	Ni ₁₂ Ti ₅₀ Zr ₃₈	12	L/ β (Ti,Zr)	46.9	31.8		54.9	45.1		...	...		...	...
	Ni ₇₀ Ti ₂₀ Zr ₁₀	12	L/TiNi ₃ /Ni ₇ Zr ₂	24.5	24.7		19.7	4.8		2.2	19.8		...	...
	Ni ₁₅ Ti ₅ Zr ₈₀	12	L/ β (Ti,Zr)	4.0	76.5		4.4	95.2		...	...		...	...
	Ni ₁₆ Ti ₂₀ Zr ₆₄	12	L/ β (Ti,Zr)	22.8	56.6		79.8	19.6		...	...		...	...
	Ni ₁₆ Ti ₄₀ Zr ₄₄	12	L/ β (Ti,Zr)	56.9	23.4		74.9	24.8		...	...		...	...
	Ni ₂₀ Ti ₂₉ Zr ₅₁	12	L/ β (Ti,Zr)	28.6	50.8		29.4	70.5		...	...		...	...
	Ni ₁₀ Ti ₈₀ Zr ₁₀	12	L/ β (Ti,Zr)	69.7	12.1		91.6	8.0		...	...		...	...
	Ni ₁₁ Ti ₇₀ Zr ₁₉	12	L/ β (Ti,Zr)	57.1	22.6		84.7	15.0		...	...		...	...
	Ni ₈₀ Ti ₄ Zr ₁₆	188	Ni ₅ Zr/TiNi ₃ /Ni ₇ Zr ₂	1.2	15.3		21.2	2.0		19.1	77.5		...	...
	Ni ₆₀ Ti ₁₀ Zr ₂₁	12	Ni ₇ Zr ₂ /L	1.8	21.3		17.6	20.9		...	...		...	...
	Ni ₈₀ Ti ₁₆ Zr ₄	188	Ni ₅ Zr/TiNi ₃ /(Ni)	6.7	11.6		23.7	1.6		12.2	0.5		...	...
	Ni ₉₁ Ti ₃ Zr ₆	12	(Ni)/L	2.1	1.8		2.0	9.2		...	...		...	...
	Ni ₄₂ Ti ₅₄ Zr ₄	12	NiTi/L	44.3	5.7		58.4	2.7		...	...		...	...
	Ni ₅₃ Ti ₄₀ Zr ₇	12	NiTi/L	43.2	5.4		36.8	9.0		...	...		...	...
	Ni ₄₄ Ti ₁₀ Zr ₄₆	12	NiZr/L	1.0	48.8		17.6	41.1		...	...		...	...
	Ni ₄₅ Ti ₅ Zr ₅₀	12	NiZr/L	0.9	49.0		8.3	49.2		...	...		...	...
	Ni ₆₅ Ti ₂₅ Zr ₁₀	12	L/TiNi ₃	27.8	11.1		23.4	1.8		...	...		...	...
	Ni ₂₄ Ti ₄₅ Zr ₃₁	12	Liquid	...	...		...	...		...	...		...	...
	Ni ₃₀ Ti ₂₀ Zr ₅₀	12	Liquid	...	...		...	...		...	...		...	...
	Ni ₆₀ Ti ₂₀ Zr ₂₀	12	Liquid	...	...		...	...		...	...		...	...
	Ni ₂₄ Ti ₅₀ Zr ₂₆	12	Liquid	...	...		...	...		...	...		...	...
	Ni ₅₅ Ti ₃₀ Zr ₁₅	12	Liquid	...	...		...	...		...	...		...	...
	Ni ₄₄ Ti ₃₀ Zr ₂₆	12	Liquid	...	...		...	...		...	...		...	...
	Ni ₄₀ Ti ₂₅ Zr ₃₅	12	Liquid	...	...		...	...		...	...		...	...

Fig. 4 Experimentally determined isothermal sections of the Ni-Ti-Zr system at (a) 1000 and (b) 1200 °C

Fig. 4(a) on the basis of the results above and the previous investigations.^[19-21]

In the isothermal section at 1200 °C (Fig. 4b), one liquid region and four three-phase regions were experimentally determined in this work. It should be noted that the area of liquid increases with the increase of the temperature from 1000 to 1200 °C. The result shows that the liquid region at 1200 °C is in accordance with the previous investigations reported from Eremenko.^[19-21]

Results further show the solubility of Zr in the NiTi phase is found to be about 35 at.%, which reduces to about 10 at.% as temperature range from 1000 to 1200 °C. According to the previous investigations^[14], Zr content increases from ~5 to ~43 at.% in the NiTi phase as temperature range from 700 to 1160 °C. However, Zr content reduces to 0 at.% until NiTi phase transforms to liquid when the temperature increases to 1310 °C.

Fig. 5 DSC heating curve of the (a) $\text{Ni}_{24}\text{Ti}_{50}\text{Zr}_{26}$ (at.%), (b) $\text{Ni}_{24}\text{Ti}_{45}\text{Zr}_{31}$ (at.%) and (c) $\text{Ni}_{30}\text{Ti}_{20}\text{Zr}_{50}$ (at.%) alloy

The solubility of Ni in the $\beta(\text{Ti}, \text{Zr})$ phase is about 0.2-9.9 at.% through the determined isothermal section. In addition, the solubility of Ti in the NiZr_2 phase is extremely low, the solubility of Ti in the NiZr phase is measured to be approximately 3.0 at.%, reduced to about 1.0 at.% when the temperature change to 1200 °C and the solubility of Ti in the Ni_7Zr_2 phase is measured to be about 2.2 at.%, which stays almost the same at 1200 °C.

4. Conclusions

Two isothermal sections of the Ni-Ti-Zr ternary system at 1000 and 1200 °C were experimentally determined. The area of liquid increases with the increase of the temperature from 1000 to 1200 °C. The phase equilibrium of the Ni-Ti-Zr ternary system determined by the present work will provide additional support for the thermodynamic assessment of this system and practical application for the Ni-Ti alloys.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51031003 and 51171159) and the Ministry of Education of China (Grant No. 20120121130004). The support from the Ministry of Science and Technology of China (Grant Nos. 2012CB825700 and 2014DFA53040), the Aviation Industry Corporation of China and Xiamen City Department of Science & Technology (Grant No. 3502Z20131153) are also acknowledged.

References

1. W. Tang, B. Sundman, R. Sandström, and C. Qiu, New Modelling of the B2 Phase and Its Associated Martensitic

- Transformation in the Ti-Ni System, *Acta Mater.*, 1999, **47**(12), p 3457-3468
2. Q.M. Hu, R. Yang, J.M. Lu, L. Wang, B. Johansson, and L. Vitos, Effect of Zr on the Properties of (TiZr)Ni Alloys from First-Principles Calculations, *Phys. Rev. B*, 2007, **76**(22), p 224201
3. K. Otsuka and C.M. Wayman, *Shape Memory Materials*, Cambridge University Press, Cambridge, 1999
4. K. Otsuka and X. Ren, Physical Metallurgy of Ti-Ni-Based Shape Memory Alloys, *Prog. Mater. Sci.*, 2005, **50**(5), p 511-678
5. M. Zarinejad, Y. Liu, and Y. Tong, Transformation Temperature Changes due to Second Phase Precipitation in NiTi-Based Shape Memory Alloys, *Intermetallics*, 2009, **17**(11), p 914-919
6. B.Y. Li, L.J. Rong, and Y.Y. Li, Synthesis of Porous Ni-Ti Shape-Memory Alloys by Self-Propagating High-Temperature Synthesis: Reaction Mechanism and Anisotropy in Pore Structure, *Acta Mater.*, 2000, **48**(15), p 3895-3904
7. X. Ren, N. Miura, J. Zhang, K. Otsuka, K. Tanaka, M. Koiwa, T. Suzuki, Y.I. Chumlyakov, and M. Asai, A Comparative Study of Elastic Constants of TiNi-Based Alloys Prior to Martensitic Transformation, *Mater. Sci. Eng. A*, 2001, **312**(1), p 196-206
8. J. Smith, Q. Jiang, R. Lck, and B. Predel, C_p and Fractal Phase Transformation in the Shape Memory Alloy Ni-52Ti, *Mater. Sci. Eng. A*, 1991, **149**(1), p 111-120
9. L. Meisner, V. Sivokha, and O. Perevalova, Formation Features of fine Structure of the $\text{Ni}_{50}\text{Ti}_{40}\text{Zr}_{10}$ Alloy Under Different Thermal Treatment, *Phys. B*, 1999, **262**(1), p 49-54
10. L. Meisner and V. Sivokha, Deformation of Crystal Lattice in the Process of Martensitic Transformation in Alloys of $\text{Ni}_{50}\text{Ti}_{50-x}\text{Zr}_x$, *J. Phys. IV*, 1995, **5**(8), p C8.765-C8.769
11. S.F. Hsieh and S.K. Wu, A Study on Lattice Parameters of Martensite in $\text{Ti}_{50.5-x}\text{Ni}_{49.5}\text{Zr}_x$ Shape Memory Alloys, *J. Alloys Compd.*, 1998, **270**(1), p 237-241
12. G. Firstov, J. Van Humbeeck, and Y.N. Koval, High-Temperature Shape Memory Alloys: Some Recent Developments, *Mater. Sci. Eng. A*, 2004, **378**(1), p 2-10
13. V. Eremenko, E. Semenova, and L. Tret'yachenko, The Structure of Ni-Zr-Ti Alloys in the Region of 0-50 at.% of Nickel at 700 °C, *Dop. Akad. Nauk Ukr. RSR A Fiz.-Mat. Tekh.*, 1988, **2**, p 76-79
14. K.P. Gupta, The Ni-Ti-Zr System (Nickel-Titanium-Zirconium), *J. Phase Equilib.*, 1999, **20**(4), p 441-448
15. M.C. Yeh, J.L. Li, P.J. Lo, and K.-C. Hsieh, Phase Equilibrium in the Ni-Ti-Zr System at 800 °C, *J. Phase Equilib.*, 2014, **35**(2), p 157-162
16. H. Okamoto, Ni-Zr (Nickel-Zirconium), *J. Phase Equilib.*, 2007, **28**(4), p 409
17. P. Bellen, K.C.H. Kumar, and P. Wollants, Thermodynamic Assessment of the Ni-Ti Phase Diagram, *Z. Metallk.*, 1996, **87**(12), p 972-978
18. K.C.H. Kumar, P. Wollants, and L. Delacy, Thermodynamic Assessment of the Ti-Zr System and Calculation of the Nb-Ti-Zr Phase Diagram, *J. Alloys Compd.*, 1994, **206**(1), p 121-127
19. V.N. Eremenko, E.L. Semenova, and L.A. Tret'yachenko, Liquidus Surface and Solidification Scheme for Alloys of the System Ti-Ni-Zr Containing Up to 50% Ni, *Powder Metall. Met. Ceram.*, 1991, **30**, p 664-668
20. V.N. Eremenko, E.L. Semenova, and L.A. Tret'yachenko, Projection of the Solidus Surface and Reactions During Solidification of Ti-Ni-Zr Alloys in the Ti-TiNi-ZrNi-Zr Region, *Russ. Akad. Nauk Metall.*, 1992, **6**, p 138-143 (in Russian)
21. V.N. Eremenko, E.L. Semenova, and L.A. Tret'yachenko, Constitution of the Ternary Ni-Zr-Ti Alloys Along the TiNi-ZrNi Section, *Izv. V.U.Z. Tsvetn. Metall.*, 1990, **6**, p 85-88