Enthalpy of mixing of liquid Ni–Ti–Zr alloys at 1873 K

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ABSTRACT

The enthalpies of mixing of liquid Ni–Ti–Zr alloys were determined at 1873 K by means of a high-temperature isoperibolic calorimeter. The investigations were performed along sections $x_{Ni}/x_{Ti} = 4/1$ and $x_{Ni}/x_{Zr} = 4/1$ in the corresponding composition ranges $x_{Zr} = 0$–0.41 and $x_{Ti} = 0$–0.48. The limiting partial enthalpy of mixing of undercooled liquid zirconium in liquid Ni–Ti alloy is (-192 ± 8) kJ mol^{-1}. The limiting partial enthalpy of mixing of undercooled liquid titanium in liquid Ni–Zr alloy is (-130 ± 12) kJ mol^{-1}. The integral mixing enthalpies are negative over the investigated composition range. An analytical expression for the representation of the integral mixing enthalpy was obtained and used for the calculation of the function in the whole composition range.

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1. Introduction

The Ni–Ti–Zr system is known for the formation of metallic glasses [1–4] and icosahedral quasicrystalline phase [5–8]. From the technological point of view, the formation of a stable and well-ordered icosahedral phase may give challenging opportunities for potential application in stationary hydrogen fuel cell applications or in Ni-metal hydride batteries due to its ability to absorb considerable amounts of hydrogen [9,10]. To overcome the usual brittleness of quasicrystals, the researchers focused on the development of composites with nanocrystalline icosahedral phase dispersed in the amorphous matrix [11–14]. Such composite structures can be produced either by rapid quenching technique or in the course of partial devitrification of initial rapidly quenched amorphous ribbons [11–14]. The Ni–Ti–Zr system is also of great interest for the creation of the Ni-based bulk metallic glasses [15,16] and high-entropy multielement amorphous alloys [17].

To clarify high glass-forming ability and strong tendency towards quasicrystals formation, the investigation of the structural, physical, and thermodynamic properties of the liquid phase is mandatory. The structure and physical properties such as surface tension and viscosity of liquid and supercooled liquid alloys were

investigated in a number of works [18–22]. The thermodynamic properties of liquid binary alloys were also studied. Lück et al. [23] at 1741 K and 1838 K, Thiedemann et al. [24] at 1800 K and 1980 K, Turchanin et al. [25] at 1873 K, and Esin et al. [26] at 2000 K investigated the integral mixing enthalpy, $\Delta_{mix}H$, of liquid Ni–Ti alloys. In the later work [27], Wang and Lück fitted their experimental data obtained in the previous study [23] using the simple polynomials. All authors reported large exothermic heats of mixing. The experimental results [23,25] agree well though there are noticeable discrepancies between the values of the mixing enthalpies reported in [23,25] and [24,26]. For the Ni–Zr system, the integral mixing enthalpy of liquid alloys was investigated by Witusiewicz and Sommer [28] at 1565 K, Wang and Lück [27] and Arpshofen et al. [29] at (1740 and 1838) K, Turchanin et al. [25,30] at 1873 K, Sidorov et al. [31] at 1963 K, and Rösner-Kuhn et al. [32] at 1916 and 2270 K. Highly negative values were observed for this thermodynamic function. According to the experimental results at different temperatures [25,29–32], the mixing enthalpy of liquid Ni–Zr alloys shows dependence on temperature. Only data of Witusiewicz and Sommer [28] contradicts this tendency. Thiedermann et al. [33] studied the mixing enthalpy of liquid Ti–Zr alloys in the temperature range 2111–2347 K. In the investigated temperature range, this thermodynamic function shows negative values and does not depend on temperature. The information on the thermodynamics of the ternary alloys is limited to the isenthalpic curves calculated according to a geometric model

[27], no experimental data have been reported so far. The aim of the present work is a calorimetric investigation of the mixing enthalpies of liquid Ni–Ti–Zr alloys.

2. Experimental

Partial mixing enthalpies of titanium and zirconium in liquid Ni–Ti–Zr alloys were measured by means of a high-temperature isoperibolic calorimeter designed and assembled in Laboratory of physicochemical properties of liquid metallic alloys (Donbass State Engineering Academy, Ukraine). The experimental set-up is thoroughly described in [34].

The starting materials were electrolytic nickel (0.9999 mass fraction), titanium (0.9994 mass fraction), and zirconium (0.9996 mass fraction). Tungsten (0.9996 mass fraction, A-2) was used as inert reference material. All metals were of the former USSR origin. The samples prepared from these metals had a cylindrical shape (about 5–10 mm in height, and 0.5 to 2.0 mm in diameter). Yttria-stabilized zirconia crucibles (30 mm in height, 20 mm outer diameter) were used for the measurements. All experimental runs were carried out under the spectral grade argon (99.997 vol.%) at small excess pressure. The details concerning the starting materials are given in Table 1.

The partial mixing functions of zirconium and titanium in liquid alloys were investigated at 1873 K along the sections x_{Ni}/x_{Ti} = 4/1 at x_{Zr} = 0–0.41 and x_{Ni}/x_{Zr} = 4/1 at x_{Ti} = 0–0.48 respectively. The investigated compositions related to each section are shown in Fig. 1. Before starting a series of measurements along a section, the crucible was charged with (2.4141 and 1.9974) g nickel. Ten samples of nickel were used for the calibrations at the beginning of each experiment. The masses of samples varied from (0.08 to 0.15) g. After the calibration, the additions of titanium (between (0.15 and 0.21) g each for the x_{Ni}/x_{Ti} = 4/1 section) or zirconium (between (0.21 and 0.25) g each for the x_{Ni}/x_{Zr} = 4/1 section) were introduced consequently into the bath of liquid metal to synthesize the liquid binary alloys with required composition. Then, the small zirconium or titanium samples (between (0.04 and 0.15) g each), thermostated at 298 K, were dropped into the bath of binary alloys. At the end of each series, the calorimeter was calibrated by adding six additions (approximately (0.46 and 0.66) g each) of tungsten. A revolving discharger for samples allowed dropping up to 68 samples in the course of one experimental series. The time interval between the drops was from (4 to 6) min – a period of time required for temperature/composition stabilization of alloy after a sample dissolution. After the first calibration run, the addition
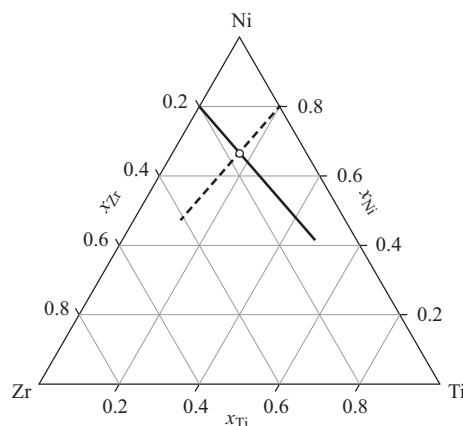

Fig. 1. Composition intervals (shown with lines) investigated in the Ni–Ti–Zr system. Symbols: ▬▬▬ x_{Ni}/x_{Zr} = 4/1 section, ▬ ▬ ▬ x_{Ni}/x_{Ti} = 4/1 section, ○ denotes the intersection point of the investigated sections.

of the second component to synthesize required liquid binary alloy, incorporation every 10 zirconium or titanium samples, and before the calibration with tungsten, the intervals about 15 min were made. The crucibles with final ingots were weighed after completion of each experiment. The weight loss during the experiment was less than 0.005 mass fractions.

The procedure of experimental data processing was described in details in [35–38]. For each experimental run, the calorimeter constant was determined as follows

$$k = -n_{Me} \cdot \Delta H^T_{298,Me} / \int \Delta T dt, \qquad (1)$$

where n_{Me} is added amount of nickel or tungsten, $\Delta H^T_{298,Me}$ is the high-temperature enthalpy content of liquid nickel or solid tungsten at the temperature of the experiment, $\int \Delta T dt$ is the area under the heat exchange curve. For each section, the experimental data on the calorimeter constant were treated by the least square fit. The results are given in Table 2. For all the sections, the calorimeter constant was accepted as a function of alloy mass (m).

The added samples of metal (titanium or zirconium) were so small that the composition change in the bath of liquid ternary alloys did not exceed Δx_{Me} = 0.01–0.015. Therefore, the partial mixing enthalpy of the component can be directly determined using the following equation

Table 1
Sample table.[a]

Chemical name	State union standard	Initial mass fraction purity	Purification method	Analysis method
Nickel	GOST849–97 Primary nickel. Specifications	0.9999	Electrolysis	CAEA[c]
Titanium	TU48-4–282-86 Titanium iodide[f]	0.9994	Iodide refining	Spectral analysis, coulometry, NAA[d], FPM[e]
Zirconium	TU95.46–82 Zirconium iodide[f]	0.9996	Iodide refining	Spectral analysis, coulometry, NAA[d], FPM[e]
Tungsten	TU48-19–57-91 High-purity metallic tungsten	0.9996	The method of hydrogen reduction	Spectral analysis
Argon	GOST10157–79 Gaseous and liquid argon. Specifications.	99.997[b]	Low-temperature rectification	Colorimetry, spectral analysis, coulometry

[a] All the materials were used in the as-received state. No additional purification or chemical analysis were conducted. The purification method and analysis method are given in accordance with state union standards.

[b] Value is given in volume percent.

[c] Chemical atomic emission analysis.

[d] Neutron activation analysis.

[e] Flame photometric analysis.

[f] Here, term 'iodide' means that the iodide process (crystal bar process) was applied for the production of pure titanium and zirconium.

Table 2

Enthalpy of metal (Me = Zr or Ti) samples solution $k \int \Delta T dt$ at added amount of metal n_{Me}, partial mixing enthalpies of metal $\Delta_{mix}\overline{H}_{Me}$ at mole fraction of metal x_{Me} for the liquid Ni–Ti–Zr alloys, high-temperature enthalpy content of undercooled liquid metal $\Delta H_{298,Me}^{1873}$, and calorimeter constant k at temperature T = 1873 K and pressure 152.00 kPa.[a]

Added metal (Me)	n_{Me}/mmol	$k \int \Delta T dt$/kJ	x_{Me} [b]	$\Delta_{mix}\overline{H}_{Me}$ [c]/(kJ mol^{-1})
The x_{Ni}/x_{Ti} = 4/1 section				
k(m)/(kJ·K^{-1}·s^{-1}) = 4.77–0.08 m[d]. Starting amount: n_{Ni}/mmol = 41.1310				
Added amount: n_{Ni}/mmol = 13.368 and n_{Ti}/mmol = 13.579. $\Delta H_{298,Zr}^{1873}$/(kJ mol^{-1}) = 70.89 [39]				
Zr	0.736	0.0943	0.005	−199.0
Zr	0.688	0.0723	0.016	−176.0
Zr	0.768	0.0633	0.026	−153.3
Zr	0.783	0.0548	0.037	−140.9
Zr	0.839	0.0587	0.047	−140.9
Zr	0.815	0.0489	0.058	−130.9
Zr	0.781	0.0559	0.069	−142.5
Zr	0.798	0.0465	0.079	−129.2
Zr	0.881	0.0531	0.089	−131.2
Zr	0.935	0.0473	0.100	−121.5
Zr	0.887	0.0543	0.111	−132.1
Zr	0.949	0.0344	0.121	−107.1
Zr	0.987	0.0264	0.132	−97.6
Zr	1.010	0.0321	0.143	−102.7
Zr	1.010	0.0184	0.154	−89.1
Zr	0.933	0.0175	0.164	−89.7
Zr	1.040	0.0284	0.174	−98.2
Zr	1.170	0.0284	0.185	−95.2
Zr	1.160	0.0022	0.196	−72.8
Zr	1.100	0.0030	0.206	−73.6
Zr	1.120	0.0043	0.217	−74.7
Zr	1.130	−0.0026	0.227	−68.6
Zr	1.210	−0.0147	0.237	−58.7
Zr	1.210	−0.0164	0.247	−57.3
Zr	1.210	−0.0237	0.257	−51.3
Zr	1.260	−0.0374	0.267	−41.2
Zr	1.270	−0.0300	0.277	−47.3
Zr	1.210	−0.0313	0.286	−45.0
Zr	1.300	−0.0329	0.295	−45.6
Zr	1.230	−0.0384	0.304	−39.7
Zr	1.350	−0.0387	0.314	−42.2
Zr	1.370	−0.0454	0.323	−37.8
Zr	1.390	−0.0440	0.332	−39.2
Zr	1.250	−0.0435	0.341	−36.1
Zr	1.270	−0.0506	0.348	−31.0
Zr	1.270	−0.0556	0.356	−27.1
Zr	1.270	−0.0428	0.364	−37.2
Zr	1.440	−0.0595	0.372	−29.6
Zr	1.470	−0.0552	0.380	−33.3
Zr	1.480	−0.0646	0.388	−27.2
Zr	1.570	−0.0690	0.397	−26.9
Zr	1.620	−0.0630	0.405	−32.0
The x_{Ni}/x_{Zr} = 4/1 section				
k(m)/(kJ·K^{-1}·s^{-1}) = 4.35–0.05 m[d]. Starting amount: n_{Ni}/mmol = 34.0313				
Added amount: n_{Ni}/mmol = 18.059 and n_{Zr}/mmol = 12.990. $\Delta H_{298,Ti}^{1873}$/(kJ mol^{-1}) = 66.82 [39]				
Ti	0.823	0.0452	0.006 [b]	−121.7
Ti	0.852	0.0522	0.019	−128.1
Ti	0.921	0.0455	0.032	−116.2
Ti	0.925	0.0459	0.045	−116.4
Ti	1.040	0.0416	0.058	−106.8
Ti	0.994	0.0291	0.072	−96.1
Ti	0.987	0.0266	0.085	−93.8
Ti	1.020	0.0316	0.098	−97.8
Ti	1.070	0.0159	0.111	−81.7
Ti	1.130	0.0081	0.124	−74.0
Ti	1.150	−0.0025	0.137	−64.6
Ti	1.050	0.0051	0.149	−71.7
Ti	1.210	−0.0094	0.162	−59.1
Ti	1.120	−0.0080	0.174	−59.7
Ti	1.300	−0.0216	0.187	−50.2
Ti	1.320	−0.0290	0.200	−44.9
Ti	1.320	−0.0285	0.213	−45.2
Ti	1.370	−0.0294	0.225	−45.4
Ti	1.440	−0.0468	0.238	−34.3
Ti	1.400	−0.0400	0.250	−38.2
Ti	1.470	−0.0530	0.263	−30.8
Ti	1.540	−0.0520	0.275	−33.1

Table 2 (*continued*)

Added metal (Me)	n_{Me}/mmol	$k \int \Delta T dt$/kJ	x_{Me}[b]	$\Delta_{mix}\bar{H}_{Me}$ [c]/(kJ mol^{-1})
The x_{Ni}/x_{Ti} = 4/1 section				
k(m)/(kJ·K^{-1}·s^{-1}) = 4.77−0.08 m[d]. Starting amount: n_{Ni}/mmol = 41.1310				
Added amount: n_{Ni}/mmol = 13.368 and n_{Ti}/mmol = 13.579. $\Delta H^{1873}_{298,Zr}$/(kJ mol^{-1}) = 70.89 [39]				
Ti	1.570	−0.0620	0.287	−27.3
Ti	1.600	−0.0635	0.299	−27.1
Ti	1.630	−0.0835	0.311	−15.6
Ti	1.650	−0.0867	0.323	−14.3
Ti	1.720	−0.0810	0.335	−19.7
Ti	1.770	−0.0820	0.346	−20.5
Ti	1.790	−0.0928	0.358	−15.0
Ti	1.810	−0.0905	0.369	−16.8
Ti	1.850	−0.1150	0.380	−4.7
Ti	1.850	−0.1115	0.391	−6.5
Ti	1.890	−0.1283	0.401	1.1
Ti	2.020	−0.1325	0.412	−1.2
Ti	2.010	−0.1340	0.422	−0.2
Ti	2.060	−0.1315	0.433	−3.0
Ti	2.070	−0.1154	0.443	−11.1
Ti	2.100	−0.1230	0.452	−8.2
Ti	2.110	−0.1270	0.462	−6.6
Ti	2.230	−0.1340	0.471	−6.7
Ti	2.300	−0.1415	0.481	−5.3

[a] Standard uncertainties u are $u(T)$ = 0.5 K, $u(p)$ = 5 kPa, $u(n)$ = 0.001 mmol, $u(k)$ = 0.01, $u(x)$ = 0.001, $u(k \int \Delta T dt)$ = 0.001 kJ, $u\left(\Delta H^{1873}_{298,Zr}\right) = u\left(\Delta H^{1873}_{298,Ti}\right)$ = 0.02 kJ mol^{-1}, and $u_r(\Delta_{mix}\bar{H}_{Me})$ = 0.08.
[b] x_{Me} is the middle point of the composition range before and after addition of the ith metal sample, $x_{Me} = 0.5(x_{Me,i-1} + x_{Me,i})$.
[c] The values are referred to undercooled liquid titanium and zirconium.
[d] Calorimeter constant as a function of alloy mass after adding the corresponding drop, m/g, in a crucible, $u(m)$ = 0.00005 g.

$$\Delta_{mix}\bar{H}_{Me} = -\Delta H^T_{298,Me} - \frac{k}{n_{Me}} \int \Delta T dt \qquad (2)$$

where $\Delta H^T_{298,Me}$ is the high-temperature enthalpy content of liquid metal undercooled to the temperature of the experiment, n_{Me} is the added amount of metal, k is calorimeter constant obtained from the calibration. The high-temperature enthalpy content was calculated using the SGTE database [39]. The results were referred to liquid nickel, undercooled liquid titanium, and zirconium.

The set of the $\Delta_{mix}\bar{H}_{Me}$ experimental points along each section was treated using least squares regression using the simple polynomial. The optimal power of the polynomial was determined using the Fisher criterion for 95% probability. The results were presented as a $\Delta_{mix}\bar{H}_{Me}(x_{Me})$ function.

The integral mixing enthalpy of liquid ternary alloys along an investigated section was calculated by Gibbs-Duhem integration

$$\Delta_{mix}H = (1 - x_{Me})\left[\Delta H_{x_{Me}=0} + \int_{x_{Me}=0}^{x_{Me}} \frac{\Delta_{mix}\bar{H}_{Me}(x_{Me})}{(1 - x_{Me})^2} dx_{Me}\right]_{x_{Ni}/x_{Me}}, \qquad (3)$$

where $\Delta H_{x_{Me}=0}$ is the integral mixing enthalpy of liquid Ni–Me (Me = Ti or Zr) alloys at the given ratio of x_{Ni}/x_{Me}. For the integration, the integral mixing enthalpy of liquid binary alloys were accepted according to [25] ($\Delta H_{x_{Me}=0}$=−32.5 ± 0.8 kJ mol^{-1} for the Ni–Ti system) and [30] ($\Delta H_{x_{Me}=0}$=−36 ± 1.3 kJ mol^{-1} for the Ni–Zr system).

3. Results and discussion

The experimental values of the $\Delta_{mix}\bar{H}_{Zr}$ and $\Delta_{mix}\bar{H}_{Ti}$ functions of the liquid Ni–Ti–Zr alloys calculated from Eq. (2) are listed in Table 2, and shown with symbols in Fig. 2 along the investigated sections. The enthalpy of solution of titanium or zirconium samples in liquid binary alloys is also given in Table 2. The composition
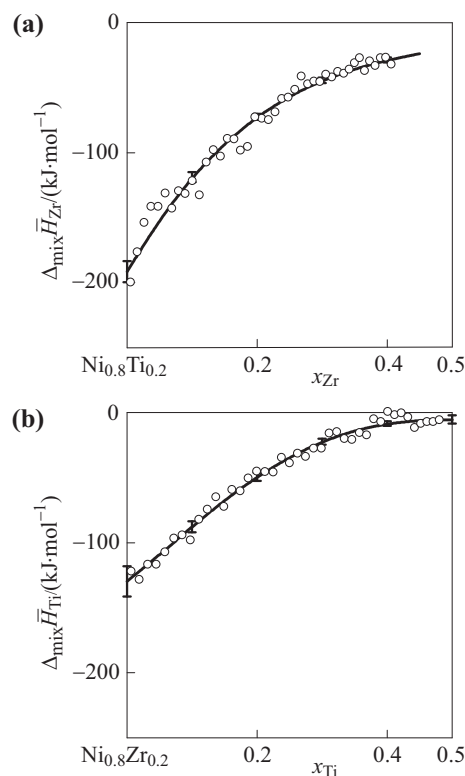

Fig. 2. The partial mixing enthalpy of zirconium $\Delta_{mix}\bar{H}_{Zr}$ and titanium $\Delta_{mix}\bar{H}_{Ti}$ in liquid Ni–Ti–Zr alloys along the investigated x_{Ni}/x_{Ti} = 4/1 (a) and x_{Ni}/x_{Zr} = 4/1 (b) sections at 1873 K. Experimental data points: ○ the present work. Line: ── calculation from Eqs. (4) and (5). The vertical bars show confidence intervals 2σ of smoothing functions. The standard states: pure liquid metals.

dependence of the corresponding partial functions is described by the following equations:the section $x_{Ni}/x_{Ti} = 4/1$

$$\Delta_{mix}\bar{H}_{Zr}(x_{Zr})/(kJ \cdot mol^{-1}) = (1-x_{Zr})^2(-191.6 + 506.4x_{Zr} - 568.5x_{Zr}^2), \tag{4}$$

the section $x_{Ni}/x_{Zr} = 4/1$

$$\Delta_{mix}\bar{H}_{Ti}(x_{Ti})/(kJ \cdot mol^{-1}) = (1-x_{Ti})^2(-129.7 + 129.4x_{Ti} + 995.8x_{Ti}^2 - 1640.4x_{Ti}^3). \tag{5}$$

The smoothed values of the $\Delta_{mix}\bar{H}_{Me}(x_{Me})$ functions calculated from these equations are given in Table 3. The corresponding fitted curves along with the confidence intervals are plotted in Fig. 2. The experimental results show that the partial mixing enthalpies of titanium and zirconium are exothermic. The limiting partial enthalpy of mixing of undercooled liquid zirconium in liquid Ni–Ti alloy is (-192 ± 8) kJ mol^{-1}. The limiting partial enthalpy of mixing of undercooled liquid titanium in liquid Ni–Zr alloy is (-130 ± 12) kJ mol^{-1}. Along all the investigated sections, the partial $\Delta_{mix}\bar{H}_{Me}(x_{Me})$ functions gradually increase with increasing concentration of the third component.

The values of the integral mixing enthalpy calculated by Gibbs-Duhem integration are listed in Table 3 and shown in Fig. 3. The $\Delta_{mix}H$ function has negative values. The investigated $x_{Ni}/x_{Ti} = 4/1$ and $x_{Ni}/x_{Zr} = 4/1$ sections have an intersection point (denoted with open circle in Fig. 1) at $x_{Ti} = x_{Zr} = 0.167$. The experimental value of the integral mixing enthalpy at this point is (-45 ± 2) kJ mol^{-1} for the $x_{Ni}/x_{Ti} = 4/1$ section and (-48 ± 1) kJ mol^{-1} for the $x_{Ni}/x_{Zr} = 4/1$ section. A good reproducibility of the results was thus achieved in the course of two independent experimental runs.

The results obtained for the integral mixing enthalpies were treated by a least square fit using the Redlich–Kister–Muggianu polynomial [40], which is given by the following equation

$$\Delta_{mix}H(x_{Ni}, x_{Ti}, x_{Zr}) = x_{Ni}x_{Ti}\sum_{i=0}^{v}{}^iL_{Ni-Ti}(x_{Ni} - x_{Ti})^i$$
$$+ x_{Ni}x_{Zr}\sum_{i=0}^{v}{}^iL_{Ni-Zr}(x_{Ni} - x_{Zr})^i$$
$$+ x_{Ti}x_{Zr}\sum_{i=0}^{v}{}^iL_{Ti-Zr}(x_{Ti} - x_{Zr})^i$$
$$+ x_{Ni}x_{Ti}x_{Zr}(x_{Ni}^0L_{Ni-Ti-Zr} + x_{Ti}{}^1L_{Ni-Ti-Zr}$$
$$+ x_{Zr}{}^2L_{Ni-Ti-Zr}), \tag{6}$$

where ${}^iL_{Ni-Ti}$, ${}^iL_{Ni-Zr}$, and ${}^iL_{Ti-Zr}$ are the interaction parameters between the elements in the corresponding binary systems, v is the power of the Redlich–Kister polynomial; ${}^0L_{Ni-Ti-Zr}$, ${}^1L_{Ni-Ti-Zr}$, and ${}^2L_{Ni-Ti-Zr}$ are the ternary interaction parameters. The binary interaction parameters for liquid Ti–Zr alloys were taken from [33] (Table 4). The remained interaction parameters were evaluated in the present work.

The least square fit was applied to obtain the binary interaction parameters for the Ni–Ti and Ni–Zr systems. The temperature dependence of the integral mixing enthalpy in the Ni–Zr system was not considered in the evaluation procedure since the experimental investigation of this feature in the ternary system was beyond the scopes of the present study. Hence, only values of the integral mixing enthalpies measured at $T = (1838, 1873,$ and $1916)$ K [25,27,29,30,32] were involved in the evaluation of the parameters for this binary system. For the Ni–Ti system, the
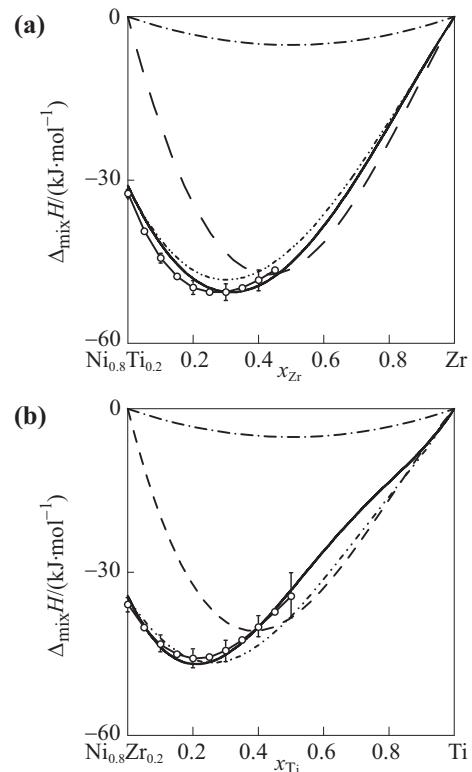

Fig. 3. The integral mixing enthalpy $\Delta_{mix}H$ of liquid Ni–Ti–Zr alloys along the investigated $x_{Ni}/x_{Ti} = 4/1$ (a) and $x_{Ni}/x_{Zr} = 4/1$ (b) sections and in the binary systems at 1873 K. Experimental data points: —O— the present work. Lines: —— the Redlich–Kister–Muggianu polynomial including ternary interaction parameters; —··— the Redlich–Kister–Muggianu polynomial without ternary interaction parameters; — — — integral mixing enthalpy of Ni–Ti liquid alloys calculated according to the present work; —— integral mixing enthalpy of Ni–Zr liquid alloys calculated according to the present work; —·—·— integral mixing enthalpy of Ti–Zr liquid alloys calculated according to [33]. The vertical bars show confidence intervals 2σ of smoothing functions. The standard states: pure liquid metals.

Table 3
The smoothed values of the partial mixing enthalpy of zirconium $\Delta_{mix}\bar{H}_{Zr}$ and titanium $\Delta_{mix}\bar{H}_{Ti}$ and integral mixing enthalpy $\Delta_{mix}H$ of liquid Ni–Ti–Zr alloys at a mole fraction of metal x_{Me} and temperature $T = 1873$ K, and pressure 152.00 kPa. Standard states: pure liquid metals.[a]

x_{Zr}	$\Delta_{mix}\bar{H}_{Zr} \pm 2\sigma$[b]/(kJ mol^{-1})	$\Delta_{mix}H \pm 2\sigma$[b]/(kJ mol^{-1})
The section $x_{Ni}/x_{Ti} = 4/1$		
0	−192 ± 8	−32 ± 1
0.05	−151 ± 6	−39 ± 1
0.10	−119 ± 4	−44 ± 1
0.15	−93 ± 3	−48 ± 1
0.20	−72 ± 2	−50 ± 2
0.25	−57 ± 2	−51 ± 2
0.30	−45 ± 2	−51 ± 2
0.35	−35 ± 2	−50 ± 2
0.40	−29 ± 2	−49 ± 2
0.45	−24 ± 2	−47 ± 2

x_{Ti}	$\Delta_{mix}\bar{H}_{Zr} \pm 2\sigma$[b]/(kJ mol^{-1})	$\Delta_{mix}H \pm 2\sigma$[b]/(kJ mol^{-1})
The section $x_{Ni}/x_{Zr} = 4/1$		
0	−130 ± 12	−36 ± 1
0.05	−109 ± 5	−40 ± 2
0.10	−88 ± 4	−43 ± 2
0.15	−67 ± 4	−45 ± 2
0.20	−49 ± 3	−46 ± 2
0.25	−34 ± 3	−46 ± 2
0.30	−22 ± 2	−44 ± 2
0.35	−14 ± 2	−43 ± 2
0.40	−8 ± 2	−40 ± 2
0.45	−6 ± 2	−37 ± 3
0.50	−5 ± 3	−34 ± 4

[a] Standard uncertainties u are $u(T) = 0.5$ K, $u(p) = 5$ kPa, $u(x) = 0.001$.
[b] The confidence interval is twice the standard deviation of the smoothed function (0.95 level of confidence).

Table 4
The binary $^iL_{Ni-Ti}$, $^iL_{Ni-Zr}$, $^iL_{Ti-Zr}$ and ternary $^iL_{Ni-Ti-Zr}$ interaction parameters for the integral mixing enthalpy $\Delta_{mix}H/(J\,mol^{-1})$ of the liquid phase of the Ni–Ti–Zr system at 1873 K.

System	Interaction parameter	Reference
Ni–Ti	$^0L_{Ni-Ti} = -153,707$	This paper
	$^1L_{Ni-Ti} = -81,825$	
	$^2L_{Ni-Ti} = 0$	
	$^3L_{Ni-Ti} = 40,000$	
Ni–Zr	$^0L_{Ni-Zr} = -185,285$	This paper
	$^1L_{Ni-Zr} = -59,538$	
	$^2L_{Ni-Zr} = 16,999$	
	$^3L_{Ni-Zr} = 681.4$	
Ti–Zr	$^0L_{Ti-Zr} = -20,800$	[33]
Ni–Ti–Zr	$^0L_{Ni-Ti-Zr} = -281,767$	This paper
	$^1L_{Ni-Ti-Zr} = 724,540$	
	$^2L_{Ni-Ti-Zr} = -40,852$	

parameters were evaluated taking into account the results [23–26]. It was found that three $^iL_{Ni-Ti}$ parameters and four $^iL_{Ni-Zr}$ parameters were required to obtain a proper description of the composition dependence of the $\Delta_{mix}H$ function in these binary systems. The $^2L_{Ni-Ti}$ parameter was set to zero to satisfactorily describe the experimental values [24] measured for the Ti-rich alloys. The results of the least square fit are given in Table 4.

The integral mixing enthalpy of liquid Ni–Ti alloys calculated using the $^iL_{Ni-Ti}$ coefficients of Redlich–Kister polynomial is shown in Fig. 4 with a solid line. The relevant experimental data are also summarized in this figure. The calculated $\Delta_{mix}H$ function is in satisfactory agreement with the results [23,25] except for the noticeable discrepancies observed at the titanium concentration higher than 0.5 mol fraction. These discrepancies arise from the necessity to obtain a reasonable fit to the experimental points of Thiedemann et al. [24] at $x_{Ti} > 0.7$. In the composition range $x_{Ti} = 0–0.5$, there is only quantitative agreement between the calculation results and the experimental dataset [24]. The calorimetric data [26] were satisfactorily fitted in the composition range up to 0.25 mol fractions of titanium. In their work, Wang and Lück [27] also obtained a quantitative and qualitative agreement between the integral mixing enthalpies calculated using the simple polynomials and the experimental data [23,25] in the composition range $x_{Ti} = 0–0.4$. However, the authors were unable to reproduce the composition dependence of the integral mixing enthalpy. The calculated minimum of this function is located at $x_{Ti} = 0.45$ that con-

tradicts the observations [23,25]. Lück et al. [23] reported that the minimum located between $x_{Ti} = 0.3$ and $x_{Ti} = 0.4$. Turchanin et al. [25], who studied the liquid alloys in the composition range up to 0.6 mol fractions titanium, observed minimum at $x_{Ti} = 0.37$. In the present work, the majority of the experimental data points was on the whole satisfactorily described and, also, a composition dependence of the integral mixing enthalpy was reproduced using the evaluated set of $^iL_{Ni-Ti}$ parameters. The calculated minimum of the $\Delta_{mix}H$ function is located at $\Delta_{mix}H = -40.8$ and $x_{Ti} = 0.4$.

The integral mixing enthalpy of liquid Ni–Zr alloys was calculated using the coefficients of Redlich–Kister polynomial evaluated in the present work (Table 4). The results are shown in Fig. 5 with a solid line. The available experimental data are also given in the figure. Since the aim of the present work is the accurate representation of the thermodynamic quantities at 1873 K, the $^iL_{Ni-Zr}$ parameters were evaluated in such a way to obtain the best fit to the experimental values at 1873 K [25,30] and to allow a reasonable representation of the data at $T = (1838, 1916)$ K [27,29,32]. This was achieved in the present work. The calculated minimum of the integral mixing enthalpy is $\Delta_{mix}H = -47.8$ at $x_{Ti} = 0.4$ that corresponds well to minimum coordinates, $\Delta_{mix}H = -46.9$ kJ mol^{-1} at $x_{Ti} = 0.38$, reported in [25].

The $\Delta_{mix}H$ of the liquid Ni–Ti–Zr alloys were, at first, calculated neglecting the fourth term of Eq. (6) that corresponds to the Muggianu geometrical model. The results are given in Fig. 3 as dashed-dot-dot lines. The agreement between the experimental and calculation results is reasonable for the $x_{Ni}/x_{Ti} = 4/1$ section up to $x_{Zr} = 0.1$ and for the $x_{Ni}/x_{Zr} = 4/1$ section up to $x_{Ti} = 0.3$. At higher concentrations, there is an underestimation of the experimental values for the $x_{Ni}/x_{Ti} = 4/1$ section and an overestimation for the $x_{Ni}/x_{Zr} = 4/1$ section. Therefore, the ternary interaction parameters of Eq. (6) must be taken into account. The results of the corresponding calculation are shown in Fig. 3 with solid lines. The experimental data are well reproduced by the Redlich–Kister–Muggianu polynomial except for the small deviations observed for the $x_{Ni}/x_{Ti} = 4/1$ section between 0.1 and 0.2 mol fractions of zirconium. Nevertheless, the Redlich–Kister–Muggianu polynomial incorporating the ternary interaction contribution gives better agreement with experimental data in comparison with the Muggianu geometrical model.

The isenthalpic curves for the ternary system calculated according to Eq. (6) are plotted on the Gibbs triangle (Fig. 6). The integral mixing enthalpy of liquid ternary alloys is negative in the whole composition range. A gradual course of isenthalpic lines shows that
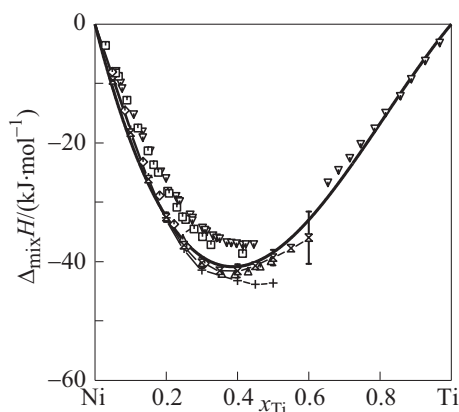

Fig. 4. The integral mixing enthalpy $\Delta_{mix}H$ of liquid Ni–Ti alloys. Experimental data points: ▲ [23] at 1741 K, ☐ [24], at 1800 K, ◇ [23] at 1838 K, —✗— [25] at 1873 K, ▽ [24] at 1980 K, – + – [26] at 2000 K. Line: —— calculation according to the present work at 1873 K. The vertical bars show confidence intervals. The standard states are pure liquid metals.
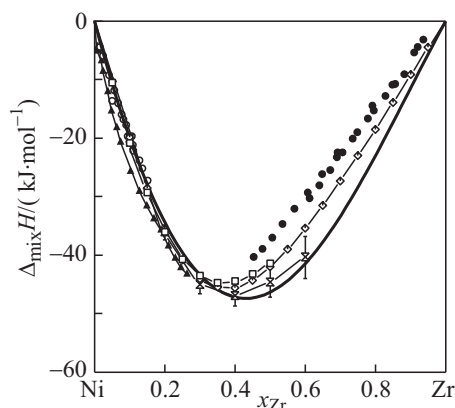

Fig. 5. The integral mixing enthalpy $\Delta_{mix}H$ of liquid Ni–Zr alloys. Experimental data points: —◇— [28] at 1565 K, ▲ [29] at 1740 K, —▲— [29] at 1838 K, —✗— [25,30] at 1873 K, ○ [32] at 1916 K, —☐— [31] at 1963 K, ● [32] at 2270 K. Line: —— calculation according to the present work at 1873 K. The vertical bars show confidence intervals. The standard states are pure liquid metals.
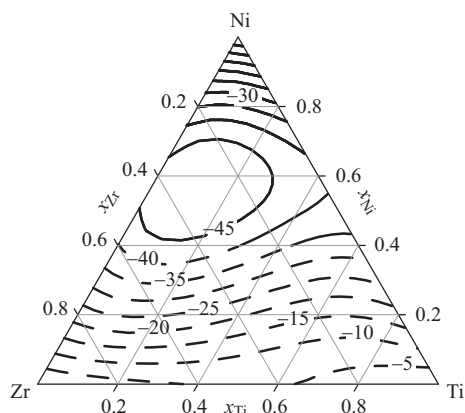
Fig. 6. Isenthalpic curves $\Delta_{mix}H/$(kJ mol^{-1}) of the liquid Ni–Ti–Zr alloys at 1873 K. The lines correspond to the calculation according to the Redlich–Kister–Muggianu polynomial. The solid lines ——— represent the results of the calculation which are in good agreement with experimental data. The dashed lines — — — correspond to the result of extrapolation according to Eq. (6). The standard states: pure liquid metals.

the composition dependence of this function is predominantly defined by the pair Ni–Ti and Ni–Zr interactions. Although, there is a minimum value of the $\Delta_{mix}H$ function located at about x_{Ni} = 0.575, x_{Ti} = 0.100, x_{Zr} = 0.325 and −50 kJ mol^{-1} in the ternary system, this local minimum is relatively weak considering the extrema in the binary Ni–Ti (−40.8 kJ mol^{-1}) and Ni–Zr (−47.8 kJ mol^{-1}) systems. The isenthalpic curves given in Fig. 6 can be compared to those calculated in [27] using a geometric model. Although the course of the isenthalpic curves calculated in the present work and [27] is on the whole similar, the $\Delta_{mix}H$ values [27] are in average by 7 kJ/mol higher comparing to the experimental and calculation results obtained in the present work. Therefore, it can be concluded that the results of prediction of thermodynamic properties out of the binary data in the frameworks of the geometric models should be treated with caution for the ternary system with such a strong interaction of the components.

4. Conclusions

The mixing enthalpies of liquid Ni–Ti–Zr r alloys have been investigated using the high-temperature isoperibolic calorimeter at 1873 K. The partial mixing enthalpies of titanium and zirconium, and the integral mixing enthalpy of liquid ternary alloys are negative in the studied composition range.

The Redlich–Kister–Muggianu polynomial and symmetric Muggianu geometric model have been used for the calculation of the integral mixing enthalpies. The best fit to the experimental values is obtained using the Redlich–Kister–Muggianu polynomial incorporating ternary interaction parameters. The isenthalpic curves have been calculated using this polynomial over the entire composition range.

The composition dependence of the integral mixing enthalpy is predominantly defined by the pair Ni–Ti and Ni–Zr interactions. Although, the $\Delta_{mix}H$ function shows a minimum of about −50 kJ mol^{-1} in the ternary system at about x_{Ni} = 0.575, x_{Ti} = 0.100, x_{Zr} = 0.325.

Acknowledgments

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