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EXPERIMENTAL INVESTIGATION AND THERMODYNAMIC MODELING OF THE ZR–Y SYSTEM

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Abstract

Based on the critical review of all the available experimental data in the literature, 8 key alloys were prepared by arc melting to investigate the phase equilibria in the Zr–Y system, These alloys, which were annealed at 5 different temperatures (800 °C, 1000 °C, 1100 °C, 1120 °C, 1160 °C), were analyzed by means of X–ray diffraction, differential scanning calorimetry, optical microscopy and scanning electron microscopy with energy–dispersive X–ray spectroscopy. The results showed that a peritectoid reaction (βZr) + (αY) = (αZr) occurs at 886 °C ± 5 °C, and an eutectic reaction L = (βZr) + (αY) occurs at 1313 °C ± 5 °C. Taking into account the experimental data obtained both from this work and the literature, the Zr–Y system was thermodynamically modeled. The previously reported temperature for the peritectic reaction of (βY) + L = (αY) at about 1490 °C is supported by our thermodynamic calculation. Comparison between the calculated and measured phase diagrams shows that the thermodynamic calculation can well account for the experimental data.

Key words: Zr–Y phase diagram, XRD, DSC, Thermodynamic calculation.

1. Introduction

Zr and Y are the important alloying elements of magnesium alloys for improving their mechanical properties. For the advanced development of the Mg–based

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alloys with high performance, knowledge of the phase equilibria and thermodynamic properties of the Zr–Y system is of fundamental importance since the Zr–Y system is one of the important subsystem of the magnesium alloys.

Table 1 lists the structures and temperatures regions of βY, αY, βZr and αZr, which are taken from Scientific Group Thermodata Europe (SGTE) database [1]. The phase equilibria in the Zr–Y system were studied by Lundin [2], Love [3], Uy et al. [4], Lundin and Klodt [5] and Wang [6, 7]. An assessed Zr–Y phase diagram was presented by Palenzona and Cirafلci [8] based on the refs. [2–5]. Figure 1 (a)–(c) shows the diagram obtained by Love [3], Lundin and Klodt[5], Palenzona and Cirafici [8], respectively. Though the Zr–Y phase diagram contains no intermediate compound and is simple, there still exists controversies and discrepancy on the invariant reactions. For instance, the (βY) ↔ (αY) transition was reported to be a peritectic reaction occurring at about 1490 ºC by Love [3] and reported to occur at 1490 ºC but via a metatectic reaction by Lundin and Klodt [5], while Uy et al. [4] suggested that this transition is lowered to an eutectoid reaction (βY) = (αY) + (αZr) occurring at 1063±10 ºC. In addition, the temperature and composition for the eutectic reaction involving the liquid phase was fixed at 1363 ±16 °C and 40.4 at.% Zr

Table 1 The structures and temperatures regions of βY, αY, βZr and αZr [1]

Phase	Temperature region, °C	Structure
βY	1479–1526	Bcc_A2
αY	<1479	Hcp_A3
βZr	866–1855	Bcc_A2
αZr	<866	Hcp_A3

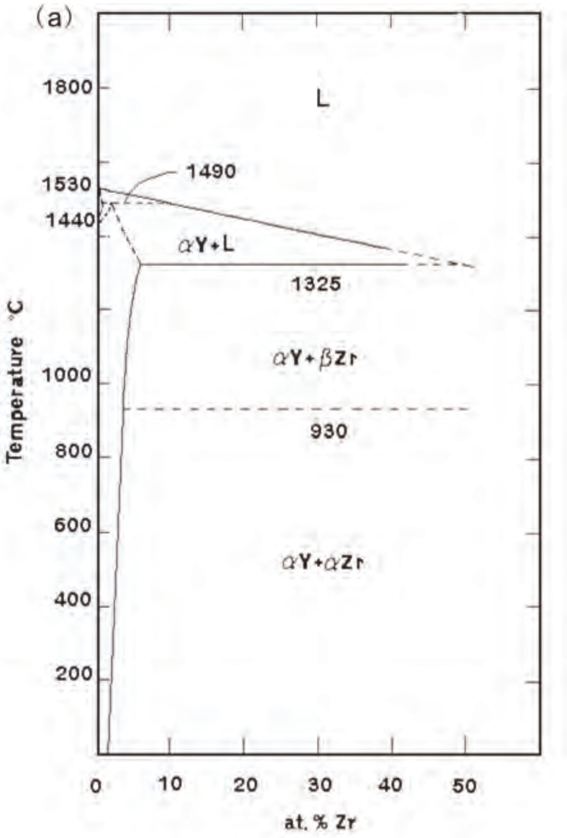

Fig. 1 (a) The experimental partial Zr-Y phase diagram from Love [3],

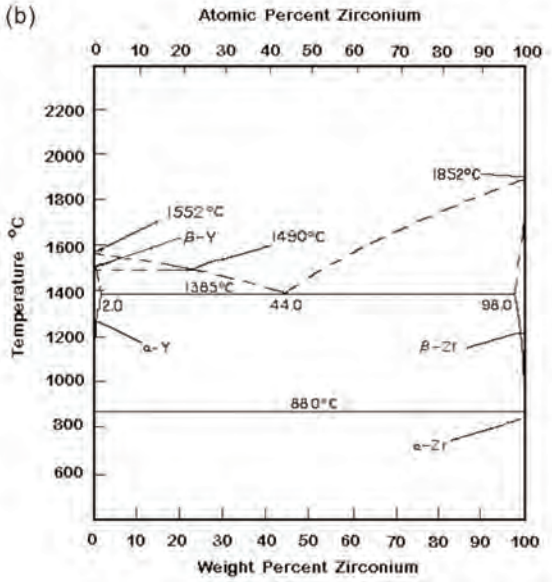

Fig. 1 (b) The experimental Zr-Y phase diagram from Lundin and Klodt [5],

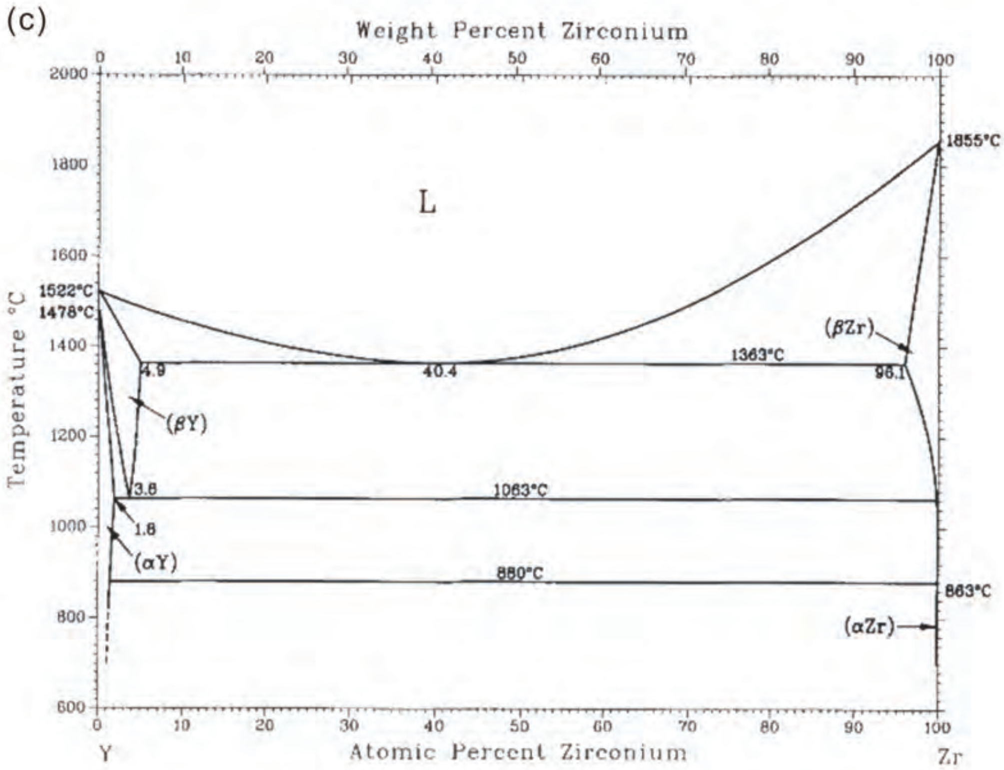

Fig. 1 (c) The assessment Zr-Y phase diagram of Palenzona and Ciraflci [8], mainly from the result of Uy et al [4]

by Uy et al [4], at 1325 °C and ~50 at.% Zr by Love [3], and at 1385 °C and 43.4 at.% Zr by Lundin and Klodt [5], respectively. It should be noted that the eutectic temperature (1363 °C) and the reaction type (eutectoid) and temperature (1063ºC) for the (βY) ↔ (αY) transition (from Uy et al. [4]) were accepted in the assessment of the Zr–Y phase diagram by Palenzona and Ciraflci [8] while the solubility limits and the peritectoid temperature of 880 °C for the (αZr) ↔ (βZr) transformation were taken from Lundin and Klodt [5].

Ding and Zhang [9] performed thermodynamic calculation of the Zr–Y system by using the thermodynamic model from Kaufman [10], but their calculated temperature for the eutectoid reaction of (βY) = (αY) + (αZr) is considerably different from the reported one by Uy et al. [4]. They suggested that (βY) cannot be described with a simple regular solution model [9]. Later on, the Zr–Y system was thermodynamically optimized by Flandorfer et al. [11] and He and Liu [12] using CALPHAD method. Due to the limited experimental information, the thermodynamic parameters for the individual phases in the Zr–Y system were evaluated by using the trial and error method.

Therefore, the major purposes of the present work are as follows: (1) to critically evaluate the experimental phase diagram data on the Zr–Y system available in the literature, especially for the transformation type between (βY) and (αY); (2) to experimentally determine the phase transition temperatures in the Zr–Y system by using differential scanning calorimetry (DSC); (3) to get an optimal set of the thermodynamic parameters for the individual phases in the Zr–Y system based on the reliable experimental data in the literature and from the present work.

2. Evaluation of literature information

By means of X–ray diffraction (XRD) analysis and differential thermal analysis (DTA), Love [3] investigated the phase equilibria in the alloys over a composition range of 0–50% at.% Y. The alloys were prepared by arc melting under an atmosphere composed of 75% helium and 25% argon. After being annealed at 800 °C and 1350 °C, some of these alloys were quenched in liquid nitrogen, and the others were slowly cooled to room temperature. The 2θ Bragg angles were determined for pure metals and for the alloys with various Zr contents. By using the Δ2θ method, the solubility of Zr in (αY) were determined to be ~1.5 at.% at room temperature, ~3.0 at.% at 800 °C, and ~5.0 at.% Zr at the eutectic temperature. The eutectic reaction L = (βZr) + (αY) was fixed at 1325 °C with a composition of ~50 at.% Zr for the liquid phase. Love [3] suggested that a peritectic reaction of (βY) + L = (αY) occurred at 1490 °C based on the DTA experiments. One thermal arrest at 930 °C was tentatively assigned to the (αZr) ↔ (βZr) transition temperature, which was expected to be not higher than the one in the Er–Zr system since the solubility of Y in Zr is less than that of Er in Zr.

Uy et al. [4] studied the Zr–Y phase diagram by means of dilatometry (DIL) and DTA using the materials of higher purity. The temperature and composition of the eutectic reaction L = (βZr) + (βY) were fixed at 1363(±16) °C and 40.4 at.% Zr with a maximum solubility of 4.9 at.% Zr in (βY) and 3.9 at.% Y in (βZr). The (αY) ↔ (βY) transition reaction was deduced to be a eutectoid reaction of (βY) = (αY) + (αZr) occurring at 1063(±10) °C and 3.6 at.% Zr for the (βY) phase based on the solubility of Zr in (αY) and in (βY). The solubility of Y in (βZr) at 888 °C and that of Y in (αZr) at 855 °C were determined to be ~0.2 at.% Y and ~1.2 at.% Y, respectively.

Lundin and Klodt [2, 5] prepared more than 100 alloys by means of arc melting in arc furnace under an atmosphere of purified argon to study the Zr–Y phase diagram over the whole composition range. Their experimental results from the examinations of the as-cast and isothermally annealed alloys and from the incipient melting studies and optical microscopic examinations (OM) showed that a eutectic reaction occurs at 43.4 at.% Zr and 1385 °C with the terminal solid solubility of Zr in (αY) and of Y in (βZr) restricted to 2.0 at.% Zr and 2.0 at.% Y, respectively. The peritectoid reaction of (βZr) + (αY) = (αZr) was fixed at 880 °C and 0.6 at.% Y for the (αZr) phase. On the basis of the similarity with the Ti–Y systems, a metatectic reaction of (βY) = (αY) + L at 1490 °C was proposed by Lundin and Klodt [2, 5] though no quantitative data were obtained concerning the (αY) ↔ (βY) transition. However, it was reported by Bare and Carlson [13] that the allotropic transition of Ti occurring at 1490 ±15 °C in the Ti–Y system was a peritectoid reaction rather than the metatectic reaction, according to the results from the microscopic and thermal analysis and from the resistometric measurements.

The data on the solidus and mutual solid solubility from Ref. [3–5] were used in the present optimization. As the result of Ref. [5] was considered by Palenzona and Ciraflci [8] to be more accurate than those of Ref. [4] because the latter were complicated by contaminants in Y–rich alloys [8], we take the composition data of the eutectic reaction and peritectoid reaction from Ref. [5]. But the temperatures for the two reactions are taken from the present results in the thermodynamic optimization.

3. Experimental procedure

Eight alloys, the nominal compositions of which are given in Table 2, were prepared by arc melting the Zr shot (99.99 wt.% purity) and Y shot (99.9 wt.% purity) in an arc furnace (WKDHL–I, Opto–electronics Co. Ltd., Beijing, China) under a high purity argon atmosphere using a non-consumable tungsten electrode. The buttons were re-melted 4 times to improve their homogeneities. The weight losses of the alloys during arc melting were generally less than 0.5 wt.%. The as-cast alloys, which were wrapped with Mo wire coils, were sealed in the evacuated quartz tubes. The quartz capsules were annealed in an L4514–type diffusion furnace at 1160 °C for 15 days and at 1120, 1100, 1000 and 800 °C for 30 days, respectively. After being annealed, the alloys were quenched in cold water.

Table 2 Summary of the composition and the annealing temperature of the alloys in the present work

Samples, #	Nominal Composition of Y in at.%	Annealing Temperature, °C
1	10	800
2	20	800
3	30	800, 1000, 1120, 1160
4	40	800, 1000, 1100, 1120
5	50	800, 1000, 1120, 1160
6	60	800, 1000, 1100, 1160
7	70	800, 1000, 1100, 1120
8	97.5	800

The metallographic samples were examined first by using a Leica DMLP optical microscope and then using a JEOL JSM6360LV scanning electron microscope (SEM) equipped with energy dispersive X–ray spectroscopy (EDX) system in backscattered electron (BSE) imaging mode. X–ray diffraction (XRD) measurements of the equilibrated alloys were performed using Cu–K_α radiation on a Rigaku D–max/2550 VB^+ X–ray diffractometer at 40kV/250mA.

DSC (DSC404C, Netzsch, Germany) measurements were carried out in Al_2O_3 crucibles at a heating rate of 5 K/min. The DSC apparatus was calibrated with the melting points of the high purity elements In, Al, Ag and Au. The accuracy of the temperature measurement using a Pt–Pt/Rh thermocouple was estimated to be ± 2 °C.

4. Experimental results and discussion

Figure 2 and figure 3 show the backscattered electron (BSE) images of alloy #3 annealed at 1120 °C for 30 days and of alloys #4 annealed at 1000 °C for 30 days, respectively. A local magnification in alloy #3 was also showed in the left upper corner in Fig. 2. The microstructures indicate that the (Zr) phase was continuous and compact while the (Y) phase was indented and porous, which could be mainly ascribed to the result of rapid galvanic corrosion of the (Y), which acts as anode with (Zr) as cathode during polishing (or exposure to the moisture).

Figure 4 is the XRD patterns of alloy #5, which was annealed at 800 °C for 30 days, at 1100 °C for 30 day and at 1160 °C for 15 days, respectively. According to the present work, (αY) and (αZr) were observed at these three temperatures, as shown in Fig. 4, such

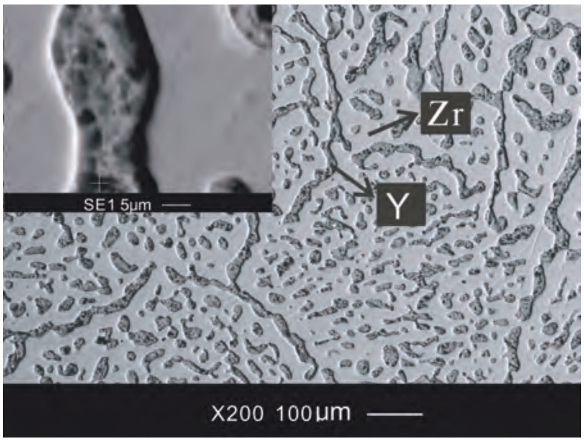

Fig. 2 The SEI micrograph of alloy #3 (30 at.%Y)annealed at 1120 °C for 30 days

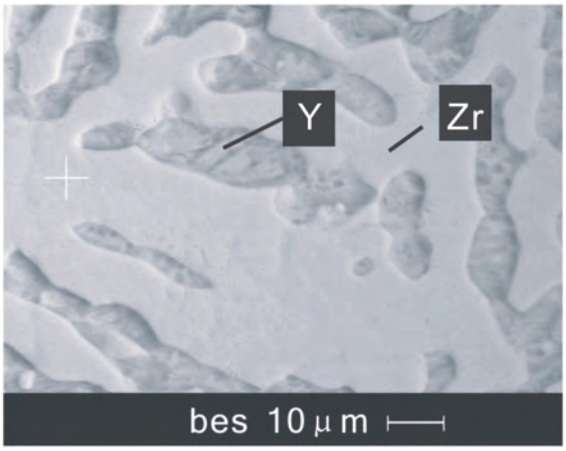

Fig. 3 The BES micrograph of alloy #4 (40 at.%Y) annealed at 1000 °C for 30 days.

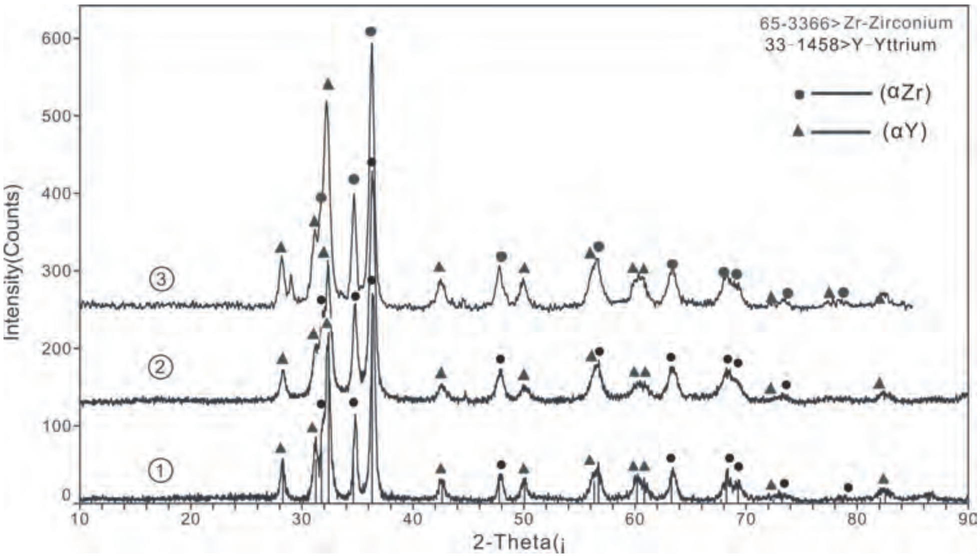

Fig. 4 The XRD patterns of (1) alloy # 5 (50 at.%Y) annealed at 800 °C for 30 days, (2) alloy #4 (40 at.%Y) annealed at 1100 °C for 30 days and (3) alloy #5 annealed at 1160 °C for 15 days

a result is not in agreement with the assessment by Palenzona and Ciraflci [8] that the constituent phases of alloy #5 at 1100 and 1160 °C should be (βZr) and (βY). The (αZr) phase occurring in the quenched samples could be ascribed to the martensitic transformation [6, 7]. Nevertheless, it should be noted that the temperature for the (αY)↔(βY) transition is still controversial in the literature. According to Love [3], a peritectic reaction of (βY) + L = (αY) occurred at 1490 °C, which support the present observation and coincides with our thermodynamic calculation presented in the next section.

Uy et al [4] reported that the reaction related to the transition between (αY) and (βY) is a eutectoid one, which occurs at 1063±10°C with a solubility of 1.8 at.% Zr in (αY). In the present work, two inconspicuous heat effects were found at about 1070 °C and 1140 °C in the DSC curve, as shown in Table 3. The similar phenomenon in the Y–Ti system was reported by Bare et al [13], but their high–temperature X–ray results indicate that there was no phase transition at the break temperature. They suggested that this kind of break may be caused by anomalous effects. Also, no evidence in this work can support that (βY) exists within this temperature region. Besides, The Zr–based alloys in molten state between 800 °C and 1200 °C were reported to have slow and weak reaction with Al_2O_3 [14, 15]. In the present work, the heating rate for the DSC measurement is 5 K/min. That is to say, the alloys are in touch with Al_2O_3 above 1000 °C for more than 70 min. So the inconspicuous effects could be produced by the reaction of the Zr and Y with the Al_2O_3 crucible wall.

Love [3] proposed that a peritectic reaction involving (βY) occurred at approximately 1490 °C while Lundin and Klodt [2, 5] suggested a metatectic reaction for the (βY) ↔ (αY) transformation at 1490 °C based on the analogy to the Y–Ti system. However, based on the fact that the allotropic transformation temperature of Y (1479 °C) is lower than 1490 °C, it can be concluded that the invariant reaction involving (βY) is peritectic rather than metatectic.

As the (αY) ↔ (βY) transition was not well determined via XRD and DSC in the present work, we accept the tentative conclusion of Love [3] that the reaction

Table 3 Summary of the phase-transition temperatures for the samples in the Zr–Y system annealed at 800 °C for 30 days [a]

Samples #	Alloy composition At % Y	Thermal arrests, °C.		Inconspicuous effect, °C.
1	10	881.2	1311.1	1142.7
2	20	884.9	1307.8	1137.9
3	30	887.6	1306	1139.6
4	40	892.5	1308.4	
5	50	892.9	1317.4	
6	60	885.5	1308.7	1092.9 1130.3
7	70	890.3	1309.3	1074.4 1134.7
8	97.5	884.8	1313.7	1070.3 1155.0

[a] Obtained on heating rate of 5 K/min

Table 4 The presently assessed compositions and temperatures data

Type of data	Reference	Experimental method	Quoted mode [b]
Invariant reactions:			
Eutectic	[3]	XRD and DTA	□
	[4]	DTA and DIL	□
	[5]	Incipient-melting	□
	This work	DSC	■
Y–rich	[3]	XRD and DTA	■
	[4]	DTA and DIL	+
Zr–rich	[3]	XRD and DTA	+
	[5]	Incipient-melting	□
	This work	DSC	■
Solidus in Zr-rich	[5]	Incipient-melting and OM	■

[b] Indicates whether the data are used or not used in the parameter optimization:
■, used;
□, not used but considered as reliable data for checking the modeling;
+, not used.

involving (βY) is a peritectic reaction of (βY) + L = (αY) occurring at 1490 °C. The presently assessed data are summarized in Table 4.

5. Thermodynamic calculation

There was no evidence for the existence of any intermediate phase in this system. (βZr), (βY) are the solid solution based on βZr, βY with bcc_A2 structure. (αZr), (αY) are the solid solution based on αZr, αY with hcp_A3 structure.

The expressions of the Gibbs energies of the pure Zr and Y are taken from the SGTE database [1].

The solution phases (αZr, αY, βZr and βY) are described by the substitution solution model, and the Gibbs energies of the phases are described by Redlich–Kister polynomials [16]:

$$\begin{aligned}&G^{\varphi} - H^{SER} = x\cdot {}^{0}G_{Zr}^{SER} + (1-x)\cdot {}^{0}G_{Y}^{SER} + \\ &+R\cdot T[x\cdot \ln x + (1-x)\cdot \ln(1-x)] + \\ &+x(1-x)[a_0 + b_0\cdot T + (1-2x)\cdot \\ &\cdot(a_1 + b_1\cdot T)]\end{aligned} \quad ...(1)$$

In which H^{SER} is the abbreviation of, $xH_{Zr}^{SER} + (1-x)H_{Y}^{SER}$ R is the gas constant and x is the mole fraction of Zr. The parameters a_i, b_i and c_i (i=0, 1, 2) are to be optimized.

The thermodynamic parameters are optimized using the PARROT module in Thermo-Calc software [17]. Due to the rather different elemental melting temperatures, two parameters were used to describe the bcc phase. For reproducing the eutectic point properly, a positive value of ${}^{1}L_{Zr,Y}^{L}$ is necessary.

In addition, two interaction parameters were employed to describe the Gibbs energy of the liquid, bcc and hcp phases. The parameters obtained in the present work are summarized in Table 5 with the parameters from Refs. [11, 12] for comparison.

The invariant reaction temperatures of the present work are listed in Table 6, compared with the measured values. Figure 5 is the presently calculated Zr–Y phase diagram. Figure 6 is the enlarged part concerning the reaction (βZr) + (αY) = (αZr), together with the experiment data of Luntin [5] for comparison. Figure 7 is the enlarged part concerning the reaction (βY) + L = (αY). Though less number of the adjustable parameters was adopted in the present work, a better reproduction of the experimental data was attained in comparison with the previous calculations [11, 12]. According to the present calculation, a peritectic reaction of (βY) + L = (αY) occurs at 1481 °C, which is in accord with Love [3].

The present work is a continuing effort of our previous attempts [18–20] to establish a thermodynamic database for Al and Mg alloys.

Table 5 The obtained parameters in Zr–Y system in the present work compared with former assessments.

Phase	Used parameters		
	Flandorfer et al. [11]	He et al. [12]	Present work
liquid	${}^{0}L^{L}_{Zr,Y} = 24000$	${}^{0}L^{L}_{Zr,Y} = 23902.389 + 0.09999T$	${}^{0}L^{L}_{Zr,Y} = 22718.358$
	${}^{1}L^{L}_{Zr,Y} = 3000$	${}^{1}L^{L}_{Zr,Y} = 3000.29996$	${}^{1}L^{L}_{Zr,Y} = 5302.237$
hcp (α)	${}^{0}L^{Hcp}_{Zr,Y} = 50000$	${}^{0}L^{Hcp}_{Zr,Y} = 50648.266 - 1.144725*T$	${}^{0}L^{Bcc}_{Zr,Y} = 40000$
bcc (β)	${}^{0}L^{Bcc}_{Zr,Y} = 40000$	${}^{0}L^{Bcc}_{Zr,Y} = 28548.038 + 6.887644*T$	${}^{0}L^{Bcc}_{Zr,Y} = 78604.723 - 14.2239*T$
	${}^{1}L^{Bcc}_{Zr,Y} = -9000$	${}^{1}L^{Bcc}_{Zr,Y} = -8716.91499$	

Table 6 Comparison between the measured and calculated invariant reaction temperatures in the Zr–Y system.

Invariant Reactions	Temperature, °C	Reference	Method
(βY) + L = (αY)	1490	[3]	DTA
	1481	This work	Calculation
L = (βZr) + (αY)	1325	[3]	DTA
	1313	This work	DSC
	1313	This work	Calculation
(βZr) + (αY) = (αZr)	880	[5]	Incipient-melting
	886	This work	DSC
	887	This work	Calculation

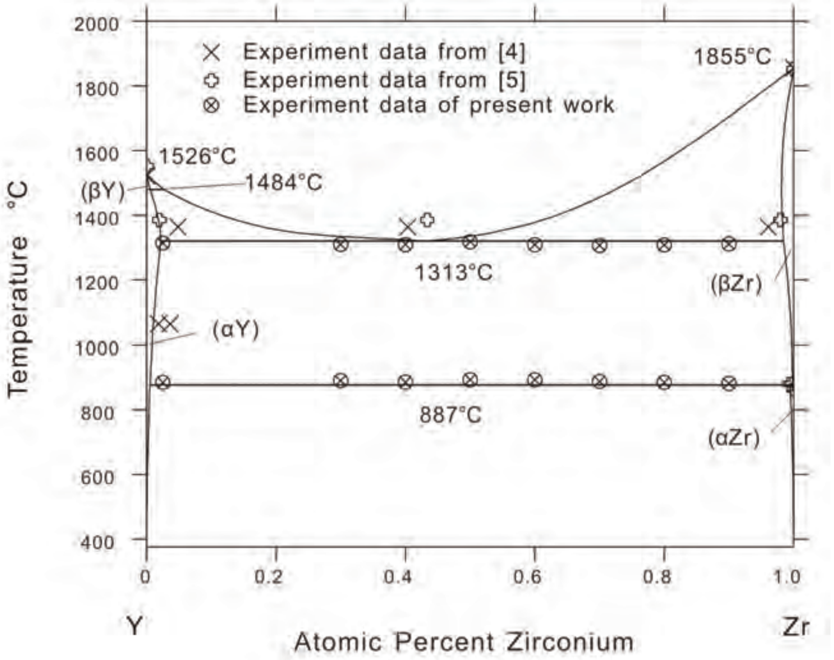

Fig. 5 The calculated phase diagram of the Zr–Y system compared with the experimental data from the literature [4, 5], and the present work

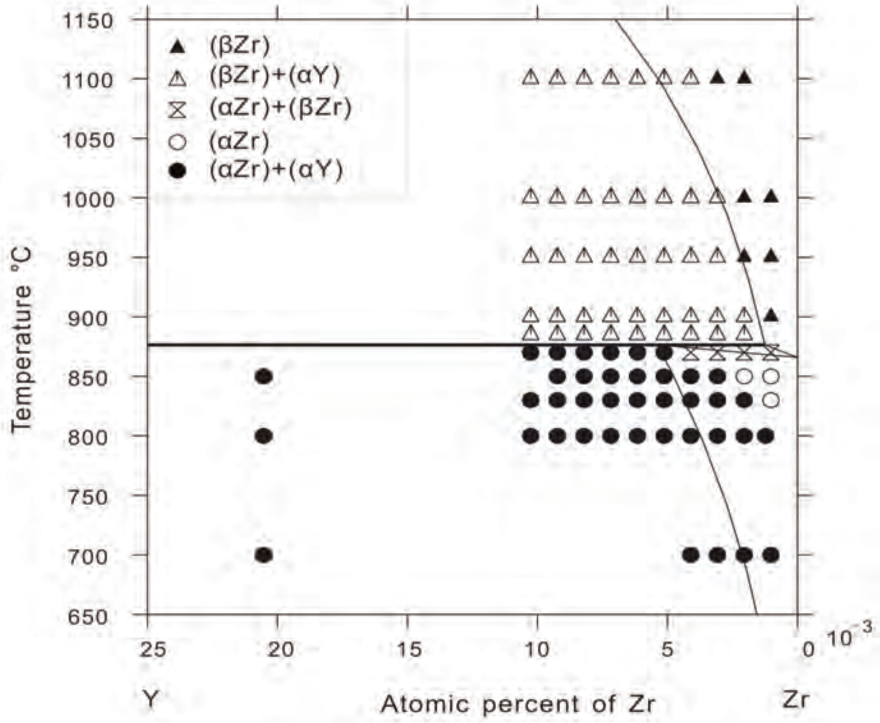

Fig. 6 The calculate Zr-rich region compared with the experiment data of [5]

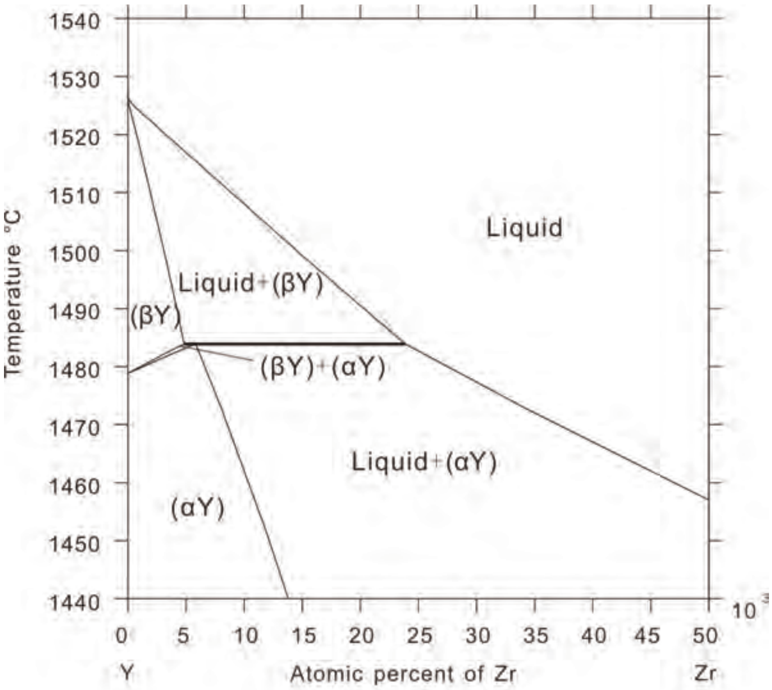

Fig. 7 The calculate Y-rich region in this work

6. Conclusion

Using DSC, the eutectic reaction of L = (βZr) + (αY) and the peritectoid reaction of (βZr) + (αY) = (αZr) were determined to occur at 1313 °C±5 °C and at 886 °C±5 °C, respectively.

A set of self-consistent thermodynamic parameters for the Gibbs energies of individual phases in the Zr–Y system was obtained by using CALPHAD approach taking into account the experimental data from the present work and literature. The peritectic reaction of (βY) + L = (αY) reported in the literature was confirmed in the present work both experimentally and thermodynamically. Compared with the previous assessments, the present modeling utilizes less number of the parameters for the liquid and bcc phases, and the present thermodynamic description can better account for the experimental data.

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