

Thermodynamic assessment of the Zn–Y and Al–Zn–Y systems

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Abstract

The phase diagram in the Zn–Y binary system has been evaluated by using the CALPHAD (Calculation of Phase Diagrams) method with the experimental data of the phase equilibria and thermodynamic properties. The Gibbs free energies of the liquid, bcc and hcp phases were described by the subregular solution model with the Redlich–Kister equation, and those of the eight stoichiometric compounds of the YZn, YZn₂, YZn₃, Y₃Zn₁₁, Y₁₃Zn₅₈, YZn₅, Y₂Zn₁₇ and YZn₁₂ were described by the sublattice model. The thermodynamic parameters in the Al–Zn–Y system were also evaluated by combining the experimental data with the parameters in three binary systems. The calculated phase equilibria and thermodynamic properties are in good agreement with the experimental data.

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Keywords: Phase diagram; Zn–Y system; Al–Zn–Y system; Thermodynamic assessment; CALPHAD method

1. Introduction

Magnesium (Mg) base alloys are potential candidates for structural, automotive and aerospace applications owing to their remarkable high specific strengths [1,2]. Rare earth elements are often added to Mg base alloys to improve the high temperature strength and creep resistance by precipitation hardening [2–4]. The Mg–Al–Zn–Y–Ce system is one of the key systems for developing high strength Mg base alloys. In order to develop the thermodynamic database of the Mg–Al–Zn–Y–Ce multicomponent system for designing Mg base alloys containing rare earth elements by the CALPHAD method which is a powerful tool to cut down on cost and time during development of materials and provides a clear guide line for materials design [5]. In the present paper, the phase diagrams in the Zn–Y and Al–Zn–Y systems were thermodynamically assessed by the CALPHAD method based on the available experimental data.

2. Thermodynamic models

2.1. Solution phases

The Gibbs free energies of the liquid, fcc, bcc and hcp phases are described by the subregular solution model, the expression of the Gibbs free energy for a phase in the Al–Zn–Y system is as follows:

$$G_m^\phi = \sum_{i=\text{Al,Y,Zn}} {}^0G_i^\phi x_i + RT \sum_{i=\text{Al,Y,Zn}} x_i \ln x_i + {}^E G_m^\phi \quad (1)$$

where ${}^0G_m^\phi$ is the molar Gibbs free energy of pure component i in the respective reference state with the ϕ phase, which is taken from the SGTE pure element database [6]. R is the gas constant, and T is the absolute temperature. The x_i denotes the mole fractions of component i . The term ${}^E G_m^\phi$ is the excess energy, which is expressed in the Redlich–Kister polynomials [7] as:

$${}^E G_m^\phi = L_{\text{AlY}}^\phi x_{\text{Al}} x_{\text{Y}} + L_{\text{AlZn}}^\phi x_{\text{Al}} x_{\text{Zn}} + L_{\text{YZn}}^\phi x_{\text{Y}} x_{\text{Zn}} + L_{\text{AlYZn}}^\phi x_{\text{Al}} x_{\text{Y}} x_{\text{Zn}} \quad (2)$$

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Table 1
The stable solid phases and the used models in the Zn–Y system

Phase	Prototype	Modeling phase	Used models
α Y	Mg	hcp	Subregular solution model
β Y	W	bcc	Subregular solution model
Y(Zn)	Mg	hcp	Subregular solution model
YZn	CsCl	(Y)(Zn)	Sublattice model
α YZn ₂	KHg ₂	(Y)(Zn) ₂	Sublattice model
β YZn ₂	–	(Y)(Zn) ₂	Sublattice model
YZn ₃	YZn ₃	(Y)(Zn) ₃	Sublattice model
Y ₃ Zn ₁₁	La ₃ Al ₁₁	(Y) ₃ (Zn) ₁₁	Sublattice model
Y ₁₃ Zn ₅₈	Gd ₁₃ Zn ₅₈	(Y) ₁₃ (Zn) ₅₈	Sublattice model
YZn ₅	EuMg ₅	(Y)(Zn) ₅	Sublattice model
Y ₂ Zn ₁₇	Th ₂ Ni ₁₇	(Y) ₂ (Zn) ₁₇	Sublattice model
YZn ₁₂	ThMn ₁₂	(Y)(Zn) ₁₂	Sublattice model

where L_{ij}^{ϕ} and L_{AlYZn}^{ϕ} are the interaction energies in binary and ternary systems, respectively, which are expressed in the following forms:

$$L_{ij}^{\phi} = {}^0L_{ij}^{\phi} + {}^1L_{ij}^{\phi}(x_i - x_j) + {}^2L_{ij}^{\phi}(x_i - x_j)^2 + \dots$$

$$= \sum_{m=0}^n {}^mL_{ij}^{\phi}(x_i - x_j)^m \quad (3)$$

$${}^mL_{ij}^{\phi} = a + bT \quad (4)$$

$$L_{AlYZn}^{\phi} = {}^0L_{AlYZn}^{\phi}x_{Al} + {}^1L_{AlYZn}^{\phi}x_{Y} + {}^2L_{AlYZn}^{\phi}x_{Zn} \quad (5)$$

$${}^nL_{AlYZn}^{\phi} = a' + b'T \quad (6)$$

where the parameters of a , b and a' , b' were evaluated based on the experimental data in binary and ternary systems, respectively.

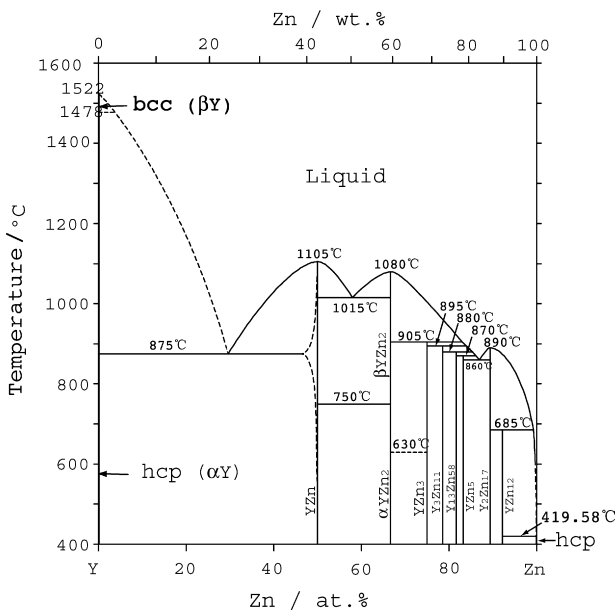


Fig. 1. The phase diagram of the Zn–Y system reviewed by Okamoto [11].

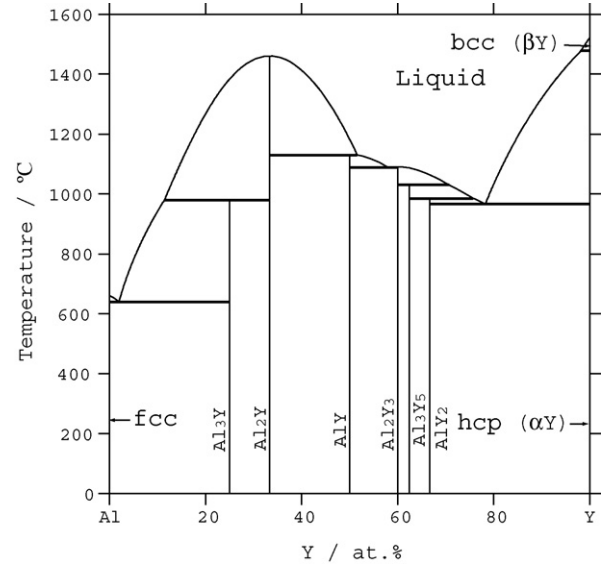


Fig. 2. The calculated phase diagram of the Al–Y system [13].

2.2. Stoichiometric intermetallic compounds

In the Zn–Y system, the intermetallic compounds YZn₂, YZn₃, Y₃Zn₁₁, Y₁₃Zn₅₈, YZn₅, Y₂Zn₁₇ and YZn₁₂ are stoichiometric compounds. The Gibbs free energy for per mole of formula unit $YpZnq$ can be expressed as:

$$G_m^{YpZnq} = \Delta^0 G_f^{YpZnq} + \frac{p}{p+q} {}^0G_Y^{\text{hcp}} + \frac{q}{p+q} {}^0G_{Zn}^{\text{hcp}} \quad (7)$$

where the ${}^0G_f^{YpZnq}$ indicates the standard Gibbs free energy for the formation of the stoichiometric compound from pure elements, which is described as:

$$\Delta^0 G_f^{YpZnq} = a'' + b''T \quad (8)$$

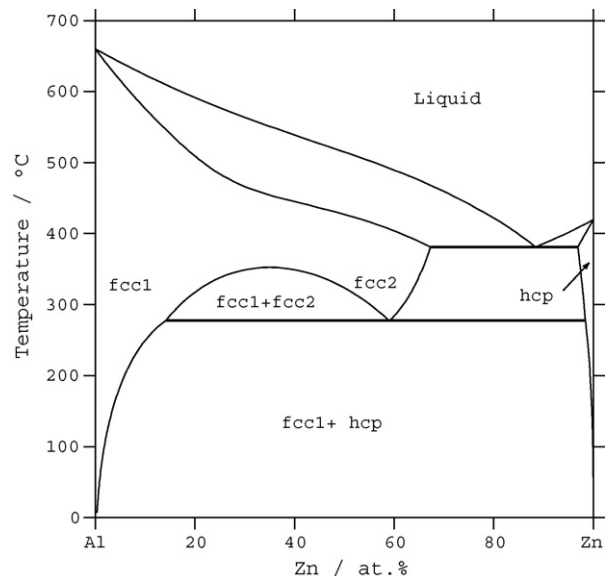


Fig. 3. The calculated phase diagram of the Al–Zn system [14].

Table 2
Thermodynamic parameters in the Al–Zn–Y system

Parameters in each phase (J/mol)	Reference
Liquid phase, format (Al, Y, Zn)₁	
${}^0L_{Al,Y}^L = -202611.28 + 4.64T$	[13]
${}^1L_{Al,Y}^L = -54350.11 + 0.28T$	[13]
${}^2L_{Al,Y}^L = +83347.01 - 34.76T$	[13]
${}^3L_{Al,Y}^L = +15488.69 - 0.80T$	[13]
${}^4L_{Al,Y}^L = -51205.9 + 30.22T$	[13]
${}^0L_{Al,Zn}^L = +10465.55 - 3.39T$	[14]
${}^0L_{Y,Zn}^L = -120443.49 + 18.85T$	This work
${}^1L_{Y,Zn}^L = +79694.1 - 37.82T$	This work
${}^2L_{Y,Zn}^L = +3471.11 + 2.88T$	This work
${}^0L_{Al,Y,Zn}^L = -20,000 - 10.235T$	This work
fcc phase (A1), format (Al, Y, Zn)₁(Va)₁	
${}^0L_{Al,Zn}^{fcc} = +7297.48 + 0.48T$	[14]
${}^1L_{Al,Zn}^{fcc} = +6612.88 - 4.59T$	[14]
${}^2L_{Al,Zn}^{fcc} = -3097.19 + 3.31T$	[14]
${}^0L_{Al,Y}^{fcc} = 0$	[13]
${}^0L_{Y,Zn}^{fcc} = 0$	This work
${}^0L_{Al,Y,Zn}^{fcc} = 100,000$	This work
bcc phase (A2), format (Al, Y, Zn)₁(Va)₃	
${}^0L_{Al,Y}^{bcc} = +90T$	[13]
${}^0L_{Y,Zn}^{bcc} = -2000$	This work
${}^0L_{Al,Y,Zn}^{bcc} = 0$	This work
hcp phase (A3), format (Al, Y, Zn)₁(Va)_{0.5}	
${}^0L_{Al,Y}^{hcp} = +90T$	[13]
${}^0L_{Al,Zn}^{hcp} = +18820.95 - 8.95T$	[14]
${}^1L_{Al,Zn}^{hcp} = -702.79$	[14]
${}^0L_{Y,Zn}^{hcp} = -2000$	This work
${}^0L_{Al,Y,Zn}^{hcp} = -2000$	This work
Al₃Y phase, format (Al)_{0.75}(Y)_{0.25}	
${}^0G_{Al:Y}^{Al_3Y} - 0.75{}^0G_{Al}^{fcc} - 0.25{}^0G_Y^{hcp} = -66865 + 11.62T$	[13]
Al₂Y phase, format (Al)_{0.667}(Y)_{0.333}	
${}^0G_{Al:Y}^{Al_2Y} - 0.667{}^0G_{Al}^{fcc} - 0.333{}^0G_Y^{hcp} = -82006 + 11.78T$	[13]
AlY phase, format (Al)_{0.5}(Y)_{0.5}	
${}^0G_{Al:Y}^{AlY} - 0.5{}^0G_{Al}^{fcc} - 0.5{}^0G_{Al}^{hcp} = -86905 + 20.435T$	[13]
Al₂Y₃ phase, format (Al)_{0.4}(Y)_{0.6}	
${}^0G_{Al:Y}^{Al_2Y_3} - 0.4{}^0G_{Al}^{fcc} - 0.6{}^0G_Y^{hcp} = -74721 + 16.882T$	[13]
Al₃Y₅ phase, format (Al)_{0.375}(Y)_{0.625}	
${}^0G_{Al:Y}^{Al_3Y_5} - 0.375{}^0G_{Al}^{fcc} - 0.625{}^0G_{Al}^{hcp} = -70559.9 + 15.965T$	[13]
AlY₂ phase, format (Al)_{0.333}(Y)_{0.667}	
${}^0G_{Al:Y}^{AlY_2} - 0.333{}^0G_{Al}^{fcc} - 0.667{}^0G_Y^{hcp} = -63636 + 14.8T$	[13]
γ phase, format (Y)_{0.5}(Al, Zn)_{0.5}	
${}^0G_{Y:Al}^{\gamma} - 0.5{}^0G_Y^{hcp} - 0.5{}^0G_{Al}^{fcc} = +50,000$	This work
${}^0G_{Y:Zn}^{\gamma} - 0.5{}^0G_Y^{hcp} - 0.5{}^0G_{Zn}^{Al} = -45,285 + 8.525T$	This work
${}^0L_{Y:Al,Zn}^{\gamma} = -249,329 + 15.481T \ln T$	This work
${}^1L_{Y:Al,Zn}^{\gamma} = 57,247 - 4.79T \ln T$	This work
αYZn₂ phase, format (Y)_{0.333}(Zn)_{0.667}	
${}^0G_{Y:Zn}^{\alpha YZn_2} - 0.333{}^0G_Y^{hcp} - 0.667{}^0G_{Zn}^{hcp} = -51016.67 + 13.41T$	This work
βYZn₂ phase, format (Y)_{0.333}(Zn)_{0.667}	
${}^0G_{Y:Zn}^{\beta YZn_2} - 0.333{}^0G_Y^{hcp} - 0.667{}^0G_{Zn}^{hcp} = -48379.33 + 10.83T$	This work
YZn₃ phase, format (Y)_{0.25}(Zn)_{0.75}	
${}^0G_{Y:Zn}^{YZn_3} - 0.25{}^0G_Y^{hcp} - 0.75{}^0G_{Zn}^{hcp} = -43,625 + 11.475T$	This work
Y₃Zn₁₁ phase, format (Y)_{0.214}(Zn)_{0.786}	
${}^0G_{Y:Zn}^{Y_3Zn_{11}} - 0.214{}^0G_Y^{hcp} - 0.786{}^0G_{Zn}^{hcp} = -39857.43 + 10.375T$	This work

Table 2 (Continued)

Parameters in each phase (J/mol)	Reference
$Y_{13}Zn_{58}$ phase, format $(Y)_{0.183}(Zn)_{0.817}$ ${}^0G_{Y:Zn}^{Y_{13}Zn_{58}} - 0.183{}^0G_Y^{hcp} - 0.817{}^0G_{Zn}^{hcp} = -36554.93 + 9.59T$	This work
YZn_5 phase, format $(Y)_{0.167}(Zn)_{0.833}$ ${}^0G_{Y:Zn}^{YZn_5} - 0.167{}^0G_Y^{hcp} - 0.833{}^0G_{Zn}^{hcp} = -34839.67 + 9.30T$	This work
Y_2Zn_{17} phase, format $(Y)_{0.105}(Zn)_{0.895}$ ${}^0G_{Y:Zn}^{Y_2Zn_{17}} - 0.105{}^0G_Y^{hcp} - 0.895{}^0G_{Zn}^{hcp} = -28368.42 + 8.25T$	This work
YZn_{12} phase, format $(Y)_{0.077}(Zn)_{0.923}$ ${}^0G_{Y:Zn}^{YZn_{12}} - 0.077{}^0G_Y^{hcp} - 0.923{}^0G_{Zn}^{hcp} = -23129.23 + 7.72T$	This work

where the parameters of a'' and b'' were evaluated in the present paper.

2.3. Binary phase extending into the ternary system

In view of the solubility of Al in YZn compound [8] in the ternary Al–Zn–Y system, in the present work, this phase is treated as the formula $(Y)_{0.5}(Al, Zn)_{0.5}$ by two sublattices with Y on the first sublattice, and Al and Zn on the second one. The Gibbs free energy for per mole of formula unit γ (YZnAl) phase is expressed as follows:

$$G_m^\gamma = y_{Al}^{II} {}^0G_{Y:Al}^\gamma + y_{Zn}^{II} {}^0G_{Y:Zn}^\gamma + 0.5RT(y_{Al}^{II} \ln y_{Al}^{II} + y_{Zn}^{II} \ln y_{Zn}^{II}) + y_{Al}^{II} y_{Zn}^{II} \sum_n {}^nL_{Y:Al,Zn}^\gamma (y_{Al}^{II} - y_{Zn}^{II})^n \quad (9)$$

where y_{Al}^{II} and y_{Zn}^{II} are the site fractions of species Al and Zn on the second sublattice, respectively. The two parameters of ${}^0G_{Y:Al}^\gamma$ and ${}^0G_{Y:Zn}^\gamma$ represent the Gibbs free energies of the γ compound when the second sublattice is occupied by only one element Al or Zn, respectively. The ternary parameter ${}^nL_{Y:Al,Zn}^\gamma$ is expressed as:

$${}^nL_{Y:Al,Zn}^\gamma = a''' + b'''T + c'''T \ln T \quad (10)$$

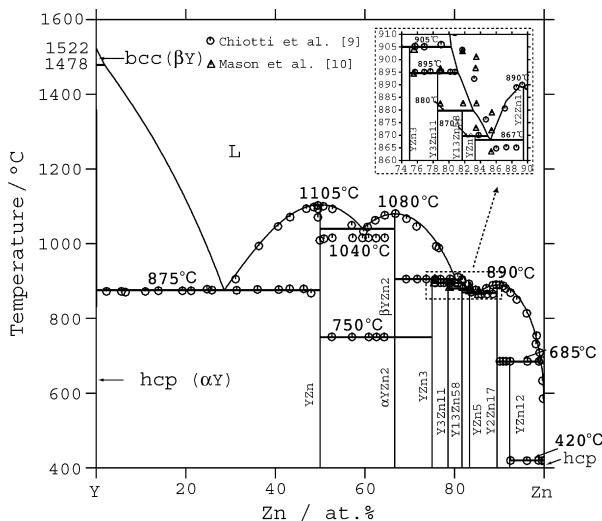
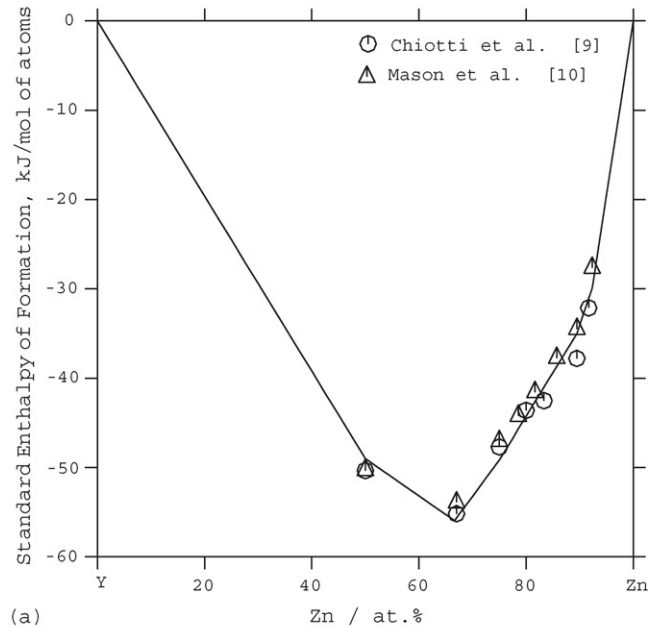
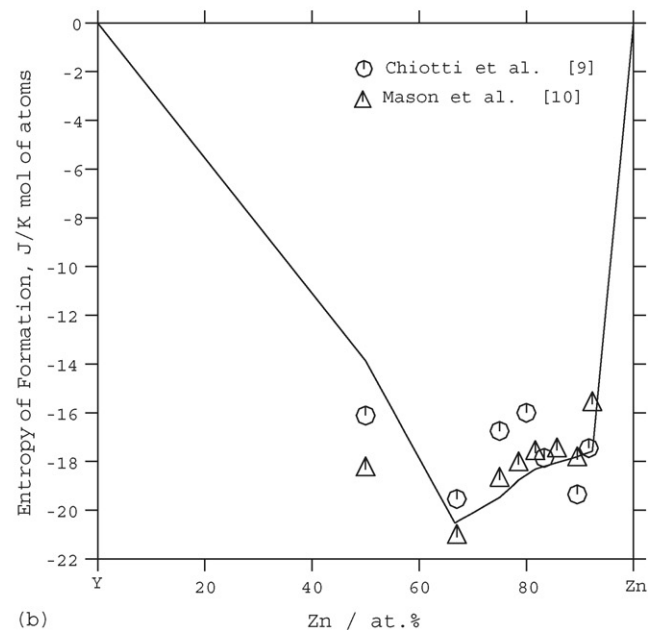


Fig. 4. The calculated phase diagram of the Zn–Y system with experimental data.



(a)



(b)

Fig. 5. The calculated enthalpy (a) and entropy (b) of formation at 500 °C compared with experimental data.

Table 3
Experimental and calculated invariant reactions in the Zn–Y system

Invariant reactions	Reaction type	Present calculation		Experimental measurements					
		T (°C)	Zn ^a (at.%)	Ref. [9]		Ref. [10]		Ref. [11]	
				T (°C)	Zn ^a (at.%)	T (°C)	Zn ^a (at.%)	T (°C)	Zn ^a (at.%)
L ↔ hcp + YZn	Eutectic	875	28.54	875	29.12	875	29.12	875	29.1
L ↔ YZn	Congruent	1105	50	1105	50	1105	50	1105	50
L ↔ YZn + βYZn ₂	Eutectic	1040	59.45	1015	59	1015	59	1015	59
L ↔ βYZn ₂	Congruent	1080	66.67	1080	66.67	1080	66.67	1080	66.67
L + βYZn ₂ ↔ YZn ₃	Peritectic	905	80.28	905	81.82	905	82	905	83
L + YZn ₃ ↔ Y ₃ Zn ₁₁	Peritectic	895	81.18	895	82.4	896	83.1	895	83.8
L + Y ₃ Zn ₁₁ ↔ Y ₁₃ Zn ₅₈	Peritectic	880	83.09	–	–	882	83.7	880	85.2
L + Y ₁₃ Zn ₅₈ ↔ YZn ₅	Peritectic	870	84.95	870	84.72	872	85.4	870	86.1
L ↔ Y ₂ Zn ₁₇ + YZn ₅	Eutectic	868	85.33	865	86	863	86	860	87
L ↔ Y ₂ Zn ₁₇	Congruent	890	89.47	890	89.47	890	89.47	890	89.47
L + Y ₂ Zn ₁₇ ↔ YZn ₁₂	Peritectic	685	99.28	685	99.43	685	99.42	685	99.33
L ↔ hcp – Zn	Congruent	420	100	419	100	420	100	419.58	100
βYZn ₂ ↔ αYZn ₂ (in the YZn–YZn ₂ region)	Polymorphic-transformation	750	–	750	–	750	–	750	–
βYZn ₂ ↔ αYZn ₂ (in the YZn ₂ –YZn ₃ region)	Polymorphic-transformation	750	–	~550	–	630	–	630	–

^a Note: Composition of the liquid phase.

where the parameters of a''' , b''' and c''' were assessed in this work.

The stable solid phases and the used models in the Zn–Y system are presented in Table 1.

3. Experimental information

3.1. The Zn–Y binary system

A detailed investigation on the phase diagram and thermodynamic properties in the Zn–Y system was firstly carried out by Chiotti et al. [9], who measured the whole composition region of the phase diagram by differential thermal analysis (DTA), and determined the phase stability of the YZn, YZn₂, YZn₃, YZn₄, YZn₅, Y₂Zn₁₇ and YZn₁₁ compounds as well as the Gibbs free energies, enthalpies and entropies of formation for these compounds at 500 °C, 700 °C and 900 °C by the dewpoint method.

Later, the phase diagram and thermodynamic properties of the Zn–Y system were comprehensively re-examined by Mason and Chiotti [10]. Eight inter-

metallic compounds, YZn, YZn₂, YZn₃, Y₃Zn₁₁, Y₁₃Zn₅₈, YZn₆, Y₂Zn₁₇ and YZn₁₂, have been identified by DTA, metallographic and X-ray diffraction techniques. Mason and Chiotti [10] measured the Gibbs free energies, enthalpies and entropies of formation for the YZn, YZn₂, YZn₃, Y₃Zn₁₁, Y₁₃Zn₅₈, YZn₆, Y₂Zn₁₇ and YZn₁₂ compounds in the range from 500 °C to 900 °C, but only given the values at 500 °C in his paper [10], where the reference states of Y and Zn are hcp and liquid phases, respectively [9,10]. Agreement on the phase diagram and thermodynamic properties was obtained between above two results reported by Chiotti et al. [9] and Mason and Chiotti [10] except that there is a larger discrepancy for the Gibbs free energies, enthalpies and entropies of the compounds with higher Zn contents.

Chiotti et al. [9] reported that the temperature of polymorphic transformation of the YZn₂ compound was 750 °C, however, Chiotti et al. [9] and Mason and Chiotti [10] gave that YZn₂ undergoes a polymorphic transformation in the YZn₂–YZn₃ region at 550 °C and 630 °C, respectively. These results seem be in contradiction with the thermodynamic rule.

Okamoto [11] reviewed the phase diagram in the Zn–Y system, in which the phase diagram was redrawn on the basis of the experimental data [9,10], as shown in Fig. 1

Table 4
Gibbs free energy of formation of intermetallic compounds in the Zn–Y system

Phase	Gibbs free energy of formation (kJ/mol of atoms)								
	500 °C		700 °C		900 °C				
	Present calculation	Experimental measurements (±1)	Present calculation	Experimental measurements (±1)	Present calculation	Experimental measurements (±1)			
		Ref. [9]	Ref. [10]		Ref. [9]	Ref. [10]	Ref. [9]	Ref. [10]	
YZn	–38.27	–38	–36	–35.5	–35	–	–32.7	–31	–
αYZn ₂	–40.1	–40	–38	–35.9	–36	–	–	–	–
βYZn ₂	–	–	–	–	–	–	–32.2	–32	–
YZn ₃	–34.1	–35	–32	–30.2	–31	–	–26.3	–27	–
Y ₃ Zn ₁₁	–31.2	–31	–30	–27.4	–28	–	–23.6	–24	–
Y ₁₃ Zn ₅₈	–28.4	–	–28	–24.8	–	–	–21.1	–	–
YZn ₅	–26.9	–29	–24	–23.4	–25	–	–19.6	–21	–
Y ₂ Zn ₁₇	–21.2	–23	–21	–17.6	–19	–	–14.1	–14	–
YZn ₁₂	–16.4	–19	–16	–12.8	–15	–	–9.4	–11	–

The reference states of pure elements of Y and Zn are hcp and liquid phases, respectively.

Table 5
Calculated invariant reactions in the Al–Zn–Y system

Reactions	Reaction type	Temperature (°C)	Phase	Composition (at.%)		
				Al	Y	Zn
$L \leftrightarrow Al_2Y + Y_2Zn_{17} + YZn_5$	E1	863	L	0.95	14.84	84.21
			Al_2Y	66.67	33.33	0
			Y_2Zn_{17}	0	10.53	89.47
			YZn_5	0	16.67	83.33
$L \leftrightarrow \beta YZn_2 + AlY + \gamma$	E2	1032	L	6.21	38.98	54.81
			βYZn_2	0	33.33	66.67
			AlY	50	50	0
			γ	3.83	50	46.17
$L \leftrightarrow AlY + \gamma + Al_2Y_3$	E3	1063	L	33.76	56.08	10.16
			AlY	50	50	0
			γ	3.34	50	46.66
			Al_2Y_3	40	60	0
$L \leftrightarrow \gamma + AlY_2 + hcp$	E4	916	L	4.13	74.79	21.08
			γ	4.55	50	45.45
			AlY_2	33.33	66.67	0
			hcp	0	99.94	0.06
$L + Al_3Y \leftrightarrow fcc + YZn_{12}$	U1	387	L	12.71	0	87.29
			fcc	34.47	0	65.53
			Al_3Y	75	25	0
			YZn_{12}	0	7.7	92.3
$L + Al_2Y \leftrightarrow Al_3Y + YZn_{12}$	U2	569	L	5.93	0.09	93.98
			Al_3Y	75	25	0
			YZn_{12}	0	7.7	92.3
			Al_2Y	66.67	33.33	0
$L + Y_2Zn_{17} \leftrightarrow YZn_{12} + Al_2Y$	U3	670	L	3.05	0.85	96.1
			YZn_{12}	0	7.7	92.3
			Al_2Y	66.67	33.33	0
			Y_2Zn_{17}	0	10.53	89.47
$L + Y_{13}Zn_{58} \leftrightarrow Al_2Y + YZn_5$	U4	864	L	0.94	15.19	83.87
			Al_2Y	66.67	33.33	0
			YZn_5	0	16.67	83.33
			$Y_{13}Zn_{58}$	0	18.31	81.69
$L + Y_3Zn_{11} \leftrightarrow Al_2Y + Y_{13}Zn_{58}$	U5	874	L	0.95	17.03	82.02
			Al_2Y	66.67	33.33	0
			$Y_{13}Zn_{58}$	0	18.31	81.69
			Y_3Zn_{11}	0	21.43	78.57
$L + YZn_3 \leftrightarrow Al_2Y + Y_3Zn_{11}$	U6	889	L	1.01	18.95	80.04
			Al_2Y	66.67	33.33	0
			Y_3Zn_{11}	0	21.43	78.57
			YZn_3	0	25	75
$L + \beta YZn_2 \leftrightarrow Al_2Y + YZn_3$	U7	900	L	5.36	20.51	74.13
			Al_2Y	66.67	33.33	0
			YZn_3	0	25	75
			βYZn_2	0	33.33	66.67
$L + Al_2Y \leftrightarrow \beta YZn_2 + AlY$	U8	1306	L	6.79	38.09	55.12
			Al_2Y	66.67	33.33	0
			βYZn_2	0	33.33	66.67
			AlY	50	50	0
$L + Al_2Y_3 \leftrightarrow \gamma + Al_3Y_5$	U9	997	L	9.14	67.63	23.23
			γ	3.71	50	46.29
			Al_2Y_3	40	60	0
			Al_3Y_5	37.5	62.5	0
$L + Al_3Y_5 \leftrightarrow \gamma + AlY_2$	U10	945	L	5.47	72.24	22.29
			γ	4.27	50	45.73
			Al_3Y_5	37.5	62.5	0
			AlY_2	33.33	66.67	0

Table 5 (Continued)

Reactions	Reaction type	Temperature (°C)	Phase	Composition (at.%)		
				Al	Y	Zn
L + YZn ₁₂ ↔ fcc + hcp	U11	381	L	11.65	0	88.35
			fcc	32.69	0	67.31
			YZn ₁₂	0	7.69	92.31
			hcp	3.1	0	96.9

3.2. The Al–Zn–Y ternary system

The phase equilibria in the Al–Zn–Y ternary system were only reported by Ganiev et al. [8], who determined the isothermal sections at 300 °C and 500 °C using X-ray phase analysis and did not find ternary compounds. In this ternary system, the experimental results indicated that there exists almost no solubility of third element in binary compounds except for the YZn compound, and the fcc phase is in equilibrium with the Al₃Y compound in the Al-rich corner.

The experimental information on the liquid phase and thermodynamic properties was not reported yet.

4. Assessment procedure

The optimization was carried out by using a PARROT program in Thermo-Calc software [12], which can handle various kinds of experimental data. The experimental data of the phase diagram and thermodynamic properties were used as input to the program. Each piece of selected information was given a certain weight by the importance of data, and changed by trial and error during the assessment, until most of the selected experimental information is reproduced within the expected uncertainty limits.

In the present thermodynamic assessment, the reference states of pure elements of Y and Zn are hcp and liquid phases, respectively, and almost all of the above experimental information was selected for the evaluation of the thermodynamic parameters. At first, the parameters of the compounds are evaluated based on the experimental data on the Gibbs free energy, enthalpy and entropy of formation, and then the parameters of the liquid phase were evaluated based on the experimental data on the liquidus line, which were measured accurately almost over the whole composition range [9,10].

In the assessment of the Al–Zn–Y ternary system, the thermodynamic parameters of the Al–Y [13] and Al–Zn [14] binary systems are adopted, and the calculated phase diagrams are shown in Figs. 2 and 3. The ternary parameters of the liquid, fcc, hcp, phases and the ternary compound γ (YZnAl) phase were assessed based on the experimental data of the isothermal sections at 300 °C and 500 °C [8]. However, the ternary parameters of the bcc phase cannot be accurately calculated because available experimental information on these phases is limited. Thus, these parameters were determined by considering the fact that the unstable phases do not appear in the calculation of phase diagrams in the ternary system. These parameters need to be evaluated based on new experimental data in the future.

All the parameters were finally evaluated together and adjustments were made to give the best description of the system. All evaluated parameters are listed in Table 2.

5. Results and discussion

The calculated phase diagram in the Zn–Y system with all experimental data used in the optimization is shown in Fig. 4. All

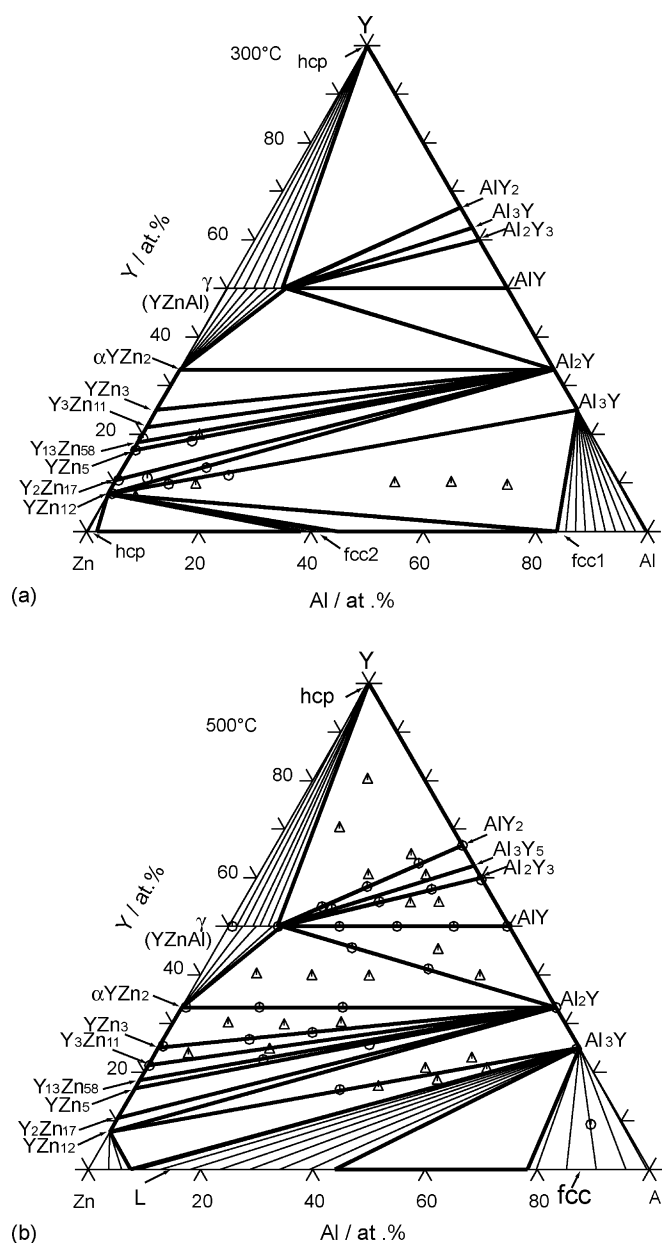


Fig. 6. The calculated isothermal sections at (a) 300 °C and (b) 500 °C of the Al–Zn–Y system with the experimental data [8]. (Δ): three-phase equilibrium; (\circ): two-phase equilibrium.

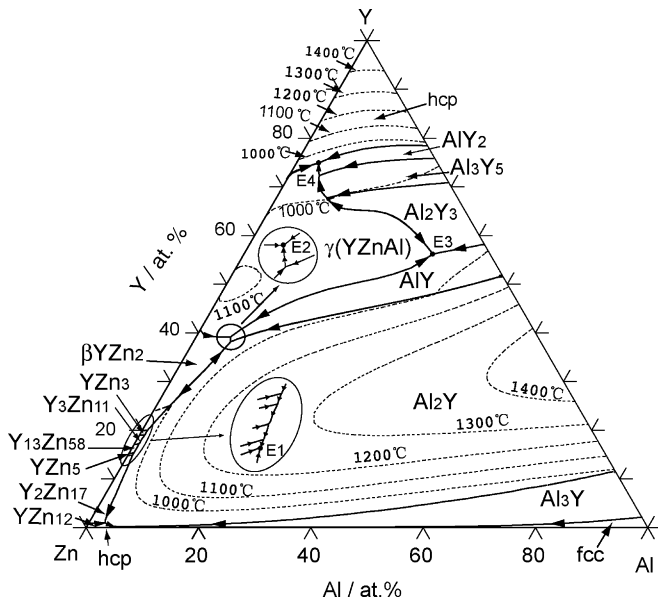


Fig. 7. The calculated liquidus project of the Al–Zn–Y system.

the invariant equilibria in the Zn–Y system are listed in Table 3. The calculated phase diagram is in excellent agreement with most of the experimental results reported by Chiotti et al. [9] and Mason and Chiotti [10]. However, a relative discrepancy on the liquidus lines in the Zn-rich region between the calculated and experimental data was observed. Great care has been taken to reduce these discrepancies, but it was found that it is difficult to fit these experimental data very well.

Fig. 5 shows the calculated enthalpy and entropy of formation in the whole compositional region at 500 °C by the present assessed thermodynamic parameters with the experimental data [9,10]. The calculated and experimental values of the Gibbs free energies of all stoichiometric compounds in the Zn–Y system at 500 °C, 700 °C and 900 °C are listed in Table 4, where good agreement is obtained between the present calculated results and experimental data [9,10].

The data on polymorphic transformation of the YZn_2 compound at 750 °C was used in the present assessment. The calculated results indicate that the two-phase regions of the YZn – YZn_2 and YZn_2 – YZn_3 were divided into two parts at 750 °C due to the polymorphic transformation of the YZn_2 compound.

More recently, Shao et al. [15] also made the thermodynamic assessment of the Zn–Y system, however, the calculated values on entropies and Gibbs free energies of compounds in the Zn–Y system and the liquidus lines in the Zn-rich region did not agree well with the experimental data [9,10].

Fig. 6 shows the calculated isothermal sections of the Al–Zn–Y ternary system at 300 °C and 500 °C with the experi-

mental data [8], in which a good agreement is obtained. Based on the evaluated thermodynamic parameters, the liquidus project is predicted, as shown in Fig. 7, where there are four ternary eutectic reactions and eleven ternary peritectic type reactions. The calculated reaction types and the corresponding compositions are listed in Table 5.

6. Conclusions

The phase diagrams and thermodynamic properties in the Zn–Y binary and Al–Zn–Y ternary systems were evaluated from the available experimental information in literature. A consistent set of optimized thermodynamic parameters has been derived for describing the Gibbs free energy of each solution phase and intermetallic compound in the Zn–Y binary system, leading to a good agreement between the calculated results and most of the experimental data found in literature. Necessary experiments are needed to validate the liquidus project in the Al–Zn–Y system.

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