Thermodynamic calculation of phase equilibria of the U–Ga and U–W systems

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ABSTRACT

The thermodynamic assessments of the U–Ga and U–W systems have been carried out by using the CALPHAD (calculation of phase diagrams) method using experimental data including thermodynamic properties and phase equilibria. Gibbs free energies of the solution phases were described by the subregular solution models with the Redlich–Kister equation, and those of the intermetallic compounds were described by the sublattice models. A consistent set of thermodynamic parameters has been derived for the Gibbs free energy of each phase in the U–Ga and U–W binary systems, respectively. The calculated phase diagrams and thermodynamic properties in the U–Ga and U–W systems are in good agreement with experimental data.

1. Introduction

Nuclear energy, as a new kind of important energy with low pollution and low cost for generating electricity, is expected to replace the traditional fossil fuel energy. The development of U-based alloys is important to develop safe nuclear reactor technology with high efficiency. The U–Ga alloys have been studied for the development of new metal reactor, either as a high-temperature application of the thermodynamic stability of actinide intermetallics, or for the liquid metal fuel reactor technology [1]. The U–W alloy system was widely investigated for developing high neutron flux research reactors with low enrichment uranium fuel [2,3].

Phase diagrams can give an important guidance in the development of the nuclear materials. At the present time, the most of the binary U-based systems have been investigated experimentally; however, the assessments whereby the thermodynamic properties and phase diagrams are connected. The development of the thermodynamic databases of the U-based systems is important and necessary.

The purpose of the present work is to carry out the thermodynamic assessments of the U–Ga and U–W systems by means of the CALPHAD method. The thermodynamic parameters of each phase in the U–Ga and U–W systems are optimized according to provide self consistent experimental data including the thermodynamic properties and computed phase diagrams.

2. Thermodynamic models

The models and the crystal structures of each stable phase in the U–Ga and U–W systems are listed in Table 1.

2.1. Solution phases

The Gibbs free energies of the solution phases in A–B (A–B: Ga–U or U–W) system are described by

$$G_m^\phi = {}^0G_A^\phi x_A + {}^0G_B^\phi x_B + RT(x_A \ln x_A + x_B \ln x_B) + {}^EG^\phi, \tag{1}$$

where G_i^ϕ is the molar Gibbs free energy of pure element i with the structure ϕ in a nonmagnetic state, which is taken from the compilation by Dinsdale [4], and the term ${}^EG^\phi$ is the excess energy, which is expressed in the Redlich–Kister polynomials [5] as

$$
\begin{aligned}
{}^EG^\phi &= {}^0L_{AB}^\phi x_A x_B + {}^1L_{AB}^\phi (x_A - x_B) x_A x_B + {}^2L_{AB}^\phi (x_A - x_B)^2 x_A x_B + \cdots \\
&= \sum_{m=0}^{n} {}^mL_{AB}^\phi (x_A - x_B)^m x_A x_B,
\end{aligned} \tag{2}
$$

where ${}^mL_{AB}^\phi$ is the interaction energy between A and B atoms, and is expressed as

$$ {}^mL_{AB}^\phi = a + bT. \tag{3} $$

The parameters of a and b are evaluated based on the experimental data in the present work.

2.2. Stoichiometric intermetallic compounds

Intermetallic compounds of the Ga_3U, Ga_2U and Ga_3U_2 in the U–Ga system are treated as stoichiometric phases. The Gibbs free energy per mole of formula unit $(Ga)_m(U)_n$ can be expressed by

$$ \Delta G_f^{Ga_mU_n} = {}^0G_{Ga:U}^{Ga_mU_n} - m^0G_{Ga}^{ref} - n^0G_U^{ref} = a' + b'T, \tag{4} $$

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Table 1
The stable phases and the models used in the U–Ga and U–W binary systems

System	Phase	Strukturbericht designation	Prototype	Modeling phase	Used model
U–Ga	α (Ga)	A11	α (Ga)	(Ga,U)	SSM
	γ (U)	A2	W	(Ga,U)	SSM
	α (U)	A20	α (U)	(Ga,U)	SSM
	β (U)	Ab	β (U)	(Ga,U)	SSM
	Ga_2U	C32	AlB_2	$(Ga)_2(U)$	SM
	Ga_3U_2	–	–	$(Ga)_3(U)_2$	SM
	Ga_3U	$L1_2$	$AuCu_3$	$(Ga)_3(U)$	SM
U–W	bcc (W)	A2	W	(U,W)	SSM
	γ (U)	A2	W	(U,W)	SSM

Note: SSM: Subregular solution model; SM: Sublattice model.

where the $\Delta G_f^{Ga_mU_n}$ denotes the standard Gibbs free energy of formation of the stoichiometric compound from the pure elements. The term $^0G_i^{ref}$ is the molar Gibbs free energy of pure element i (i = Ga or U) with its defined reference structure in a nonmagnetic state. The parameters a' and b' are evaluated in the present work.

3. Evaluation of the experimental data

3.1. The U–Ga system

The phase diagram of the U–Ga system, which consists of three intermetallic compounds Ga_3U, Ga_2U, and Ga_3U_2 and liquid phase, was determined by Buschow [6] based on thermal analysis, X-ray diffraction, and metallogrphic methods. In addition to the compounds found by Buschow [6], the existence of the GaU and Ga_5U_3 compounds were also reported by Makrov [7] and Dayan [8], however, the decomposition reaction and phase stability of these compounds are unknown. The phase equilibria in the U-rich portion were estimated by Gardie [1] from to the measured activity of Ga in the liquid phase. Based on the experimental data reported in the previous works [6–8], the phase diagram of the U–Ga system was assessed by Okamoto [9], as shown in Fig. 1.

Johnson and Feder [10] and Lebedev et al. [11] derived the thermodynamic properties of the UGa_3 compound based on fused salt EMF measurements. Alcock et al. [12] measured the Ga vapour pressures and derived the Gibbs free energies of formation of the Ga_3U, Ga_2U, and Ga_3U_2 compounds. The thermodynamic data of the U–Ga system reported in previous works [10–12] were reviewed by Chiotti et al. [13]. Recently, Prabhahara et al. [14] determined the enthalpies of formation of the intermetallic compounds Ga_3U and Ga_2U using high-temperature liquid gallium solution calorimetric measurements. In comparing the reported data [10–14], there exists disagreement among the thermodynamic data of the compounds determined by molten salt EMF [10,11], vapour pressure measurements [12] and reaction calorimetry [14] methods. After considering the experimental methods and conditions, the data reported by Gardie [1] and Prabhakara [14] were used in the present work.

3.2. The U–W system

The U–W system is characterised by limited terminal solid solubility at both ends with no intermetallic compounds. Several researchers [16–19] reported the liquidus data in the U-rich portion, and their results are in agreement with each other. Using X-ray and metallographic techniques methods, Schramm et al. [16] and Summers-Smith [20] reported the solid solubility of W in the γ (U) to be less than 1 at.% W and 0.65–1.19 at.% W, respectively. All the reported values of solid solubility of U in bcc (W) are found to be less than 1 at.% [16,20,21]. Based on the experimental
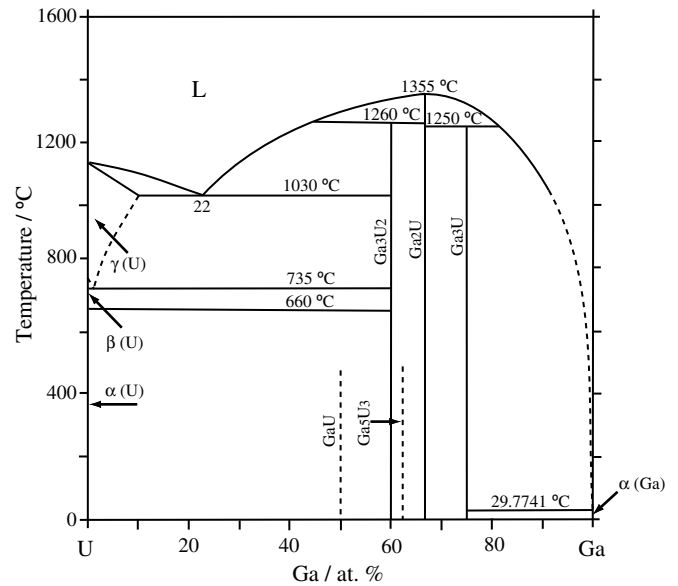

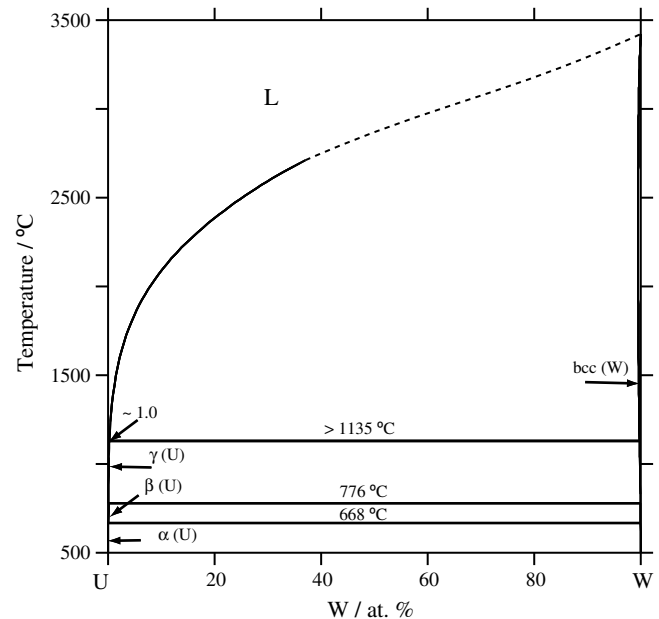**Fig. 1.** Phase diagram of the U–Ga system reviewed by Okamoto [9].

Fig. 2. Phase diagram of the U–W system reviewed by Pandian [15].

data reported in the previous works [16–21], the U–W phase diagram was reviewed by Pandian et al. [15], as shown in Fig. 2.

Miedema [22] predicted that the enthalpy of formation of type UW compound is +1 kJ/mol in the U–W system, and the enthalpy of the solution at infinite dilution for W (liquid) in U (liquid) is +4 kJ/mol. However no temperature dependence was given in the Miedema work.

4. Optimized results and discussion

The optimization was carried out using the PARROT [23] module in the Thermo-Calc software [24]. The procedure involves a weighted least-square optimization of the model parameters using experimental information on thermodynamic properties and phase

diagram. Each piece of selected information was given a certain weight according to the importance of data, and changed by trial and error during the assessment, until most of the selected experimental information was reproduced within the expected uncertainty.

4.1. The U–Ga system

The calculated phase diagram in the U–Ga system with all experimental data used in the present optimization is shown in Fig. 3. The calculated phase diagram is in good agreement with the experimental data [1,6], except for the liquid composition in the reaction of the L + $Ga_2U \rightarrow Ga_3U_2$. The calculated liquid composition in this reaction is 48.3 at.% Ga in the present works, but is 44.5 at.% Ga in Buschow's report [6].

The calculated enthalpies and entropies of formation of the compounds at 400 °C are plotted in Figs. 4 and 5. The calculated
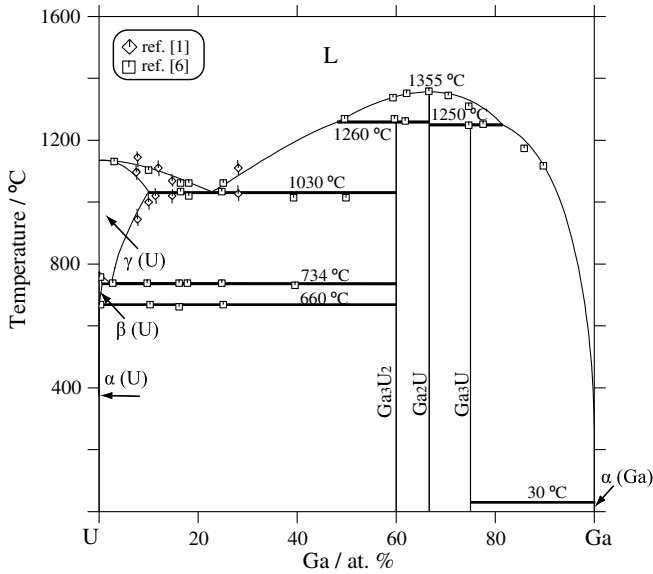

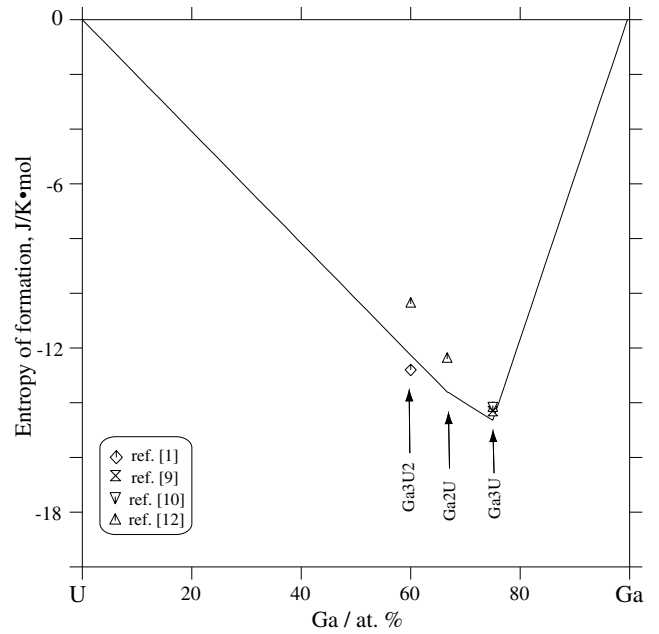**Fig. 3.** Calculated phase diagram of U–Ga system with experimental data.

Fig. 5. Calculated entropies of formation of intermetallic compounds at 400 °C in the U–Ga system compared with the experimental data [1,9–12]. (The reference states: liquid (Ga) phase and α (U) phase).
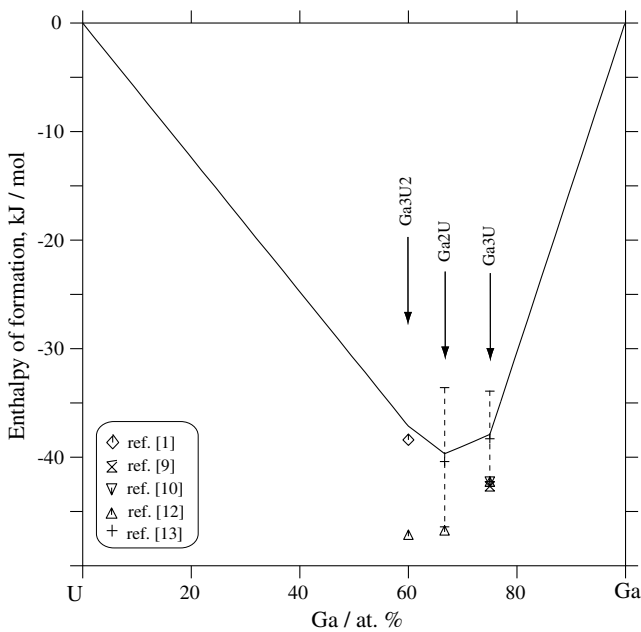

Fig. 4. Calculated enthalpies of formation of intermetallic compounds at 400 °C in the U–Ga system compared with the experimental data [1,9–13]. (The reference states: liquid (Ga) phase and α (U) phase).
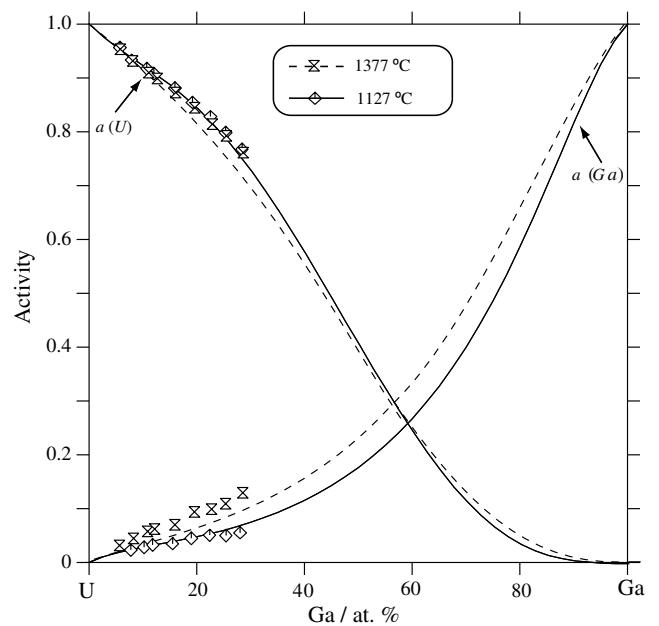

Fig. 6. Calculated activity of Ga and U in the liquid phase at 1127 °C and 1377 °C compared with experimental data [1]. (The reference states: liquid (Ga) phase and liquid (U) phase).

Table 2
Thermodynamic parameters in the Ga–U and W–U systems optimized in the present work

System	Parameters in each phase (J/mol)	
Ga–U	Liquid phase, format (Ga, U)	
	$G_{Ga}^{Liq} - G_{Ga}^{SER} = +5491.31 - 18.073718T - 7.0154 \times 10^{-17}T^7;$ $298.15 > T > 302.9$ (K) $+ 5666.446 - 18.680788T \quad - 1.64554 \times 10^{23}T^{-9};$ $302.9 > T > 4000$ (K);	Ref. [4]
	$G_U^{Liq} - G_U^{SER} = +12355.5 - 10.3239T; \quad 298.15 > T > 4000$ (K)	
	$^0L_{Ga,U}^{Liq} = -37988 + 6.292T; \quad ^1L_{Ga,U}^{Liq} = -43307 + 16.045T$	
	$^2L_{Ga,U}^{Liq} = -11520 + 5.048T; \quad ^3L_{Ga,U}^{Liq} = -20434 + 12.021T$	
	γ (U) phase, format (Ga, U)	
	$G_U^{\gamma(U)} - G_U^{SER} = -752.767 + 131.5301T - 27.5152T \times \ln T$ $- 0.00835595T^2 + 9.67907 \times 10^{-7}T^3 + 204611T^{-1};$ $298.15 > T > 1049$ (K) $- 4698.365 + 202.677635T - 38.2836T \times \ln T;$ $1049 > T > 3000$ (K);	Ref. [4]
	$G_{Ga}^{\gamma(U)} - G_{Ga}^{SER} = +4500 - 11.7T; \quad ^0L_{Ga,U}^{\gamma(U)} = -19097 + 0.204T$	
	β (U) phase, format (Ga, U)	
	$G_U^{\beta(U)} - G_U^{SER} = -5156.136 + 106.968316T - 22.841T \times \ln T - 0.01084475T^2$ $+ 2.7889 \times 10^8 T^3 + 81944T^{-1}; \quad 298.15 > T > 941.5$ (K) $- 14327.309 + 244.16002T - 42.9278T \times \ln T; \quad 941.5 > T > 3000$ (K);	Ref. [4]
	$G_{Ga}^{\beta(U)} - G_{Ga}^{SER} = +3500 - 10T; \quad ^0L_{Ga,U}^{\beta(U)} = -8500$	
	α (U) phase, format (Ga, U)	
	$G_U^{\alpha(U)} - G_U^{SER} = 0; \qquad G_{Ga}^{\alpha(U)} - G_{Ga}^{SER} = 0;$	
	$^0L_{Ga,U}^{\alpha(U)} = -7000$	
	α (Ga) phase, format (Ga, U)	
	$G_{Ga}^{\alpha(Ga)} - G_{Ga}^{SER} = 0; \qquad G_U^{\alpha(Ga)} - G_U^{SER} = 0;$	
	$^0L_{Ga,U}^{\alpha(Ga)} = 2000$	
	Ga_3U_2 phase, format $(Ga)_{0.6}(U)_{0.4}$	
	$\Delta G_f^{Ga_3U_2} = -33747 + 1.007T$	
	Ga_2U phase, format $(Ga)_{0.667}(U)_{0.333}$	
	$\Delta G_f^{Ga_2U} = -35903 + 1.082T$	
	Ga_3U phase, format $(Ga)_{0.75}(U)_{0.25}$	
	$\Delta G_f^{Ga_3U} = -33644 + 0.561T$	
W–U	Liquid phase, format (U, W)	
	$G_W^{Liq} - G_W^{SER} = +52160.584 - 14.10999T - 2.713468 \times 10^{-24}T^7;$ $298.15 > T > 3695$ (K) $+ 52432.75 - 14.187335T \quad - 1.528621 \times 10^{33}T^{-9};$ $3695 > T > 6000$ (K);	Ref. [4]
	$G_U^{Liq} - G_U^{SER} = +12355.5 - 10.3239T; \quad 298.15 > T > 4000$ (K)	
	$^0L_{U,W}^{Liq} = 12500 + 7.500T; \quad ^1L_{U,W}^{Liq} = 30794 - 11.460T$	
	γ (U) phase, format (U, W)	
	$G_U^{\gamma(U)} - G_U^{SER} = -752.767 + 131.5301T - 27.5152T \times \ln T - 0.00835595T^2$ $+ 9.67907 \times 10^{-7}T^3 + 204611T^{-1}; \quad 298.15 > T > 1049$ (K) $- 4698.365 + 202.677635T - 38.2836T \times \ln T; \quad 1049 > T > 3000$ (K);	Ref. [4]
	$G_W^{\gamma(U)} - G_W^{SER} = 0; \qquad ^0L_{U,W}^{\gamma(U)} = 36500 + 24.500T$	

Table 2 (*continued*)

System	Parameters in each phase (J/mol)	
$G_U^{SER} = -8407.734 + 130.947151T - 26.9182T \times \ln T$ $+ .00125156T^2 - 4.42605 \times 10^{-6}T^3 + 38568T^{-1};$ $298.15 > T > 955\ (K)$ $- 22521.8 + 292.113093T - 48.66T \times \ln T;\quad 955 > T > 3000\ (K)$		Ref. [4]
$G_{Ga}^{SER} = -21312.331 + 585.263691T - 108.228783T \times \ln T$ $+ .227155636T^2 - 1.18575257 \times 10^{-4}T^3 + 439954T^{-1};$ $20 > T > 302.92\ (K)$ $- 7055.646 + 132.7302T - 26.0692906T \times \ln T$ $+ 1.506 \times 10^{-4}T^2 - 4.0173 \times 10^{-8}T^3 - 118332T^{-1} + 1.64554E + 23T^{-9};$ $302.92 > T > 4000\ (K);$		Ref. [4]
$G_W^{SER} = -7646.311 + 130.4T - 24.1T \times \ln T - .001936T^2 + 2.07 \times 10^{-7}T^3$ $+ 44500T^{-1} - 5.33 \times 10^{-11}T^4;\quad 298.15 > T > 3695\ (K)$ $- 82868.801 + 389.362335T - 54T \times \ln T + 1.528621 \times 10^{+33}T^{-9};$ $3695 > T > 6000\ (K);$		Ref. [4]

Table 3
Invariant reactions in the Ga–U system

Reaction type	Reaction	Ga (at.%)			T (°C)	Reference
Eutectic	L → γ (U) + Ga₃U₂	22.0	9.2	60	1030	[6]
		21.4	9.9	60	1030	Present work
Peritectic	L + Ga₂U → Ga₃U₂	44.5	66.7	60	1260	[6]
		48.3	66.7	60	1260	Present work
Congruent	L → Ga₂U	66.7			1355	[6]
		66.7			1355	Present work
Peritectic	L + Ga₂U → Ga₃U	81.5	66.7	75	1250	[6]
		81.5	66.7	75	1250	Present work
Eutectoid	γ (U) → Ga₃U₂ + β (U)	~1	60	~0.1	735	[6]
		3	60	0.1	734	Present work
Eutectoid	β (U) → Ga₃U₂ + α (U)	–	60	–	660	[6]
		0.05	60	0.01	660	Present work

Table 4
Invariant reactions in the W–U system

Reaction type	Reaction	W (at.%)			T (°C)	Reference
Eutectic	L → γ (U) + bcc (W)	–	–	–	>1135	[15]
		0.26	0.24	99.7	1134.5	Present work
Eutectoid	γ (U) → β (U) + bcc (W)	–	–	–	776	[15]
		0.1	0	99.7	774.5	Present work
Congruent	β (U) → γ (U) + bcc (W)	–	–	–	668	[15]
		0	0	99.7	669	Present work

Table 5
The calculated mixing enthalpy of liquid phase (J/mol)

Composition (at.%)	Temperature (°C)			
	3500	3600	3700	3800
90	3400	3320	3340	3330
70	5200	5220	5200	5210
50	3170	3190	3140	3120
30	20	49	78	49

The reference states: liquid (W) phase and liquid (U) phase.

activities of Ga and U in the liquid phase at 1127 °C and 1377 °C compared with experimental data are shown in Fig. 6. Reasonable agreement is observed.

All optimized thermodynamic parameters for the U–Ga system in the present assessment are listed in Table 2. All invariant reactions in the U–Ga system with the experimental data are summarized in Table 3.

4.2. The U–W system

Since no experimental thermodynamic data in the U–W binary system are available, the optimization was carried out based on the experimental determined data of phase diagram [16–19] and the thermodynamic data estimated by Miedema [22]. The calculated phase diagram with experimental data is shown in Fig. 7. All invariant reactions in the U–W system are summarized in Table 4. The calculated results are in agreement with the experimental data by Schramm et al. [16–19]. The calculated mixing enthalpies of the liquid phase at 3500–3800 °C are summarized in Table 5,
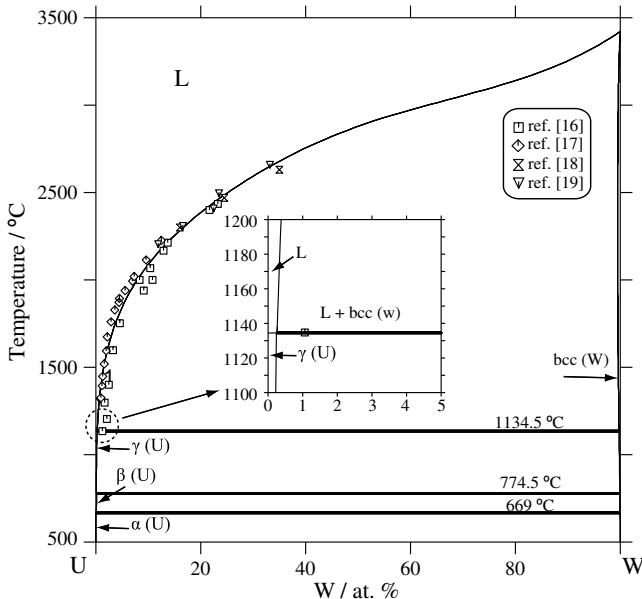
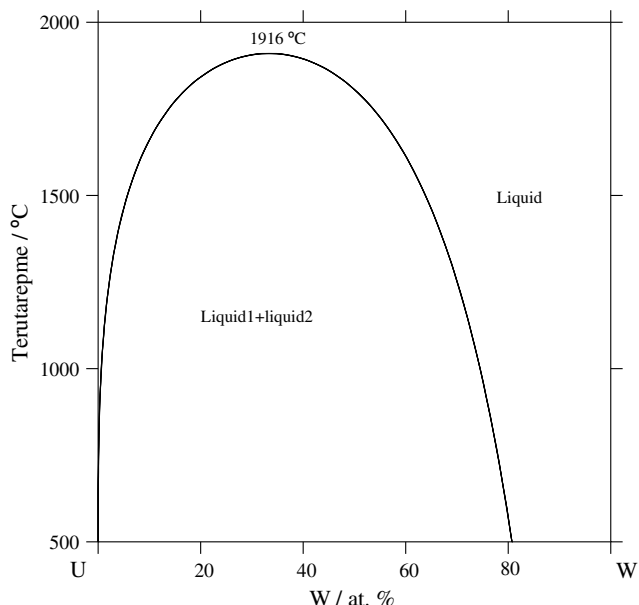**Fig. 7.** Calculated phase diagram of the U–W binary system with experimental data [21].

Fig. 8. Calculated metastable miscibility gap of the liquid phase in the U–W binary system.

which is reasonable in agreement with Miedema [22]. According to the calculated results in Table 5, the mixing enthalpies between the W and U atoms are large and positive, which implies that there is large repulsion between the U and W atoms in the liquid phase, leading to a metastable miscibility gap in the liquid phase. Based on the thermodynamic parameters optimized in the present work, the calculated metastable miscibility gap of the liquid phase in the U–W system is shown in Fig. 8. The calculated critical temperature and composition of the metastable miscibility gap of the liquid phase are 1916 °C and 32 at.% W. All thermodynamic parameters of the U–W system optimized in the present work are summarized in Table 2.

More thermodynamic data in U–W binary system need to be determined, and the thermodynamic assessment work should be carried out with new thermodynamic data in the future.

5. Conclusions

The phase diagrams and thermodynamic properties in the U–Ga and U–W systems were thermodynamically assessed by combining thermodynamic models with available experimental information. A consistent set of thermodynamic parameters has been derived to describe the Gibbs free energies of each solution phase and intermetallic compounds in the U–Ga and U–W binary systems. This leads to a good agreement between the calculated phase diagrams and most of the experiment data found in the literature.

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