



Thermodynamic assessment of Ni–Yb binary system

Dai-man ZHU¹, Chang-rong LI¹, Cui-ping GUO¹, Zhen-min DU¹, Jun-qin LI²

1. School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China;

2. Shenzhen Key Laboratory of Special Functional Materials, Shenzhen University, Shenzhen 518060, China

Received 16 April 2015; accepted 26 August 2015

Abstract: On the basis of the experimental data of phase equilibria and thermochemical properties available from literatures, a critical assessment for the Ni–Yb binary system was carried out using the CALPHAD (calculation of phase diagrams) method. The liquid phase is modeled as the associate model with the constituent species Ni, Yb and YbNi₃, owing to the sharp change of the enthalpy of mixing of liquid phase at the composition of around 25% Yb (mole fraction). The terminal solid solutions FCC_A1 (Ni/Yb) and BCC_A2 (Yb) are described by the substitutional solution model with the Redlich–Kister polynomial. The intermetallic compounds, Yb₂Ni₁₇, YbNi₅, YbNi₃, YbNi₂, α -YbNi and β -YbNi, are treated as strict stoichiometric compounds, since there are no noticeable homogeneity ranges reported for these compounds. A set of self-consistent thermodynamic parameters for the Ni–Yb binary system are obtained. According to the presently assessed results, the thermochemical properties and the phase boundary data can be well reproduced.

Key words: Ni–Yb system; thermodynamic assessment; CALPHAD technique

1 Introduction

During the last few decades, the investigation of intermetallic compounds between rare earth (RE) and transition metals has attracted a great deal of attention. In the Ni–RE series, the Ni–Yb system may be of special interest for its extensive applications as thermoelectric, amorphous and catalytic materials. The Ni electrode is a good electrode candidate for the filled skutterudite Yb_{0.3}Co₄Sb₁₂ thermoelectric devices working in air at high temperature [1]. The aluminum–nickel–ytterbium (Al–Ni–Yb) alloys, with the Al-rich precipitates and the Ni and Ni–Yb clusters coexisted, have good glass-forming abilities of metallic glasses with excellent mechanical properties [2,3]. The Ni–Yb/SiO₂ and Ni/Yb₂O₃ catalysts deliver high conversions for the reaction of gas phase phenol hydrogenation and the oxidation of CH₄, respectively [4,5]. Therefore, to better understand the thermochemical properties and the phase equilibrium relations concerning the Ni–RE binary systems will play an important role in the development of Ni-based materials with RE elements, and the Ni–Yb

binary system is one of such systems.

According to the literature review, there have been one evaluation and one computation for the Ni–Yb binary system so far [6,7]. The former [6] summarized the experimental work conducted by PALENZONA and CIRAFICI [8] using X-ray diffraction (XRD), differential thermal analysis (DTA) and metallography measurement. The latter [7] reported the calculated Ni–Yb phase diagram besides the measured data of the mixing enthalpy of the liquid phase, but neither the assessed method nor the optimized parameters were reported. More importantly, the phase diagram presented by Ref. [7] is much different from the one determined experimentally by PALENZONA and CIRAFICI [8].

The present work is to assess the Ni–Yb binary system thermodynamically by the calculation of phase diagrams (CALPHAD) method, mainly considering the phase equilibrium data in Ref. [8], the phase diagram evaluation in Ref. [6], the enthalpies of formation of the compounds in Ref. [9] and the mixing enthalpy of the liquid phase in Ref. [7]. The self-consistent thermodynamic parameters are optimized for calculating the phase equilibria and the thermochemical properties of

the Ni–Yb binary system.

2 Evaluation of available information

The experimental information of Ni–Yb system is limited. Using XRD, BUSCHOW [10] firstly studied the five intermetallic compounds, YbNi, YbNi₂, YbNi₃, YbNi₅ and Yb₂Ni₁₇, existed in the system. Later on, PALENZONA and CIRAFICI [8] measured the phase diagram in the whole composition range by XRD, differential thermal analysis (DTA) and metallography. In Ref. [8], the β -YbNi and YbNi₃ compounds melt congruently at 1308 and 1583 K, respectively, while β -YbNi shows a polymorphic transformation of α -YbNi $\leftrightarrow\beta$ -YbNi at the solid state and 1273 K. The compounds YbNi₂, YbNi₅ and Yb₂Ni₁₇ are formed by the peritectic reactions $L+YbNi_3\leftrightarrow YbNi_2$ at 1528 K, $L+YbNi_3\leftrightarrow YbNi_5$ at 1568 K and $L+YbNi_5\leftrightarrow Yb_2Ni_{17}$ at 1518 K, respectively. Three eutectic transformations were defined, $Liq\leftrightarrow FCC_A1+Yb_2Ni_{17}$ at 1503 K and

$\sim 7.5\%$ Yb (mole fraction), $Liq\leftrightarrow YbNi_2+\alpha$ -YbNi at 1263 K and $\sim 46.0\%$ Yb, and $Liq\leftrightarrow\alpha$ -YbNi+ FCC_A1 at 1063 K and $\sim 98.0\%$ Yb. According to Ref. [8], from about 55% to 90% Yb, Yb and YbNi give rise to an miscibility gap at liquid state, which extends well above 1298 K. The Ni–Yb alloys in this composition range are always two-layered after rapidly cooled by water quenching from 1773 K to room temperature. The different metallographic images of the two layers from the same sample can be considered to be the microstructures formed from the two immiscible Liquids 1 and 2 with different mass densities. Based on the metallographic images of the sample with 75% Yb quenched from 1773 K and the densities of Yb (6.97 g/cm³) and YbNi (10.08 g/cm³) [8], the compositions of the Yb-rich Liquid 1 (the upper part of the solidified alloy) and the YbNi-rich Liquid 2 (the lower part) were approximately calculated, which are 85% and 66% Yb, respectively. The details of the invariant reactions in the Ni–Yb binary system are shown in Table 1.

Table 1 Invariant reactions in Ni–Yb system

Invariant reaction	<i>T</i> /K	Reaction type	$x(Yb)_{liq}$	Experiment method	Reference
$Liq\leftrightarrow FCC_A1+Yb_2Ni_{17}$	1503	Eutectic	0.08	XRD/ DTA/ Metallography	[8]
	1503	Eutectic		Evaluated	[6]
	NA	Eutectic		Calculated	[7]
	1510	Eutectic	0.085	Calculated	This work
$Liq+YbNi_5\leftrightarrow Yb_2Ni_{17}$	1518	Peritectic	0.085	XRD/ DTA/ Metallography	[8]
	1518	Peritectic		Evaluated	[6]
	NA	Peritectic		Calculated	[7]
	1518	Peritectic	0.104	Calculated	This work
$Liq+YbNi_3\leftrightarrow YbNi_5$	1568	Peritectic	0.152	XRD/ DTA/ Metallography	[8]
	1568	Peritectic		Evaluated	[6]
$Liq+YbNi_5\leftrightarrow YbNi_3$	NA	Peritectic		Calculated	[7]
$Liq\leftrightarrow YbNi_5+YbNi_3$	1568	Eutectic	0.209	Calculated	This work
$Liq+YbNi_3\leftrightarrow YbNi_2$	1528	Peritectic	0.345	XRD/ DTA/ Metallography	[8]
	1528	Peritectic		Evaluated	[6]
	NA	Peritectic		Calculated	[7]
	1528	Peritectic	0.343	Calculated	This work
$Liq\leftrightarrow YbNi_2+\alpha$ -YbNi	1263	Eutectic	0.455	XRD/ DTA/ Metallography	[8]
	1263	Eutectic		Evaluated	[6]
$Liq+YbNi_2\leftrightarrow\beta$ -YbNi	NA	Peritectic		Calculated	[7]
α -YbNi $\leftrightarrow\beta$ -YbNi	1273	Polymorphic		XRD/ DTA/ Metallography	[8]
	NA	Polymorphic		Calculated	[7]
	1273	Polymorphic		Calculated	This work
$Liq1\leftrightarrow Liq2+\beta$ -YbNi	1298	Monotectic	0.536/0.909	XRD/ DTA/ Metallography	[8]
	1298	Monotectic		Evaluated	[6]
	NA	Monotectic		Calculated	[7]
	1308	Monotectic	0.568/0.937	Calculated	This work
$Liq\leftrightarrow\alpha$ -YbNi+FCC_A1	1063	Eutectic	0.981	XRD/ DTA/ Metallography	[8]
	1078	Eutectic		Evaluated	[6]
	NA	Eutectic	0.993	Calculated	[7]
	1088	Eutectic		Calculated	This work

Note: NA, not available exactly

BRUTTI et al [9] reported the enthalpies of formation at 298 K of the solid compounds $\text{Yb}_2\text{Ni}_{17}$, YbNi_5 , YbNi_3 , YbNi_2 and $\alpha\text{-YbNi}$ by tensimetric measurements (Knudsen effusion (KE)–mass spectrometry and Knudsen effusion–weight loss) and calorimetric measurements (direct reaction calorimetry). Using direct synthesis calorimetry (DSC), BORZONE et al [11] tested the enthalpy of formation of the YbNi_2 phase, which is larger than that obtained by BRUTTI et al [9]. NIESSEN et al [12] and BAYANOV [13] calculated the values of the enthalpies of formation of all of the compounds of the system. Those data available from literatures are collected in Table 2.

Table 2 Enthalpies of formation of intermetallic compounds in Ni–Yb system

Intermetallic compound	Enthalpy of formation/ ($\text{kJ}\cdot\text{mol}^{-1}$)	T/K	Experiment method	Reference
YbNi	–27.8	298	Miedema model	[12]
	–28.0±2.0	298	DSC	[9]
	–29.9	298	SCM	This work
YbNi ₂	–33.6	298	Miedema model	[12]
	–30	298	DSC	[11]
	–32.0±4.6	298	KE method	[9]
	–30	298	SCM	This work
	–28.8	298	Miedema model	[12]
YbNi ₃	–26.0±4.8	298	KE method	[9]
	–30.1	298	SCM	This work
	–20.2	298	Miedema model	[12]
YbNi ₅	–16.4	298	Crystal-chemical	[13]
	–20.9±4.4	298	KE method	[9]
	–20.9	298	SCM	This work
	–12.7	298	Miedema model	[12]
Yb ₂ Ni ₁₇	–13.9±0.3	298	KE method	[9]
	–13.9	298	SCM	This work

Note: SCM, stoichiometric compound model

Recently, BEREZUTSKII et al [7] investigated the mixing enthalpy of melts of the Ni–Yb binary system at 1300–1750 K using the isoperibolic calorimetry. Then, they constructed the models of the liquid and solid alloys and calculated the phase diagram which is much different from the one determined experimentally by PALENZONA and CIRAFICI [8]. On the basis of the experimental measurement, Ref. [7] proposed some suspicious points about the doubtful questions to the shape of liquidus and the melting points of compounds without further experimental confirmation.

In the present assessment of Ni–Yb binary system, the phase equilibrium data in Ref. [8], the phase diagram

evaluation in Ref. [6], the enthalpies of formation of the compounds in Ref. [9] and the mixing enthalpy of the liquid phase in Ref. [7] are mainly under consideration with high weighting factors. The comment in Ref. [7] is also taken into account that the most refractory compound in the Ni–Yb binary system should be YbNi_5 most probably since LnNi_5 is the most refractory compound in all other Ni–Ln systems [14–16].

3 Thermodynamic models

The information about the stable solid phases of Ni–Yb binary system [8], including the prototypes, the sublattices and the models used in the present assessment, is listed in Table 3.

Table 3 Stable solid phases and used models in Ni–Yb binary system

Phase	Strukturbericht designation	Prototype	Sublattice	Used model
($\alpha\text{-Ni}$) ^a	A1	Cu	(Ni%,Yb) ^b	SSM
$\text{Yb}_2\text{Ni}_{17}$		$\text{Th}_2\text{Ni}_{17}$	(Yb) _{0.105} (Ni) _{0.895}	SCM
YbNi_5	D2 _d	CaCu_5	(Yb) _{0.167} (Ni) _{0.833}	SCM
YbNi_3		PuNi_3	(Yb) _{0.25} (Ni) _{0.75}	SCM
YbNi_2	C15	MgCu_2	(Yb) _{0.333} (Ni) _{0.667}	SCM
$\alpha\text{-YbNi}$	B27	FeB	(Yb) _{0.5} (Ni) _{0.5}	SCM
$\beta\text{-YbNi}$			(Yb) _{0.5} (Ni) _{0.5}	SCM
($\beta\text{-Yb}$)	A1	Cu	(Ni,Yb%)	SSM
($\gamma\text{-Yb}$)	A2	W	(Ni,Yb%)	SSM

Note: ^a The phases with homogeneity ranges are indicated with the round brackets as (phase name); ^b The component with a larger amount is denoted by the symbol “%”; SSM, substitutional solution model

3.1 Pure elements

For the function of Gibbs free energy for a pure element, the reference state is the enthalpy of the element in its most stable form at the standard state pressure and 298.15 K. The Gibbs free energy of the pure element i in its stable or metastable state of the phase φ is described by an equation of the following form:

$${}^0G_i^\varphi(T) = G_i^\varphi(T) - H_{i,\text{SER}}(298.15\text{K}) = a + bT + cT \ln T + dT^2 + eT^{-1} + fT^3 + gT^7 + hT^{-9} \quad (1)$$

where i represents the pure element Ni or Yb; $H_{i,\text{SER}}$ (298.15 K) is the molar enthalpy of the element i at 298.15 K in its standard element reference (SER) state, FCC_A1 for both Ni and Yb; and a to h are the coefficients. The molar Gibbs free energy of the element i , in its SER state, is denoted by $G_{i,\text{SER}}$ as follows:

$$G_{\text{Ni/Yb,SER}} = {}^0G_{\text{Ni/Yb}}^{\text{FCC_A1}}(T) = G_{\text{Ni/Yb}}^{\text{FCC_A1}}(T) - H_{\text{Ni/Yb}}^{\text{FCC_A1}}(298.15\text{K}) \quad (2)$$

The molar Gibbs free energy functions of pure elements are taken from the SGTE (Scientific Group Thermodata Europe) compiled by DINSDALE [17].

3.2 Solution phases

3.2.1 Terminal solid solution phases

The molar Gibbs free energies of FCC_A1 and BCC_A2 phases in the Ni–Yb binary system are described by the substitutional solution model (SSM) as follows:

$$G_m^\varphi = \sum_{i=\text{Ni, Yb}} x_i {}^0G_i^\varphi + RT \sum_{i=\text{Ni, Yb}} x_i \ln x_i + \Delta^e G_m^\varphi + \Delta^{\text{mag}} G_m^\varphi \quad (3)$$

where x_i is the mole fraction of the pure element i , ${}^0G_i^\varphi$ is the molar Gibbs free energy of the pure element i in the state of φ phase, which is taken from the SGTE database [16], R is the mole gas constant, T is the thermodynamic temperature, $\Delta^e G_m^\varphi$ is the excess molar Gibbs free energy, and $\Delta^{\text{mag}} G_m^\varphi$ is the magnetic contribution to the molar Gibbs free energy which equals zero if there is no magnetic contribution, such as Yb.

The excess Gibbs free energy is written as a Redlich–Kister polynomial [18]:

$$\Delta^e G_m^\varphi = x_{\text{Ni}} x_{\text{Yb}} \sum_{n=0}^m {}^n L_{\text{Ni, Yb}}^\varphi (x_{\text{Ni}} - x_{\text{Yb}})^n \quad (4)$$

where ${}^n L_{\text{Ni, Yb}}^\varphi$ is the n th interaction parameter between the components Ni and Yb, which is the function of temperature:

$${}^n L_{\text{Ni, Yb}}^\varphi = a + bT + cT \ln T + dT^2 + eT^{-1} + fT^3 + gT^7 + hT^{-9} \quad (5)$$

In most cases, only the first one or two terms of the above equation are used.

The magnetic contribution is considered for the phase (α -Ni). It is described according to the model proposed by HILLERT and JARL [19]:

$$\Delta^{\text{mag}} G_m^\varphi = RT(\ln \beta^\varphi + 1) f(\tau^\varphi) \quad (6)$$

where β^φ is the Bothr magneton number, $f(\tau^\varphi)$ is a polynomial with $\tau^\varphi = T/T_c^\varphi$, and T_c^φ is the Curie temperature of solution for ferromagnetic ordering. β^φ and T_c^φ for the phase (α -Ni) are taken from the SGTE database [17].

3.2.2 Liquid phase

For the Ni–Yb binary system, the diagram of the enthalpy of mixing of liquid phase constructed by BEREZUTSKII et al [7] is characterized by a sharp change around the compound YbNi₃. This implies that some types of complex or associate are formed inside the liquid at this critical composition [20]. Therefore, the associate model [21] was proposed for the liquid phase

description with the constituent species of Ni, Yb and YbNi₃. The molar Gibbs free energy is expressed with the following expression [18]:

$$G_m^{\text{liq}} = \sum_{i=1}^3 x_i {}^0G_i^{\text{liq}} + RT \sum_{i=1}^3 x_i \ln x_i + \sum_{i=1}^2 \sum_{j=i+1}^3 x_i x_j \sum_{n=0}^m {}^n L_{i,j}^{\text{liq}} (x_i - x_j)^n \quad (7)$$

where ${}^0G_i^{\text{liq}}$ and x_i are the molar Gibbs free energy and the mole fraction of the pure species i ($i=1,2,3$ represent Ni, YbNi₃ and Yb, respectively) at the liquid state; ${}^n L_{i,j}^{\text{liq}}$ is the n th interaction parameter ($n=0,1,2$ in the present work) between the species i and j ($j=2,3$ represent YbNi₃ and Yb, respectively at the liquid state), which is a function of temperature as ${}^n L_{i,j}^{\text{liq}} = a_n + b_n T$ and the coefficients a_n and b_n are the parameters to be optimized.

3.3 Stoichiometric compounds

The intermetallic compounds YbNi, YbNi₂, YbNi₃, YbNi₅ and Yb₂Ni₁₇ in the Ni–Yb binary system are stoichiometric phases. YbNi undergoes a polymorphic transformation between the low and high temperature phases, α -YbNi and β -YbNi. The Gibbs free energy per mole atom of Yb _{p} Ni _{q} is expressed as follows:

$$G_m^{\text{Yb}_p\text{Ni}_q} = \frac{p}{p+q} G_{\text{Yb, SER}} + \frac{q}{p+q} G_{\text{Ni, SER}} + \Delta G_f^{\text{Yb}_p\text{Ni}_q}(T) \quad (8)$$

where $\Delta G_f^{\text{Yb}_p\text{Ni}_q}(T)$ is the Gibbs free energy of formation of the stoichiometric compound Yb _{p} Ni _{q} from the pure elements in their SER states. Owing to no thermochemical measurements available for these compounds, it is assumed that the Neumann–Kopp rule [22] applies to the heat capacity description, i.e., $\Delta C_p = 0$. Thus, $\Delta G_f^{\text{RE}_p\text{Ni}_q}(T)$ is described as

$$\Delta G_f^{\text{RE}_p\text{Ni}_q}(T) = a + bT \quad (9)$$

where the coefficients a and b are the parameters to be optimized.

4 Results and discussion

With the lattice stabilities of all pure elements from the study of DINSDALE [17] and the PARROT module of the Thermo-Calc software [23,24], the phase relations and the thermochemical properties of the Ni–Yb binary system were carefully assessed based on the experimental data available from literatures.

The parameters were optimized step by step. It works by minimizing an error of sum with each piece of selected information given a certain weight. The weight was given and adjusted based on the original data uncertainty and the personal evaluation. Based on the

experimental thermochemical and phase equilibrium data, the parameters related to the solution phases, the liquid phase and the terminal solid solution phases, are optimized firstly. A higher weight is given to the equilibria related to the miscibility gap than others when optimizing the liquid phase, to make the miscibility gap exist at the Yb-rich side. Then, the intermetallic compound phases are optimized according to their enthalpies of formation to match their equilibrium relations.

Table 4 lists the optimized thermodynamic parameters for the Ni–Yb binary system. Using these

parameters, the calculations can well reproduce most of the thermochemical properties and phase boundary data. For checking the results, the phase diagram of the Ni–Yb binary system was also calculated using Pandat software [25].

The calculated phase diagram is shown in Fig. 1 together with the experimental data obtained by PALENZONA and CIRAFICI [8] and all the invariant temperatures labeled. The reversible polymorphic transition of the compound YbNi, α -YbNi $\leftrightarrow\beta$ -YbNi, is at 1273 K. The calculated incongruent melting temperatures of the intermetallic compounds Yb₂Ni₁₇,

Table 4 Thermodynamic parameters of Ni–Yb binary system

Phase	Model	Parameter
Liquid	(Ni, YbNi ₃ , Yb) ₁	${}^0G_{\text{YbNi}_3}^{\text{liq}} = -33208.283 - 32.892T + G_{\text{Yb,SER}} + 3G_{\text{Ni,SER}}$
		${}^0L_{\text{Ni,Yb}}^{\text{liq}} = +4000.2389 - 10.2398T$
		${}^0L_{\text{Ni,YbNi}_3}^{\text{liq}} = -58000.293 + 18.238T$
		${}^1L_{\text{Ni,YbNi}_3}^{\text{liq}} = -3500.2389 - 2.343T$
		${}^0L_{\text{Yb,YbNi}_3}^{\text{liq}} = -38000.289 - 18.2839T$
		${}^1L_{\text{Yb,YbNi}_3}^{\text{liq}} = +58321.892 - 37.605054T$
		${}^2L_{\text{Yb,YbNi}_3}^{\text{liq}} = +10000.239 + 36.295515T$
FCC_A1(Ni/Yb)	(Ni, Yb) ₁ (Va) ₁	${}^0T_{\text{c,Ni:Va}}^{\text{FCC_A1}} = +633, {}^0\beta_{\text{Ni:Va}}^{\text{FCC_A1}} = +0.52$
BCC_A2(Yb)	(Ni, Yb) ₁ (Va) ₃	${}^0L_{\text{Ni,Yb:Va}}^{\text{FCC_A1}} = +60000$
		${}^0T_{\text{c,Ni:Va}}^{\text{BCC_A2}} = +575, {}^0\beta_{\text{Ni:Va}}^{\text{BCC_A2}} = +0.85$
Yb ₂ Ni ₁₇	(Yb) _{0.105} (Ni) _{0.895}	${}^0G_{\text{Yb:Ni}}^{\text{Yb}_2\text{Ni}_{17}} = -13900.283 - 0.1562T + 0.105G_{\text{Yb,SER}} + 0.895G_{\text{Ni,SER}}$
		${}^0G_{\text{Yb:Ni}}^{\text{YbNi}_5} = -20900.723 - 0.628T + 0.167G_{\text{Yb,SER}} + 0.833G_{\text{Ni,SER}}$
YbNi ₅	(Yb) _{0.167} (Ni) _{0.833}	${}^0G_{\text{Yb:Ni}}^{\text{YbNi}_3} = -28800.329 + 1.658T + 0.25G_{\text{Yb,SER}} + 0.75G_{\text{Ni,SER}}$
YbNi ₃	(Yb) _{0.25} (Ni) _{0.75}	${}^0G_{\text{Yb:Ni}}^{\text{YbNi}_2} = -29500 + 1.3201T + 0.333G_{\text{Yb,SER}} + 0.667G_{\text{Ni,SER}}$
YbNi ₂	(Yb) _{0.333} (Ni) _{0.667}	${}^0G_{\text{Yb:Ni}}^{\alpha\text{-YbNi}} = -29900.029 + 6.5216T + 0.5G_{\text{Yb,SER}} + 0.5G_{\text{Ni,SER}}$
α -YbNi	(Yb) _{0.5} (Ni) _{0.5}	${}^0G_{\text{Yb:Ni}}^{\beta\text{-YbNi}} = -26373.238 + 3.7508T + 0.5G_{\text{Yb,SER}} + 0.5G_{\text{Ni,SER}}$
β -YbNi	(Yb) _{0.5} (Ni) _{0.5}	

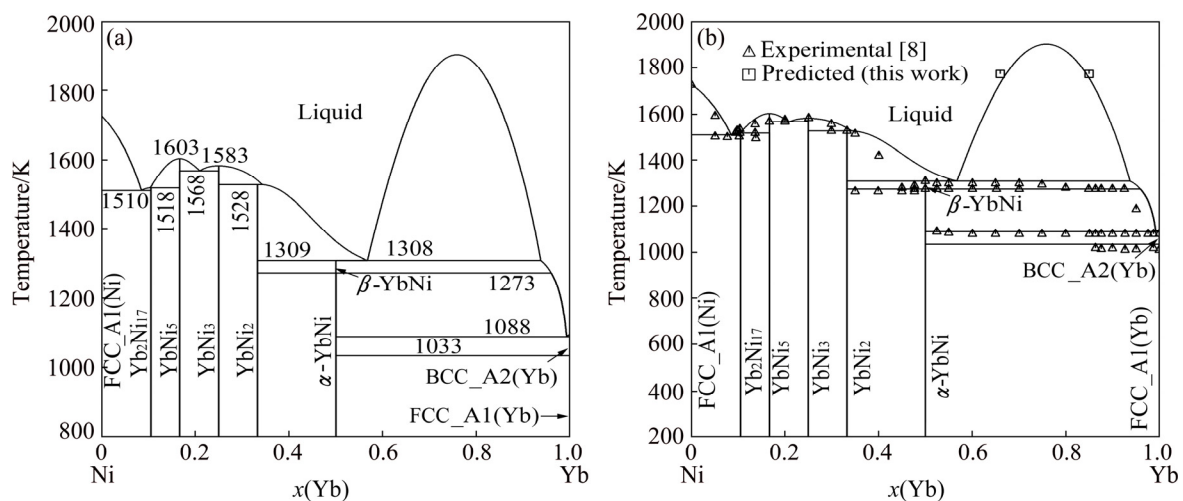


Fig. 1 Ni–Yb binary phase diagram calculated with present description (a) and compared with experimental data (b)

YbNi_2 and $\beta\text{-YbNi}$ are 1518, 1528 and 1309 K, respectively, and the calculated congruent melting temperatures of YbNi_5 and YbNi_3 are 1603 and 1583 K, respectively. The eutectic reaction temperatures for $\text{Liq} \leftrightarrow \text{FCC_Al}(\text{Ni}) + \text{Yb}_2\text{Ni}_{17}$, $\text{Liq} \leftrightarrow \text{YbNi}_5 + \text{YbNi}_3$ and $\text{Liq} \leftrightarrow \alpha\text{-YbNi} + \text{BCC_A2}(\text{Yb})$ are 1510, 1568, and 1088 K, respectively. A good agreement between the temperatures of the present calculated and the experimentally determined invariant reactions is obtained.

There is a lack of experimental data for the top boundary of the liquid miscibility gap between YbNi and Yb , and the only support is the present prediction at 1773 K based on the metallographic images reported in Ref. [8]. The phase equilibrium measurements about this region need further clarification for a better assessment of the system. The rest of the phase diagram shows very good agreement with the experimental data.

The enlargements of the Ni–Yb phase diagram around compounds YbNi_5 and YbNi_2 are shown in Figs. 2 and 3, respectively. When calculating Fig. 2, the parameter related to the enthalpy of formation of the compound YbNi_5 , denoted by a , is first fixed to fit the experimental data in Ref. [9]. Then, the parameter related to the entropy of formation of YbNi_5 , denoted by b , is given different values to find the appropriate one to accord with the experimentally determined solidification temperatures of the compounds YbNi_5 and $\text{Yb}_2\text{Ni}_{17}$ in Ref. [8], i.e., their related invariant reaction temperatures, 1568 K for the peritectic reaction $\text{Liq} + \text{YbNi}_3 \leftrightarrow \text{YbNi}_5$ and 1518 K for the peritectic reaction $\text{Liq} + \text{YbNi}_5 \leftrightarrow \text{Yb}_2\text{Ni}_{17}$. The similar way is used to calculate the data in Fig. 3 to determine approximately the liquidus around the compound YbNi_2 . Figure 2 shows that the melting temperature (T_m) of YbNi_5 is selected as 1603 K, which is 20 K higher than that of the YbNi_3 . The reasons are the following three points: 1) the calculated formation enthalpy of the compound YbNi_5 needs to match the experimental data measured in Ref. [9]; 2) the temperature of the invariant eutectic reaction between the compounds YbNi_5 and YbNi_3 was determined experimentally to be 1568 K in Ref. [8]; 3) the melting point of YbNi_5 is probably higher than that of YbNi_3 as Ref. [7] suggested. As shown in Fig. 2, if the two-phase region of $\text{Liq} + \text{YbNi}_5$ is changed to be broader to accord with the experimental data in Ref. [8], the temperature of the invariant reaction $\text{Liq} \leftrightarrow \text{YbNi}_5 + \text{YbNi}_3$ increases much higher than the experimental one. Figure 3 shows the variation of the liquidus line around the compound YbNi_2 with the change of its entropy of formation. The thermodynamic parameters of YbNi_2 are determined with the consideration of the following three points: 1) the assessed mixing enthalpy of the liquid phase around the compound YbNi_2 is consistent with the

experimental data determined in Ref. [7]; 2) the assessed temperature of the invariant reaction $\text{L} + \text{YbNi}_3 \leftrightarrow \text{YbNi}_2$ is 1528 K which is the same as the one determined experimentally in Ref. [8]; 3) the assessed formation enthalpies of the compound YbNi_2 are in good agreement with the experimental values measured in Ref. [9]. As shown in Fig. 3, if the two-phase region of $\text{YbNi}_2 + \text{Liq}$ is changed to be narrower to accord with the experimental data in Ref. [8], the temperature of the peritectic reaction (T_p) $\text{Liq} + \text{YbNi}_3 \leftrightarrow \text{YbNi}_2$ decreases much lower than the experimental one.

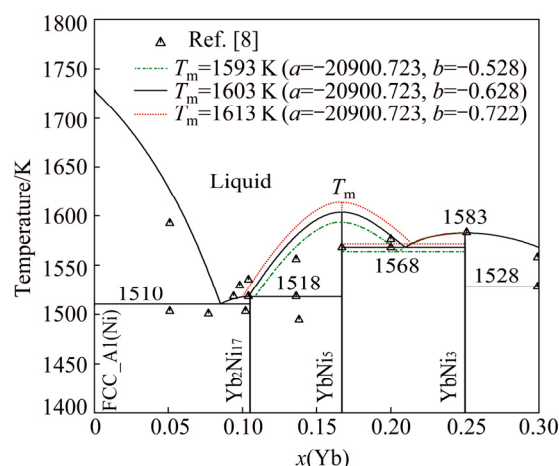


Fig. 2 Calculated enlargement of Ni–Yb phase diagram around compound YbNi_5

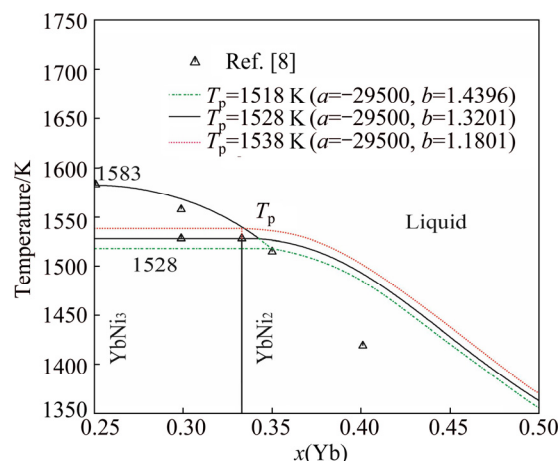


Fig. 3 Calculated enlargement of Ni–Yb phase diagram around compound YbNi_2

Figure 4 gives the calculated mixing enthalpy of the liquid phase at 1500 K, which shows good agreement with the experimental data measured at 1750, 1600, 1480 and 1300 K [7], and the asymmetry enthalpy line around the stoichiometric compound YbNi_3 implies the reasonable selection of the constituent species of the liquid phase as Ni , Yb and YbNi_3 . The calculated fractions of the species Ni , YbNi_3 and Yb in the liquid phase at 1073, 1773 and 2473 K are shown in Fig. 5. The fraction of YbNi_3 increases with the decrease of

temperature, and passes through a maximum of approximately 40% at compositions of around 30% Yb.

Figure 6 shows the calculated enthalpies of

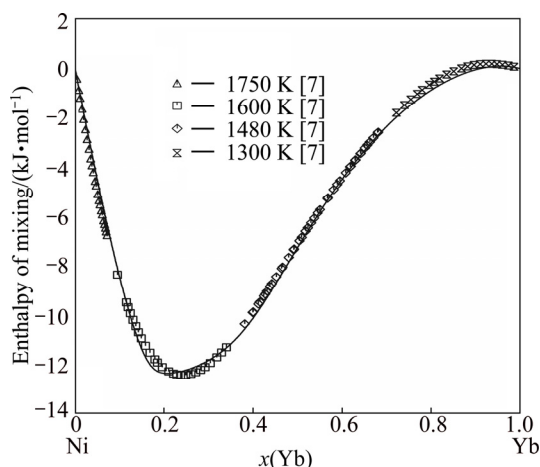


Fig. 4 Enthalpy of mixing of liquid Ni–Yb solution at 1500 K with reference states, Ni (liquid) and Yb (liquid)

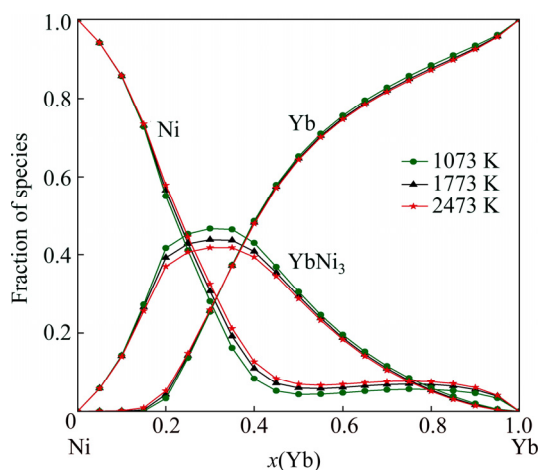


Fig. 5 Calculated fractions of species in liquid phase at 1073, 1773 and 2447 K as function of Yb content

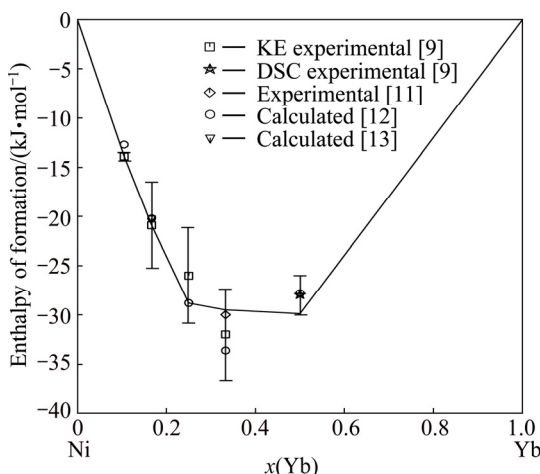


Fig. 6 Enthalpies of formation of intermetallic compounds in Ni–Yb binary system at 298 K with reference states, Ni (FCC_A1) and Yb (FCC_A1)

formation of all intermetallic compounds at 298 K, which are compared with the experimental data [9,11] and the predicted data [12,13]. The calculated values agree very well with the experimental results.

5 Conclusions

1) In order to describe reasonably the sharp change of the enthalpy of mixing of the liquid phase around the stoichiometric compound YbNi_3 in the Ni–Yb binary system, the associate model is used and the results are in good agreement with experimental data achieved.

2) There is no direct experimental data available for the top boundary of the liquid miscibility gap between YbNi and Yb. The metallographic images of the upper and lower parts of the same sample obtained by rapid cooling are considered to be the microstructures formed from the two immiscible Liquids 1 and 2 with different mass densities, from which the boundary of the liquid miscibility gap at the experimental annealing temperature of 1773 K is determined.

3) A set of self-consistent thermodynamic parameters for the Ni–Yb binary system are obtained. The comprehensive comparisons show that the calculated phase diagrams and the thermochemical properties agree reasonably with the available experimental data.

Acknowledgements

The authors thanks the Royal Institute of Technology Sweden and CompuTherm LLC for supplying Thermo-Calc software and Pandat Software packages, respectively.

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Ni–Yb 二元系的热力学评估

朱代漫¹, 李长荣¹, 郭翠萍¹, 杜振民¹, 李均钦²

1. 北京科技大学 材料科学与工程学院, 北京 100083;

2. 深圳大学 深圳特殊功能材料重点实验室, 深圳 518060

摘 要: 基于文献报道的相平衡和热化学实验数据, 利用相图计算(Calphad)方法对 Ni–Yb 二元系进行热力学评估。考虑到液相混合焓在 25% Yb(摩尔分数)附近有急剧变化, 液相采用缔合物模型, 组份为 Ni、YbNi₃ 和 Yb; 端际固溶体相包括 FCC_A1 (Ni)、FCC_A1 (Yb)和 BCC_A2 (Yb), 均采用亚规则溶体模型, 并按照 Redlich–Kister 多项式进行描述; 中间化合物 Yb₂Ni₁₇、YbNi₅、YbNi₃、YbNi₂、 α -YbNi 和 β -YbNi 都没有明显的固溶度实验数据, 均按严格计量比处理。优化得到的 Ni–Yb 二元系热力学参数自洽合理, 能够很好地再现该体系的热化学性质和相图数据。

关键词: Ni–Yb 二元系; 热力学评估; 相图计算技术

(Edited by Mu-lan QIN)