

Thermodynamic assessment of the Pd–Y binary system

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Abstract. The Pd–Y system was critically assessed using the CALPHAD technique. The solution phases (liquid, b.c.c., f.c.c. and h.c.p.) were modeled using the Redlich–Kister equation. The intermetallic compounds Pd₃Y and PdY, which have homogeneity ranges, were treated as the formula (Pd, Y)_{0.75}(Pd, Y)_{0.25} and (Pd, Y)_{0.5}(Pd, Y)_{0.5} by a two-sublattice model with a mutual substitution of Pd and Y on both sublattices. The optimization was carried out in two steps. In the first treatment, Pd₃Y and PdY are assumed to be stoichiometric compounds; in the second treatment they are treated by a sublattice model. The parameters obtained from the first treatment were used as starting values for the second treatment. The calculated phase diagram and the thermodynamic properties of the system are in satisfactory agreement with the experimental data.

1. INTRODUCTION

The rare earth elements exhibiting a good combination of magnetic, optical, electrical and thermal properties have been paid increasing attention and widely used to prepare new high performance functional materials, such as permanent magnet, magnetic refrigerant and hydrogen storage material [1–3]. The CALPHAD technique, which has been recognized to be an important tool to significantly reduce time and cost during the development of materials, can provide a clear guidance for the materials design [4–6]. In order to develop the thermodynamic database of the rare earth alloys for reliable predictions of liquidus, phase fraction, equilibrium and non-equilibrium solidification behavior, etc. The thermodynamic assessment of the Pd–Y binary system was carried out by means of the CALPHAD method.

2. REVIEW OF EXPERIMENTAL DATA

The phase diagram of the Pd–Y system was first measured by Loebich and Raub [7]. They found seven intermetallic compounds in the Pd–Y system and called them Pd₃Y, Pd₂Y, Pd₅Y₄, PdY, PdY₃, Pd₃Y₂ and Pd₂Y₅, where Pd₃Y, PdY and Pd₅Y₄ melted congruently and Pd₃Y₂, Pd₂Y and Pd₂Y₃ formed by peritectic reactions. Later, Pd₅Y₄ was identified to be Pd₄Y₃ by Palenzona and Iandelli [8]. Pd₇Y and PdY₃ were found to exist by Sanjines-Zeballos et al. [9] and Takao et al. [10], respectively. The results obtained have been taken by Massalski [22] to draw a phase diagram. Kuentzler and Loebich [11] presented a revised phase diagram and discussed the stability of the existing ordered structures. The homogeneity range of the intermetallic compound Pd₃Y and the solubility of Y in f.c.c.(Pd) were measured by Loebich and Raub [7] and Harris and Norman [12]. No appreciable solid solubility of Pd in Y was observed [7]. Loebich and Raub [7] indicated the presence of polymorphic transformation and a small range of homogeneity for PdY (51–52 at.% Y). Considering, however, the subsequent work of Kuentzler and Loebich [11] and Palenzona and Cirafici [13], the

homogeneity range of PdY should be 50–51 at.% Y and the maximum melting point attributed to the ideal 50 at.% Y composition [14].

3. THERMODYNAMIC MODELS

3.1. Pure elements

The Gibbs energy function

$$G_i(T) = {}^\circ G_i - H_i^{\text{SER}}(298.15 \text{ K}) \quad (1)$$

(298.15) for the element i ($i = \text{Pd, Y}$) in the phase φ ($\varphi = \text{Liquid, HCP_A3, BCC_A2 and FCC_A1}$) is described by an equation of the following form:

$$G_i(T) = a + bT + cT \ln T + dT^2 + eT^3 + fT^7 + gT^{-1} + hT^{-9}. \quad (2)$$

Where $H_i^{\text{SER}}(298.15 \text{ K})$ is the molar enthalpy of the element i ($i = \text{Pd, Y}$) at 298.15 K in its standard element reference (SER) state, FCC_A1 for Pd and HCP_A3 for Y.

In this article, the Gibbs energy functions are taken from the SGTE compilation of Dinsdale [15].

3.2. Solution phases

The solution phases [(FCC_A1) Pd, HCP_A3 (α Y), BCC_A2 (β Y) and liquid] were modeled as substitutional solutions according to the polynomial Redlich–Kister model [16]. The Gibbs energy of one mol of formula unit of phase φ is expressed as the sum of the reference part ${}^{\text{ref}}G^\varphi$, the ideal part ${}^{\text{id}}G^\varphi$, and the excess part ${}^{\text{exc}}G^\varphi$:

$$G_m^\varphi = {}^{\text{ref}}G^\varphi + {}^{\text{id}}G^\varphi + {}^{\text{exc}}G^\varphi. \quad (3)$$

As used in the thermo-calc software [17]:

$${}^{\text{ref}}G^\varphi(T) = ({}^0G_{\text{Pd}}^\varphi(T) - H_{\text{Pd}}^{\text{SER}}(298.15 \text{ K}))_{x_{\text{Pd}}} + ({}^0G_{\text{Y}}^\varphi(T) - H_{\text{Y}}^{\text{SER}}(298.15 \text{ K}))_{x_{\text{Y}}} \quad (4)$$

$${}^{\text{id}}G^\varphi = RT(x_{\text{Pd}} \ln x_{\text{Pd}} + x_{\text{Y}} \ln x_{\text{Y}}) \quad (5)$$

Where R is the gas constant, T the temperature, in Kelvin, Warning: x_{Pd} and x_{Y} are the fraction of elements Pd and Y, respectively.

The excess terms of all the solution phases were modeled by the Redlich-Kister [16] formula:

$${}^{\text{exc}}G_m^\varphi(T) = x_{\text{Pd}}x_{\text{Y}}[{}^0L_{\text{Pd,Y}}^\varphi(T) + {}^1L_{\text{Pd,Y}}^\varphi(T)(x_{\text{Pd}} - x_{\text{Y}}) + L_{\text{Pd,Y}}^\varphi(T)(x_{\text{Pd}} - x_{\text{Y}})^2 + \dots] \quad (6)$$

$${}^iL_{\text{Pd,Y}}^\varphi(T) = a_i + b_i T. \quad (7)$$

Where ${}^iL_{\text{Pd,Y}}^\varphi(T)$ is the interaction parameter between the elements Pd and Y, which is evaluated in the presented work, a_i and b_i are the coefficients to be optimized.

3.3. Stoichiometric compounds and intermediate phases

The Gibbs energy of the stoichiometric compounds A_pB_q is expressed as follows:

$${}^0G_{A_pB_q} = \frac{p}{p+q} {}^0G_A + \frac{q}{p+q} {}^0G_B + a + bT. \quad (8)$$

Where 0G_A and 0G_B are the Gibbs energy of the pure elements Pd and Y, respectively, a and b are parameters to be determined.

The Pd_3Y (C14 Laves, isotypic with AuCu_3) and PDY are treated by a two-sublattice model [18, 19]. The Gibbs energy function per mole (m) of the formula unit is the following:

$$\begin{aligned} G_m^{\text{Pd}_3\text{Y}} &= y'_{\text{Pd}}y''_{\text{Pd}} {}^0G_{\text{Pd:Pd}} + y'_{\text{Pd}}y''_{\text{Y}} {}^0G_{\text{Pd:Y}} + y'_{\text{Y}}y''_{\text{Pd}} {}^0G_{\text{Y:Pd}} \\ &+ y'_{\text{Y}}y''_{\text{Y}} {}^0G_{\text{Y:Y}} + pRT(y'_{\text{Pd}} \ln y'_{\text{Pd}} + y'_{\text{Y}} \ln y'_{\text{Y}}) \\ &+ pRT(y''_{\text{Pd}} \ln y''_{\text{Pd}} + y''_{\text{Y}} \ln y''_{\text{Y}}) \\ &+ py'_{\text{Pd}}y'_{\text{Y}} \left[y''_{\text{Pd}} \sum_n {}^nL_{\text{Pd,Y:Pd}}(y'_{\text{Pd}} - y'_{\text{Y}})^n \right. \\ &\left. + y''_{\text{Y}} \sum_n {}^nL_{\text{Pd,Y:Y}}(y'_{\text{Pd}} - y'_{\text{Y}})^n \right] \\ &+ qy'_{\text{Pd}}y''_{\text{Y}} \left[y'_{\text{Pd}} \sum_n {}^nL_{\text{Pd:Pd,Y}}(y''_{\text{Pd}} - y''_{\text{Y}})^n \right. \\ &\left. + y'_{\text{Y}} \sum_n {}^nL_{\text{Y:Pd,Y}}(y''_{\text{Pd}} - y''_{\text{Y}})^n \right] \\ G_m^{\text{PdY}} &= y_{\text{Pd}} {}^0G_{\text{Pd:Y}} + y_{\text{Y}} {}^0G_{\text{Y:Y}} + RT(y_{\text{Pd}} \ln y_{\text{Pd}}) \\ &+ y_{\text{Y}} \ln y_{\text{Y}} \\ &+ y_{\text{Y}} \sum_n {}^nL_{\text{Pd,Y:Y}}(y_{\text{Pd}} - y_{\text{Y}})^n \end{aligned}$$

Where y'_i and y''_j are the site fraction of component i and j ($i, j = \text{Pd, Y}$) located on sublattice I and II, respectively, and the parameter ${}^0G_{i,j}$ represents the Gibbs free energy of the compound phase when the two sublattices are

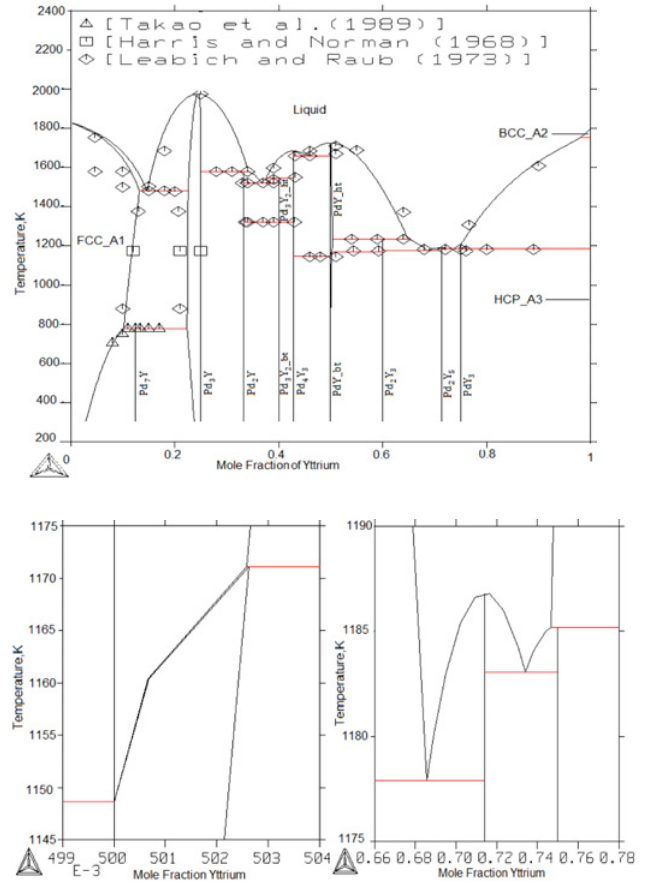


Figure 1. Comparison of the Pd-Y calculated phase diagram with the experimental data. (b) Enlarged section of (Fig. 1).

occupied by element i or j . $L_{i,\text{Pd,Y}}$ and $L_{\text{Pd,Y},j}$ are the interaction parameters between Pd and Y in the second or first sublattice, when the other sublattice is occupied by element i or j . ${}^0G_{i,j}$, $L_{i,\text{Pd,Y}}$ and $L_{\text{Pd,Y},j}$ were evaluated in the present work.

4. RESULTS AND DISCUSSIONS

The evaluation of the phase diagram was carried out with the computer Thermo-Calc software [17] which makes it possible to optimize the formation Gibbs energies of the system phases by means of the least squares method using simultaneously thermodynamic and phase diagram data. The calculated phase diagram is shown in Fig. 1. It is compared with the numerous experimental data in Fig. 1. A good agreement is noted.

All the parameters were evaluated and listed in Table 1. For the intermetallic compounds Pd_3Y , Pd_4Y_3 , PdY_{ht} , the coefficients a and b in Eq. (7), were adjusted according to the enthalpies of formation measured by [22].

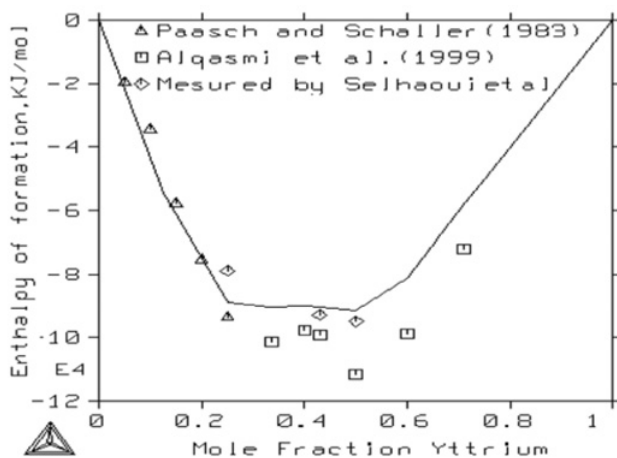
The calculated invariant equilibria in the Pd-Y system are listed in Table 2, where the largest uncertainty is about 4°C in the invariant temperature of the reaction $\text{Liq} \leftrightarrow \text{Pd}_2\text{Y}_5 + \text{Pd}_2\text{Y}_3$. In the reaction $\text{Liq} \leftrightarrow \text{Pd}_2\text{Y}_5 + \text{Pd}_2\text{Y}_3$, the uncertainty in the invariant temperature is about 13°C [11]. In view of the estimated experimental

Table 1. The optimized thermodynamic parameters of the Pd-Y system.

Phase	Thermodynamic models	Parameters in SI
Liquid	(Pd, Y) ₁	${}^0L^{liq} = -344376.073 + 21.686T$ ${}^1L^{liq} = -209832.431 + 54.045T$
BCC_A2	(Pd, Y) ₁ (Va) ₃	No excess term
HCP_A3	(Pd, Y) ₁ (Va) ₅	No excess term
FCC_A1		${}^0L^{FCC.A1} = -640143 + 17.95T$
Pd ₇ Y	(Pd) _{0.875} :(Y) _{0.125}	$G_{Pd:Y}^{Pd_7Y} - 0.875 {}^{298}H_{Pd}^{FCC.A1} - 0.125 {}^{298}H_Y^{HCP.A3}$ $= 0.875G_{Pd}^{FCC.A1} + 0.125G_Y^{HCP.A3} - 54709 + 10.815T$
Pd ₃ Y	(Pd) _{0.75} :(Y) _{0.25}	$G_{Pd:pd}^{Pd_{0.75}Y_{0.25}} - H_{Pd}^{FCC.A1} = 80000 + GHSERPd$ $G_{Pd:Y}^{Pd_{0.75}Y_{0.25}} - 0.75H_{Pd}^{FCC.A1} - 0.25 H_Y^{HCP.A3}$ $= + 0.25 GHSERPd + 0.75 GHSERY - 88887.7$ $+ 6.135T$ $G_{Y:pd}^{Pd_{0.75}Y_{0.25}} - 0.75H_{Pd}^{FCC.A1} - 0.25H_Y^{HCP.A3}$ $= + 75000 + 0.75GHSERPd + 0.25 GHSERY$ $+ 88887.7 - 6.135T$ $G_{Y:Y}^{Pd_{0.75}Y_{0.25}} - H_Y^{HCP.A3} = 75000 + GHSERY$
Pd ₂ Y	(Pd) _{0.667} :(Y) _{0.333}	${}^0L_{Pd:Y,Pd}^{Pd_{0.75}Y_{0.25}} = -103331.7 - 0.86T$ $G_{Pd:Y}^{Pd_2Y} - 0.667 {}^{298}H_{Pd}^{FCC.A1} - 0.333 {}^{298}H_Y^{HCP.A3}$ $= + 0.667 {}^{298}H_{Pd}^{FCC.A1} + 0.333 {}^{298}H_Y^{HCP.A3} - 90302.78 + 3.7T$
Pd ₃ Y ₂ .bt	(Pd) _{0.6} :(Y) _{0.4}	$G_{Pd:Y}^{Pd_3Y_2.bt} - 0.6H_{Pd}^{FCC.A1} - 0.4H_Y^{HCP.A3}$ $= 0.6H_{Pd}^{FCC.A1} + 0.4H_Y^{HCP.A3} - 90425 + 2.08T$
Pd ₃ Y ₂ .ht	(Pd) _{0.6} :(Y) _{0.4}	$G_{Pd:Y}^{Pd_3Y_2.ht} - 0.6H_{Pd}^{FCC.A1} - 0.4H_Y^{HCP.A3}$ $= 0.6G_{Pd}^{FCC.A1} + 0.4H_Y^{HCP.A3} - 90107.45 + 1.84T$
Pd ₄ Y ₃	(Pd) _{0.571} :(Y) _{0.429}	$G_{Pd:Y}^{Pd_4Y_3} - 0.571H_{Pd}^{FCC.A1} - 0.429H_Y^{HCP.A3}$ $= 0.571G_{Pd}^{FCC.A1} + 0.429G_Y^{HCP.A3} - 90509 + 1.493T$
PdY.bt	(Pd) _{0.5} :(Y) _{0.5}	$G_{Pd:Y}^{Pd_{0.5}Y_{0.5}} - 0.5H_{Pd}^{FCC.A1} - 0.5H_Y^{HCP.A3}$ $= + 0.5 GHSERPd + 0.5 GHSERY - 91389.8748$ $+ 3.16T$
PdY.ht	(Pd) _{0.5} :(Y) _{0.5}	$G_{Y:Y}^{Pd_{0.5}Y_{0.5}} - H_Y^{HCP.A3} = 153095.5 + GHSERY$ ${}^0L_{Pd:Y:Y}^{Pd_{0.5}Y_{0.5}} = -141542.47$ $G_{Pd:Y}^{Pd_{0.5}Y_{0.5}} - 0.5H_{Pd}^{FCC.A1} - 0.5H_Y^{HCP.A3}$ $= + 0.5 GHSERPd + 0.5 GHSERY - 91389.8743$ $+ 3.16T$
Pd ₂ Y ₃	(Pd) _{0.4} :(Y) _{0.6}	$G_{Y:Y}^{Pd_{0.75}Y_{0.25}} - H_Y^{HCP.A3} = + 183383.5 - 7.7T + GHSERY$
Pd ₂ Y ₅	(Pd) _{0.286} :(Y) _{0.714}	${}^0L_{Pd:Y:Y}^{Pd_{0.5}Y_{0.5}} = -162924.4$
PdY ₃	(Pd) _{0.25} :(Y) _{0.75}	$G_{Pd:Y}^{Pd_2Y_3} - 0.4H_{Pd}^{FCC.A1} - 0.6H_Y^{HCP.A3}$ $= 0.4G_{Pd}^{FCC.A1} + 0.6G_Y^{HCP.A3} - 81146.17 + 7.23T$ $G_{Pd:Y}^{Pd_2Y_5} - 0.286H_{Pd}^{FCC.A1} - 0.714H_Y^{HCP.A3}$ $= 0.286G_{Pd}^{FCC.A1} + 0.714G_Y^{HCP.A3} - 57513.8 + 3.47T$ $G_{Pd:Y}^{PdY_3} - 0.25H_{Pd}^{FCC.A1} - 0.75H_Y^{HCP.A3}$ $= 0.25G_{Pd}^{FCC.A1} + 0.75G_Y^{HCP.A3} - 50238.5 + 2.914T$

Table 2. Invariant reactions in the Pd-Y system.

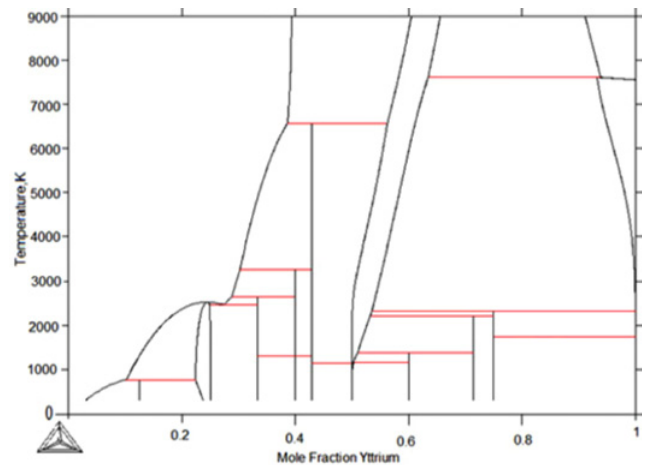
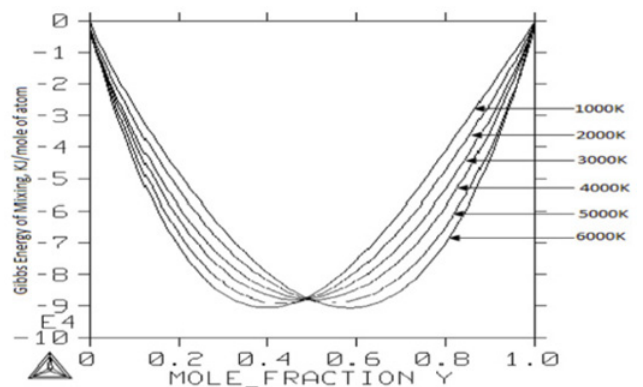
Reaction	Present work		Ref [7]	
	T(K)	X(Y)	T(K)	X(Y)
Liq + BCC_A2 \leftrightarrow HCP_A3	1751	0.980	1751	0.980
Liq + HCP_A3 \leftrightarrow PdY ₃	1185	0.746	1181	0.745
Liq \leftrightarrow Pd ₂ Y ₅ + PdY ₃	1183	0.734	1168	0.730
Liq \leftrightarrow Pd ₂ Y ₅	1187		1188	–
Liq \leftrightarrow Pd ₂ Y ₅ + Pd ₂ Y ₅	1178	0.685	1176	0.700
Liq + PdY_ht \leftrightarrow Pd ₂ Y ₅	1233	0.649	1233	0.660
Liq \leftrightarrow PdY_ht	1723		1723	0.500
Liq \leftrightarrow PdY_ht + Pd ₄ Y ₃	1658	0.453	1658	0.470
Liq \leftrightarrow Pd ₄ Y ₃	1683		1683	–
Liq + Pd ₄ Y ₃ \leftrightarrow Pd ₃ Y ₂ _ht	1546	0.376	1547	0.380
Liq \leftrightarrow Pd ₃ Y ₂ _ht + Pd ₂ Y	1519	0.367	1518	0.370
Liq + Pd ₃ Y \leftrightarrow Pd ₂ Y	1578	0.342	1578	0.340
Liq \leftrightarrow Pd ₃ Y	1973		1973	0.250
Liq \leftrightarrow Pd ₃ Y + FCC_A1	1478	0.147	1478	0.150
		FCC		
		0.132		
		Pd3Y		
		0.225		
FCC_A1 + Pd ₂ Y \leftrightarrow Pd ₇ Y		FCC		
	777	0.101	777	0.105
		Pd3Y		
		0.224		
Pd ₃ Y ₂ _ht \leftrightarrow Pd ₃ Y ₂ _bt	1318	0.369	1318	–
PdY_ht + Pd ₂ Y ₃ \leftrightarrow PdY_b	1171	–	1173	0.520
PdY_ht \leftrightarrow Pd ₄ Y ₃ + PdY_b	1149	–	1143	0.510

**Figure 2.** Calculated and measured enthalpies of formation of the intermetallic compounds.

errors (about 1–2 at. %), all experimental invariant reaction compositions in the Pd–Y system are well reproduced.

The assessed enthalpies of formation of the intermetallic compounds compared with experimental measurements are plotted in Fig. 2. The calculated enthalpies agree well with the experimental data [20–22].

As mentioned by [23] in order to check that the optimized thermodynamic parameters of the intermetallic compounds are satisfactory, we verified that when the liquid phase is suspended during the calculation of the Pd–Y phase diagram, the stoichiometric phases disappear

**Figure 3.** Calculated Pd-Y phase diagram when the liquid phase is suspended.**Figure 4.** Gibbs energy of mixing of the liquid phase at different temperature.

at high temperatures. A terminal solid solutions and a two-phase domain existing between them are found to be stable (Fig. 3).

Figure 4 shows the evolutions of Gibbs energy for the liquid phase as a function of temperature (T) with our optimization, when T is increasing up to 6000 K, the Gibbs energy for the liquid phase decreases.

The reference states were Pd and Y liquids.

5. CONCLUSIONS

All of the experimental phase equilibria and thermodynamic data of the Pd–Y system from the available literature have been critically evaluated. Within the regime of CALPHAD technique, the Redlich–Kister polynomial, the sublattice-compound energy model and the temperature dependant expression were adopted to describe the solution phases, the non-stoichiometric phases and the stoichiometric compounds, respectively. A set of self-consistent thermodynamic parameters has been obtained, which can reproduce satisfactorily most of the experimental data on thermodynamic properties and phase diagram within experimental uncertainties.

References

- [1] K.H.J. Buschow, Rep. Progr. Phys. 1977; 40: 1179–1256.
- [2] L. Schlapbach, A. Züttel, Nature. 2001; 414: 353–358.
- [3] V.K. Pecharsky, K.A. Gschneidner, Phys. Rev. Lett. 1997; 78: 4494–4497.
- [4] L. Kaufman, H. Bernstein, Computer Calculation of Phase Diagram, Academic Press, New York, 1970.
- [5] N. Saunders, A.P. Miodownik, CALPHAD – A Comprehensive Guide, Pergamon Press, Oxford, UK, 1998.
- [6] H. Lukas, S.G. Fries, B. Sundman, Computational Thermodynamics—The Calphad Method, Cambridge University Press, Cambridge, UK, 2007.
- [7] Q. Loebich Jr., E. Raub, J. Less-Common Met. 1973; 30: 47–62.
- [8] A. Palenzona, A. Iandelli, J. Less-Common Met. 1974; 34: 121–124.
- [9] R. Sanjines-Zeballos, B. Chabot, E. Parthe, J. Less-Common Met. 1980; 72: 17–20.
- [10] K. Takao, Y. Sakamoto, M. Yoshida, J. Less-Common Met. 1989; 152: 115–125.
- [11] R. Kuentzler, O. Loebich, J. Less-Common Met. 1985; 106: 335–348.
- [12] I.R. Harris, M. Norman, J. Less-Common Met. 1968; 15: 285–298.
- [13] A. Palenzona, S. Cirafici, Thermochem. Acta. 1975; 12: 267–275.
- [14] G. Borzone, G. Cacciamani, R. Ferro, CALPHAD 1990; 14: 139–149.
- [15] AT. Dinsdale, SGTE data for pure elements. Calphad 1991; 15: 317–425.
- [16] O. Redlich, AKister. IndEng Chem. 1948; 40: 345–8.
- [17] B. Sundman, B. Jansson, JO. Andersson. The Thermo-Calc databank system. CALPHAD. 1985; 9: 153–90.
- [18] M. Hillert, L.I. Staffansson, Acta Chem. Scand. 1970; 24: 3618.
- [19] B. Sundman, J. Agren, J. Phys. Chem. Solids. 1981; 42: 297–301.
- [20] S. Paasch, H.-J. Schaller, Ber. Bunsenges. Phys. Chem. 1983; 87: 812.
- [21] R.A. Alqasmi, S. Paasch, H.J. Schaller, J. Alloys Comp. 1999; 283: 173–177.
- [22] N. Selhaoui, O. J. Kleppa, J. Alloys Comp. 1993; 191.
- [23] S.L. Chen, S. Daniel, F. Zhang, Y.A. Chang, W.A. Oates, R. Schmid-Fetzer, J. Phase Equilib. 2001; 22: 373.
- [24] Binary Alloy Phase Diagrams, Second Edition, Ed. T.B. Massalski, ASM International, Materials Park, Ohio. 1990; 3: 3065–3068.