JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 15, No. 11-12, November - December 2013, p. 1280 - 1285

Thermodynamic reassessment of the Sn–Y system

A. IDDAOUDI*, N. SELHAOUI, M. AIT AMAR, S. KARDELLASS, L. BOUIRDEN
Laboratory of Thermodynamics and Energy (L.T.E), Faculty of science, B. P. 8106, Ibn Zohr University, Agadir, Morocco

The phase diagram of the Sn-Y and thermodynamic system has been critically assessed by means of CALPHAD technique. The solution phases (liquid, hcp and bcc) are modeled with the Redlich-Kister equation, and the intermetallic compounds (Sn_4Y_5, $Sn_{10}Y_{11}$, Sn_2Y, Sn_5Y_2 and Sn_3Y) are treated as stoichiometric compounds. The Sn_3Y_5 sub-stoichiometric intermetallic compound, which have a homogeneity range, were treated with the formula $(Sn)_{0.375}(Sn,Y\%)_{0.625}$ by a two-sublattice model with Sn on the first sublattice and Sn and Yon the second one. The calculated phase diagram and the thermodynamic properties of the system are in satisfactory agreement with the majority of the experimental data.

(Received September 28, 2013; accepted November 7, 2013)

Keywords: Sn-Y system, Phase diagram, Thermodynamic assessment, Calphad method

1. Introduction

The recent study of superconductivity in Sn_3Y at 7K can be explained by intermediate strength conventional electron-phonon coupling [1,2]. A complete thermodynamic description of the Sn-Y system is needed.

The present work is a part of a thermodynamic description of R-Sn(R=Sc [3], Yb[4] and La[5]) already calculated in our laboratory which is required to give a better understanding of the constitutional properties and potential technological applications of these alloys.

The objective of this work is to develop a thermodynamic description of the Sn-Y binary system by means of the CALPHAD [6] technique.

2. Review of experimental data

The phase diagram of the Sn-Y system was first investigated by Schmidt and McMaters [7] using metallography, x-ray diffraction and differential thermal analysis. Four intermetallic compounds were described: Sn_3Y_5, Sn_4Y_5, $Sn_{10}Y_{11}$, Sn_2Y and Sn_3Y. For the Sn_3Y_5 compound a congruent melting was determined at 1940°C, while the Sn_4Y_5, $Sn_{10}Y_{11}$, Sn_2Y and Sn_3Y compounds, a peritectic formation was reported, respectively, at 1790°C, 1600°C, 1140°C and 515°C.

Later, Palenzona and Manfrinetti [8] reinvestigated the phase diagram in the range 60 to 100 at. % Y. A new compound Sn_5Y_2 with the peritectic reaction temperature of 430°C was discovered.

Recently, the evaluated Sn-Y phase diagram by Okamoto [9] (Fig. 1) is based on the work of Schmidt and McMaters [7] and Palenzona and Manfrinetti [8] according to this assessment. Six intermetallic compounds were reported: Sn_3Y_5, Sn_4Y_5, $Sn_{10}Y_{11}$, Sn_2Y, Sn_5Y_2 and Sn_3Y. The crystal structures of various phases are reported in Table 1.

Tang et al. [10] established a thermodynamic optimization of the Sn-Y binary system with the Thermo-Calc software [11], but without considering that the Sn_3Y_5 is a sub-stoichiometric intermetallic compound.

Borzone et al. [12] measured the enthalpies of formation for the intermetallic compounds Sn_3Y and Sn_2Y using the dynamic differential calorimetry method. Witusiewicz et al. [13] determined the enthalpies of formation of the Sn_5Y_2, Sn_4Y_5 and Sn_2Y. Meschel and Kleppa [14] and Borsese et al. [15] measured the standard enthalpy of formation of Sn_3Y_5 using the dynamic differential calorimetry method. Colinet and Pasturel [16] calculated the enthalpies of formation for four intermetallic compounds: Sn_3Y_5, Sn_4Y_5, Sn_2Y and Sn_3Y.

Gorbachuk and Bolgar [17] determined the molar heat capacities of the compound Sn_3Y in the range 298–2300 K.

Table 1. Symbols and crystal structures of the stable solid phases in the Sn-Y system.

Diagram symbol	Composition at.% Y	Pearson symbol	Symbol used in thermo-calc data file	Prototype
(βSn)	0	tI4	BCT_A5	β-Sn
(αSn)	0	cF8	Diamond	C
Sn_3Y	25	cP4	Sn_3Y	Cu_3Al
Sn_5Y_2	28.6	oP14	Sn_5Y_2	Ge_5Er_2
Sn_2Y	33.3	oC12	Sn_2Y	Si_2Zr
$Sn_{10}Y_{11}$	52.4	tI84	$Sc_{11}Sn_{10}$	$Ge_{10}Ho_{11}$
Sn_4Y_5	55.6	oP36	Sn_4Y_5	Ge_4Sm_5
Sn_3Y_5	62.5	hP16	Sn_3Y_5	Si_3Mn_5
(βY)	100	cI2	BCC_A2	W
(αY)	100	hP2	HCP_A3	Mg

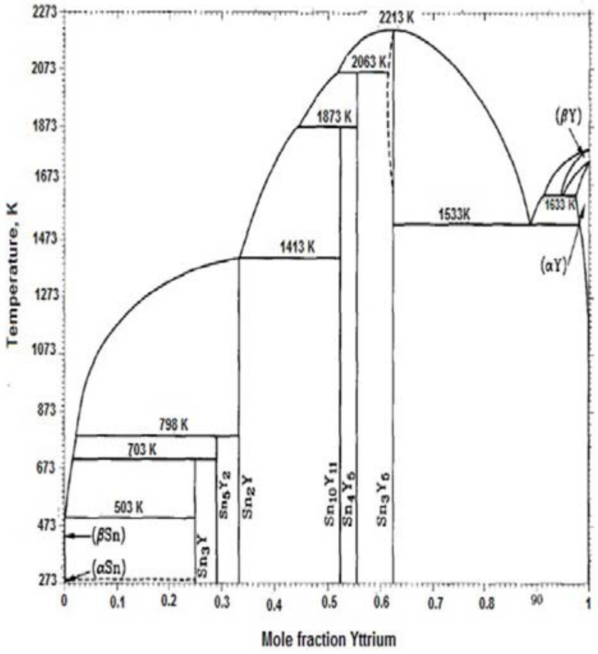

Fig. 1. The phase diagram of the Sn-Y system reviewed by Okamoto [9].

3. Thermodynamic models

For the calculation of phase equilibria in a multicomponent system, it is necessary to minimize the total Gibbs energy G, of all the phases that take part in this equilibrium:

$$G = \sum_{i=1}^{p} n_i G_i^{\varphi}(T) = \text{minimum} \qquad (1)$$

Where ni is the number of moles and $G_i^{\varphi}(T)$ the Gibbs energy of phase φ.

The Gibbs energy is represented as a power series in terms of temperature T in the form:

$$G_i^{\varphi}(T) = a + bT + cTln(T) + \sum dT^n \qquad (2)$$

Where a, b, c and d are coefficients and n represents a set of integers. A number of such expressions are usually required for a given phase to cover the whole temperature range of interest. From this expression for the Gibbs energy other thermodynamic functions can be evaluated:

$$S = -b - c - cTln(T) - \sum ndT^{n-1} \qquad (3)$$

$$H = a - cT - \sum (n-1)dT^n \qquad (4)$$

$$C_p = -c - \sum n(n-1)dT^{n-1} \qquad (5)$$

3.1 Pure elements

The Gibbs energy of the pure element i (i= Y, Sn) in the phase φ (φ =Liquid, HCP_A3, BCT_A5 and DIAMOND_A4), referred to the enthalpy of its stable state at 298.15 K, is described as a function of temperature by

$$G_i^{\varphi}(T) = {}^0G_i^{\varphi} - H_i^{SER}(298.15K)$$
$$= a + bT + cTlnT + dT^2 + eT^3 + fT^7 + gT^{-1} + hT^{-9} \qquad (6)$$

Where $H_i^{SER}(298.15\ K)$ is the molar enthalpy of the element i at 298.15 K in its standard element reference (SER) state, HCP_A3 for Y and BCT_A5 for Sn.

In this paper, The Gibbs energy functions are taken from the SGTE compilation of Dinsdale [18].

3.2. Solution phases

The solution phases, (φ =Liquid and HCP_A3) were modeled as substitutional solutions according to the polynomial Redlich–Kister model [19]. The solid BCT_A5 (β-Sn) and Diamond_A4 (α-sn) with negligible solubilities are considered as pure elements. The Gibbs energy of one mol of formula unit of phase φ is expressed as the sum of the reference part ${}^{ref}G^{\varphi}$, the ideal part ${}^{id}G^{\varphi}$, and the excess part ${}^{exc}G^{\varphi}$:

$$G_m^{\varphi} = {}^{ref}G^{\varphi} + {}^{id}G^{\varphi} + {}^{exc}G^{\varphi} \qquad (7)$$

As used in the Thermo-Calc software [11]:

$$\begin{aligned} {}^{ref}G^{\varphi}(T) = {} & ({}^0G_Y^{\varphi}(T) - H_Y^{SER}(298.15K))x_Y + \\ & ({}^0G_{Sn}^{\varphi}(T) - H_{Sn}^{SER}(298.15K))x_{Sn} \end{aligned} \qquad (8)$$

$${}^{id}G^{\varphi} = RT(x_Y \ln x_Y + x_{Sn} \ln x_{Sn}) \qquad (9)$$

Where R is the gas constant, T the temperature, in Kelvin, x_Y and x_{Sn} are the fraction of elements Y and Sn, respectively. The excess ${}^{exc}G^{\varphi}$ energy part in Eq. 7 is given by the Redlich-Kister polynomial [19] formula:

$${}^{exc}G_m^{\varphi}(T) = y_i y_j \sum_{\lambda=0}^{\lambda} {}^{\lambda}L_{i,j}^{\varphi}(y_i - y_j)^{\lambda} \qquad (10)$$

With i and j are indices which correspond to the two species Yttrium and Tin.

The binary interaction parameters of the ${}^{\lambda}L_{i,j}^{\varphi}$ type assessed in this study were temperature dependent as follows:

$${}^{\lambda}L_{i,j}^{\varphi} = a_{\lambda} + b_{\lambda}T \qquad (11)$$

a_{λ} and b_{λ} are the coefficients to be optimized.

3.3 Stoichiometric compounds

The Gibbs energy of the stoichiometric compounds (Sn_4Y_5, $Sn_{10}Y_{11}$, Sn_2Y, Sn_5Y_2 and Sn_3Y) noted as ${}^{0}G_{A_pB_q}$ was expressed as follows:

$$ {}^{0}G_{A_pB_q} = \frac{p}{p+q}\,{}^{0}G_A + \frac{q}{p+q}\,{}^{0}G_B + a + bT \qquad (12) $$

Where ${}^{0}G_A$ and ${}^{0}G_B$ are the Gibbs energy of the pure elements Sn and Y, respectively, a and b are parameters to be determined.

3.4. Intermediate phases

The Sn_3Y_5 intermetallic compounds have an experimental small homogeneity range, they were treated by a two-sublattice model as $(Sn)_{0.375}(Sn,Y\%)_{0.625}$ The symbol % denotes the major component in the considered sublattice. The Gibbs energy function per mole (m) of the formula unit $(Sn)_{0.375}(Sn,Y\%)_{0.625}$ is the following:

$$ \begin{aligned} G^{0.375Sn0.625Y} - H^{SER}_{0.375Sn0.625Y} + = y^{1}_{Sn} y^{2}_{sn}\,{}^{0}G^{Sn:Sn} \\ + y^{1}_{Sn} y^{2}_{Y}\,{}^{0}G^{Sn:Y} + RT[0.375 y^{1}_{Sn} \ln y^{1}_{Sn} + \\ 0.625(y^{2}_{Sn} \ln y^{2}_{Sn} + y^{2}_{Y} \ln y^{2}_{Y})] + {}^{xs}G_m \end{aligned} \qquad (13) $$

$$ H^{SER}_{Sn0.375Y0.625} = 0.375 H^{SER}_{Sn} + 0.625 H^{SER}_{Y} \qquad (14) $$

where $y^{1}_{Sn} = 1$ denotes the site fraction of tin the first sublattice, y^{2}_{Sn} and y^{2}_{Y} the site fractions of tin and Yttrium in the second sublattice, ${}^{0}G^{0.375Sn0.625Y}$ is the Gibbs energy of the hypothetical compound $Sn_{0.375}Y_{0.625}$ ${}^{xs}G_m$ is the excess Gibbs energy expressed by the following expression:

$$ {}^{xs}G_m = y^{2}_{Sn} y^{2}_{Y} (L^{\lambda}_{Sn:Sn,Y}) \qquad (15) $$

Where $L^{\lambda}_{Sn:Sn,Y}$ represents the interaction parameters between the elements Sn and Y in the second sublattice while the first sublattice is only occupied by the element Sn.

These excess parameters are temperature dependent as:

$$ L^{\lambda}_{Sn:Sn,Y} = a_{\lambda} + b_{\lambda} T \qquad (16) $$

In order to avoid the occurrence of the hypothetical compound $Sn_{0.375}Sn_{0.625}$ during the phase diagram calculation, the value +5000 J/mol of atoms was added to the function GHSERSN, see Table 2.

4. Results and discussions

The interaction parameters of the thermodynamic assessment of the Sn–Y binary system were optimized using the Parrot module [20] in ThermoCalc [11] with the CALPHAD [6] technique. This module works by minimizing the square sum of the differences between the experimental data and calculated values.

Most of the experimental data which are mentioned in ‘‘Review of experimental data’’ are used in this work. In this parameter optimization procedure, for modeling the liquid phase we first imposed the conditions $d^2G/dx^2>0$ (additional constraints to avoid the appearance of an unwanted inverted miscibility gap in the liquid phase during the phase diagram calculation as recommended in [21–23]). The congruent intermetallic compound is going to be investigated next. The other compounds were consequently optimized by using phase diagram data reported by Okamoto [9] and thermodynamic information of the compounds. All the parameters were evaluated and listed in Table 2.

The calculated Sn–Y phase diagram compared with the experimental data is showed in Fig. 2. A satisfactory agreement is noted in most of experimental data [7, 8].

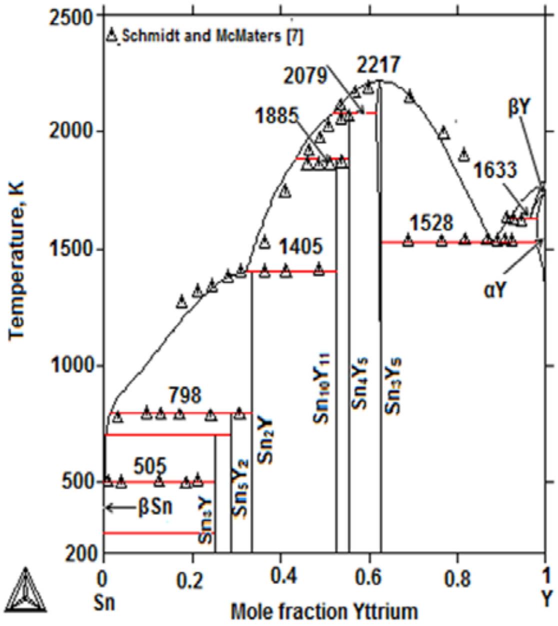

Fig. 2. Comparison of the Sn-Y calculated phase diagram with the experimental data

Table 2 The optimized thermodynamic parameters of the Sn-Y system

phase	Thermodynamic models	Parameters in SI
Liquid	$(Sn,Y)_1$	$^{0}L^{liq} = -211504 + 19.353T$ $^{1}L^{liq} = -58029 + 46.633T$ $^{2}L^{liq} = 89354 - -28.416T$
HCP_A3	$(Sn,Y)_1(Va)_{0.5}$	$^{0}L^{HCP\_A3} = 2898 - 106.370T$
BCC_A2	$(Sn,Y)_1(Va)_3$	$^{0}L^{BCC-A2} = -7117$-51.579T
BCT_A5	(Sn)	No excess term
DIAMOND_A4	(Sn)	No excess term
Sn_3Y	$(Sn)_{0.25} : (Y)_{0.75}$	$G^{Sn3Y}_{Sn:Y} - 0.75\,{}^{298}H^{BCT\_A5}_{Sn} - 0.25\,{}^{298}H^{HCP\_A3}_{Y}$ $= 0.75G^{BCT\_A5}_{Sn} + 0.25G^{HCP\_A3}_{Y} - 52504 + 7.055T$
Sn_5Y_2	$(Sn)_{0.286} : (Y)_{0.714}$	$G^{Sn5Y2}_{Sn:Y} - 0.714\,{}^{298}H^{BCT\_A5}_{Sn} - 0.286\,{}^{298}H^{HCP\_A3}_{Y}$ $= 0.714G^{BCT\_A5}_{Sn} + 0.286G^{HCP\_A3}_{Y} - 59873 + 9.151T$
Sn_2Y	$(Sn)_{0.333}: (Y)_{0.667}$	$G^{Sn2Y}_{Sn:Y} - 0.667\,{}^{298}H^{BCT\_A5}_{Sn} - 0.333\,{}^{298}H^{HCP\_A3}_{Y}$ $= 0.667G^{BCT\_A5}_{Sn} + 0.333G^{HCP\_A3}_{Y} - 69319 + 11.015T$
$Sn_{10}Y_{11}$	$(Sn)_{0.524}: (Y)_{0.476}$	$G^{Sn10Y11}_{Sn:Y} - 0.476\,{}^{298}H^{BCT\_A5}_{Sn} - 0.524\,{}^{298}H^{HCP\_A3}_{Y}$ $= 0.476G^{BCT\_A5}_{Sn} + 0.524G^{HCP\_A3}_{Y} - 72641 + 3.349T$
Sn_4Y_5	$(Sn)_{0.555}: (Y)_{0.445}$	$G^{Sn4Y5}_{Sn:Y} - 0.444\,{}^{298}H^{BCT\_A5}_{Sn} - 0.556\,{}^{298}H^{HCP\_A3}_{Y}$ $= 0.444G^{BCT\_A5}_{Sn} + 0.556G^{HCP\_A3}_{Y} - 72709 + 2.908T$
Sn_3Y_5	$(Sn)_{0.625}: (Y)_{0.375}$	$G^{Sn3Y5}_{Sn:Sn} - {}^{298}H^{BCT\_A5}_{Sn} = G^{BCT\_A5}_{Sn} + 5000$ $G^{Sn3Y5}_{Sn:Y} - 0.375\,{}^{298}H^{BCT\_A5}_{Sn} - 0.625\,{}^{298}H^{HCP\_A3}_{Y}$ $= 0.375G^{BCT\_A5}_{Sn} + 0.625G^{HCP\_A3}_{Y} - 73000 + 3.4303T$ $^{0}L^{Sn3Y5}_{Sn:Sn,Y} = -22205 - 5.347T$

Table 4. Calculated and measured enthalpies of formation of the intermetallic compounds

Phase	$\Delta H_{formation}$ (kJ mol^{-1} at^{-1})	Technique used	Reference
Sn_3Y_5	-72.8±2.9	Calorimetry	[14]
	-87.9±4.2	Calorimetry	[15]
	-63	Estimation	[16]
	-73	Optimization	This work
Sn_4Y_5	-69.3±6.5	Estimation	[13]
	-69	Estimation	[16]
	-72.7	Optimization	This work
Sn_2Y	-71.8±0.9	Emf	[12]
	-60	Estimation	[16]
	-65.95±4.2	Calorimetry	[13]
	-69.3	Optimization	This work
Sn_3Y	-52.3±2.1	Calorimetry	[12]
	-46	Estimation	[16]
	-52.5	Optimization	This work
Sn_5Y_2	-62.6±5	Calorimetry	[13]
	-59.8	Optimization	This work
$Sn_{10}Y_{11}$	-72.6	Optimization	This work

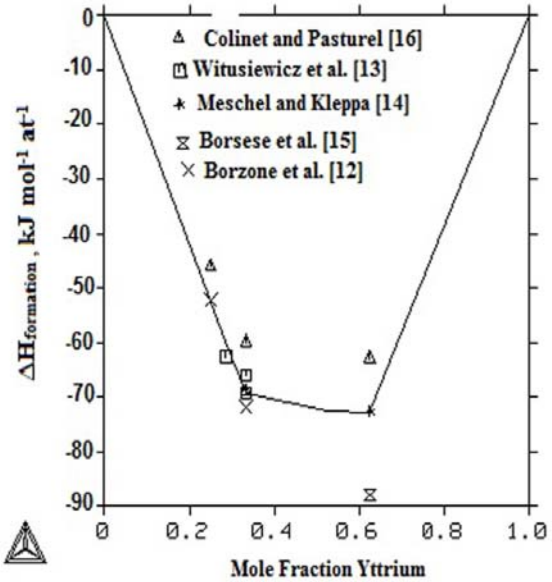

Fig. 3. Calculated and measured enthalpies of formation of thei ntermetallic compounds.

The calculated invariant reactions of the Sn-Y system are listed in table 3 and compared with the experimental results from [7, 8].

The calculated standards of formation of the intermetallic compounds compared with experimental measurements are presented in Fig. 3 and Table 4. The calculated enthalpies agree well with the experimental data [12-16].

Table 3 Invariant reactions in the Sn–Y system

Reactions	T (K)	x_Y^{Liq}	Reference
Liq ↔ βSn+ Sn_3Y	503	0.001	[7]
	503	0.001	[8]
	505	0	This work
Liq + Sn_3Y ↔ Sn_5Y_2	703	0.004	[8]
	704	0.001	This work
Liq + Sn_5Y_2 ↔ Sn_2Y	798	0.014	[8]
	798	0.013	This work
Liq + Sn_2Y ↔ $Sn_{10}Y_{11}$	1413	0.31	[7]
	1405	0.32	This work
Liq + $Sn_{10}Y_{11}$ ↔ Sn_4Y_5	1873	0.445	[7]
	1885	0.43	This work
Liq + Sn_4Y_5 ↔ Sn_3Y_5	2063	0.52	[7]
	2079	0.52	This work
Liq ↔ Sn_3Y_5	2213	-	[7]
	2217	-	This work
Liq ↔ αY + Sn_3Y_5	1533	Liq:0.89 αY 0.98	[7]
	1528	Liq 0.88 αY 0.97	This work
βY ↔ αY + Liq	1633	βY 0.94 αY 0.97	[7]
	1633	βY 0.96 αY 0.98	This work

As mentioned in [24], 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 Sn-Y phase diagram, the stoichiometric phases disappear at high temperatures. A terminal solid solutions and a two-phase domain existing between them are found to be stable (see Fig. 4).

5. Conclusions

The present work reviewed critically the experimental information on phase diagram and thermodynamic properties. A consistent set of thermodynamic parameters has been optimized and most of the experimental information can be satisfactorily reproduced on the basis of the optimized thermodynamic parameters.

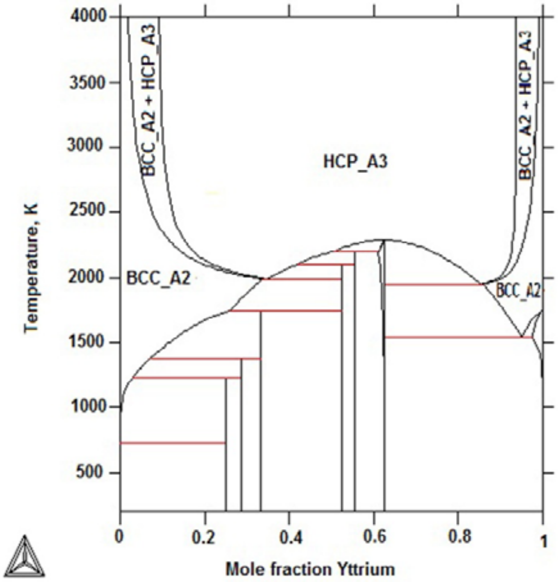

Fig.4. Calculated Sn–Y phase diagram when the liquid phase is suspended

References

[1] K. Kawashima, M. Maruyama, M. Fukuma, J. Akimitsu, Phys. Rev. B **67**, 094517 (2010).
[2] S. B. Dugdale, Phys. Rev. B **83**, 012502 (2011).
[3] A. Iddaoudi, N. Selhaoui, M. Ait Amar, S. Kardellass, R. Karioui, L. Bouirden, Calphad, **41**, 71 (2013).
[4] M. Idbenali, C. Servant, J. Therm. Anal. Calorim **103**, 131 (2011).
[5] M. Idbenali, C. Servant, N. Selhaoui, L. Bouirden, Calphad, **33**, 398 (2009).
[6] L. Kaufman and H.Bernstein, Computer Calculations of Phase Diagrams, Academic Press, New-York, NY, (1970).
[7] F. A. Schmidt, O. D. McMasters, J. Less-Common Met. **15**, 1 (1968).
[8] A. Palenzona, P.Manfrinetti, J. Alloys Compd. **201**, 43 (1993).
[9] H. Okamoto, J. Phase Equilib.**16**, 104 (1995).
[10] C. Tang , B. Hu, Y. Du, D. Zhao, P. Zhou, F. Zheng, Q. Gao, J. Wang, CALPHAD **39**, 91 (2012).
[11] B. Sundman, J-O. Andersson, Calphad **9**, 153 (1985).
[12] G .Borzone, A. Borsese, R. Forro, Z. Anorg. Allg. Chem. **501**, 199 (1983).
[13] V. T. Witusiewicz,V. R. Sidorko, J. Alloys Compd. **248**, 233 (1997).
[14] S. V. Meschel, O. J. Kleppa, J. Alloys Compd. **238**, 180 (1996).
[15] A. Borsese, G.Borzone, R. Forro, J. Less-Common Met. **70**, 213 (1980).
[16] C. Colinet, A. Pasturel, J. Less-Common Met. **102**, 167 (1984).

[17] N. P. Gorbachuk, A. S. Bolgar, Power Metallutgy and Ceramics. **41**, 55 (2002).
[18] A. T. Dinsdale, SGTE data for pure elements. Calphad **15**, 317 (1991).
[19] O. Redlich, A. Kister, Ind. Eng. Chem **40**, 345 (1948).
[20] B Jansson, Thesis, Stockholm: Royal Institute of Technology, 1984.
[21] C. H. Lupis, Chemical Thermodynamics of Metals, Prentice-Hall Inc. North-Holland, NY, 1983.
[22] G. Kaptay, Calphad **28**, 115 (2004).
[23] K.C. Kumar, P. Wollants, J. Alloys Compounds **320**, 189 (2001).
[24] S.L. Chen, S.Daniel, F. Zhang, Y.A.Chang, W.A.Oates, R. Schmid-Fetzer, J. Phase Equilib. **22**, 373 (2001).

---

[*] Corresponding author: iddaoudi19@gmail.com