Thermochimica Acta 507–508 (2010) 35–44

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

New thermodynamic assessment of nickel–tin solid and liquid alloys

Vassili P. Glibin [a,*], Tatyana N. Vorobyova [b], Boris V. Kuznetsov [b]

[a] Department of Chemical and Biochemical Engineering, University of Western Ontario, 1151 Richmond Street, London, Ontario, N6A 5B9, Canada
[b] Department of Chemistry, Belarusian State University, 14 Leningradskaya St., Minsk, 220050, Belarus

ARTICLE INFO

Article history:
Received 15 February 2010
Received in revised form 30 April 2010
Accepted 30 April 2010
Available online 10 May 2010

Keywords:
Thermodynamics
Nickel–tin alloys
Modified quasi-chemical model
Wilson's model

ABSTRACT

Standard enthalpies of formation, $\Delta_f H^\circ(298.15)$, entropies, $S^\circ(298.15)$, and molar heat capacities, $C^\circ_{p,m}(298.15)$, for a number of phases of Ni–Sn system have been estimated by graphical and analytical methods. The $\Delta_f H^\circ(298.15)$, $S^\circ(298.15)$ and $C^\circ_{p,m}(298.15)$ values of a new metastable $NiSn_9$ compound were found equal to $-85.0 \pm 5\,kJ\,mol^{-1}$, $420.7 \pm 5\,J\,K^{-1}\,mol^{-1}$ and $228\,J\,K^{-1}\,mol^{-1}$, respectively. New, reassessed value of $\Delta_f H^\circ(298.15)$ for metastable NiSn was obtained equal to $-54.0 \pm 4\,kJ\,mol^{-1}$. The limiting partial enthalpies of Ni in solid Sn ($\bar{H}_{\mathrm{lim}}(\mathrm{Ni}) = -3 \pm 1\,kJ\,mol^{-1}$) and Sn in solid Ni ($\bar{H}_{\mathrm{lim}}(\mathrm{Sn}) = -49 \pm 4\,kJ\,mol^{-1}$) at 298.15 K were determined by graphical method. The calculated $C^\circ_{p,m}(298.15)$ values of NiSn and Ni_3Sn_4 are equal $45.1\,J\,K^{-1}\,mol^{-1}$ and $160.3\,J\,K^{-1}\,mol^{-1}$, respectively. Using different methods, the standard entropy values $S^\circ(298.15)\,(\mathrm{NiSn}) = 71.7 \pm 2$ and $S^\circ(298.15)\,(Ni_3Sn_4) = 256.4 \pm 5\,J\,K^{-1}\,mol^{-1}$ were calculated. It has been shown that the combined approach based on a modified quasi-chemical model and the Tsuboka–Katayama–Wilson's equations reproduce with good approximation the experimental data on the thermodynamic functions of mixing for liquid Ni–Sn alloys. This method takes into consideration the effects of the short range ordering and the temperature on the thermodynamic functions of mixing, and has the advantage that prior knowledge of experimental values of mixing quantities is not required. The extension of this approach to the binary systems, where volume effect is inherent, is motivated.

1. Introduction

Thermodynamic modeling of alloy systems is needed for the interpretation and prediction of metastable phase formation obtained by rapid solidification and mechanical alloying. By electrodeposition it is also possible to obtain alloy phases of metastable structure; however, these phases may differ considerably from alloys of the same composition obtained by metallurgical methods [1–12]. Particularly, the electroplated Ni–Sn coatings together with Cu–Ni and Cu–Sn analogues are of an especial scientific and practical interest when possessing thermodynamic properties identical to their metallurgical alloys [1–5,11,12]. Another practical application is linked to the soldering technology for microelectronics [13,14].

The enthalpy of formation is the most important among the thermodynamic constants which can be derived from theoretical models of intermetallic compounds. This thermodynamic constant can be derived from the cohesive energies of the considered compound and its constituent elements. Using a tight binding model, Watson and Bennett [15] and Colinet et al. [16] proposed methods for predictions of the enthalpies of formation of disordered binary alloys of transition metals. In addition, more sophisticated methods based on the calculation of the energies of formation of perfectly ordered compounds, applicable to a large variety of alloys, are used [17–19]. The properties at non zero temperature are obtained by the cluster variation method [18] to treat the ordering effects with introduction of vibrational, relaxation and elastic contributions, if it is necessary.

The field of molten alloys has been less studied, presumably due to higher complexity of the liquid alloys structure compared to intermetallic compounds. In numerous liquid alloys the presence of strong short range order has often been quoted. The most popular interpretation of the thermodynamic data in systems which display a strong non-ideal mixing behavior consists in assuming the existence of chemical complexes or associates. Extensive work using such assumptions has been done for the modeling of the enthalpy of mixing in all kinds of alloys: simple metal alloys, transition metal alloys, *d* metal – *sp* metal alloys, and in semi metal alloys [20–28]. However, direct evidence of the existence and the form of such associates in liquid alloys is still lacking.

The purpose of this work was to broaden and specify data on thermodynamic constants of intermetallic phases formed in the Ni–Sn system via metallurgical and electrodeposition methods and develop a combined approach of modified quasi-chemical and the Tsuboka–Katayama–Wilson models for prediction of the thermo-

---

* Corresponding author. Tel.: +1 519 661 2111x88237; fax: +1 519 661 3498.
E-mail addresses: vglibin@yahoo.ca, vglibin@uwo.ca (V.P. Glibin), vorob@bsu.by (T.N. Vorobyova), boris_1979@rambler.ru (B.V. Kuznetsov).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.04.026

dynamic mixing quantities of liquid alloys. The Ni–Sn system was used as an example of a specific system where the end-members have a large difference in molar volumes.

2. Solid alloys

2.1. Literature data

Hultgren et al. [29] and later Nash and Nash [30], taking the numerous literature data, have constructed an assessed Ni–Sn phase diagram. Further thermodynamic assessments and phase diagram calculations using CALPHAD procedure were published by Kattner [14], Nash et al. [31], Ghosh [32] and Liu et al. [33]. The Ni–Sn diagram revised according to the results of the experimental investigation was reported in [13]. The presence of three intermediate phases Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4 was established. Ni_3Sn, Ni_3Sn_2 melt congruently at temperature around 1462 K and 1553 K, respectively, and Ni_3Sn_4 forms by a peritectic reaction at 1071 K [13]. Ni_3Sn and Ni_3Sn_2 exist under two crystalline forms: low-temperature (λ-) and high-temperature (η-) forms. The high-temperature η-form of Ni_3Sn is stable between 1220 K and 1462 K and the low-temperature λ-form is stable below 1184 K [13].The transformation of η-Ni_3Sn to λ-Ni_3Sn is of the order–disorder type [34]. There are also two forms of Ni_3Sn_2: the η-Ni_3Sn_2 is stable between 781 K and 1553 K, the λ-Ni_3Sn_2 is stable below 781 K [13]. The standard enthalpies of formation were determined for a number of equilibrium intermetallic compounds in the system Ni–Sn by means of solution calorimetry in liquid tin [13,35–37] and direct reaction calorimetry [38].

The Ni–Sn alloys obtained by electrodeposition had significant differences with respect to equilibrium structure [1–4,6–10]. The presence of the following phases was established in electrodeposited alloys: fcc solid solution within values of the Sn solubility in the range of 10–18 at.% compared to 0–10.6 at.% Sn [1,10] in the equilibrium system; a metastable NiSn with NiAs type of structure, present in a wide range of Ni fraction with respect to the equiatomic composition [6–8,10]; a phase identified with the equilibrium compound Ni_3Sn_4, which could be obtained as a single phase in the concentration range 60–75 at.% Sn [1,10]; a new metastable phase of composition close to $NiSn_9$ observed in multiphase Sn–Ni electrodeposits in the concentration range 3–34 at.% Ni [9]; and a bct-Sn with negligible Ni solubility [1,10]. The enthalpies of formation of Ni–Sn electrodeposits were measured in [6,12] using solution calorimetry (with aqueous solvent). A single phase electrodeposit compositions obtained between 47.5 at.% and 60.3 at.% Ni had enthalpies of formation at 298 K best represented as linear function of the Ni content. The interpolation from these results to the equiatomic composition (NiSn) yields $-58 \pm 4\,\mathrm{kJ\,mol^{-1}}$. It was established that NiSn electrodeposit decomposes slowly above 575 K with formation of Ni_3Sn_2 and Ni_3Sn_4 [6–8]. Accordingly to Schwitzgebel's et al. [8] the question whether NiSn is metastable composition outside the equilibrium range of Ni_3Sn_2 (Ni vacancies or Sn substitutions) or merely a quenched like form of Ni_3Sn_2 in its normal composition range, is still open. The high-tin $NiSn_9$ phase decomposes at 373 K into bct-Sn and Ni_3Sn_4 [9].

2.2. Estimation of thermodynamic constants of the intermetallic phases in Ni–Sn system at 298 K

The values of the partial enthalpy of nickel dissolution in solid tin, $\bar{H}_{\mathrm{lim}}(\mathrm{Ni})$ and the partial enthalpy of tin dissolution in solid nickel at infinite dilution, $\bar{H}_{\mathrm{lim}}(\mathrm{Sn})$, were found (Fig. 1) by extrapolation to the molar (atomic) fractions $X_{\mathrm{Ni}} = 0$ and $X_{\mathrm{Sn}} = 0$ of the plots of enthalpy of alloys formation (referred to mole of Ni or Sn atoms) versus molar fraction of the tin. To construct the diagram the values of standard enthalpies of formation of NiSn, Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4 reported (Table 1) in literature [6–8,12,13,35–38] and reference books [29,39,40] were used. Thus, we estimated the $\bar{H}_{\mathrm{lim}}$ Sn in solid nickel at 298 K is equal to $-49 \pm 4\,\mathrm{kJ\,mol^{-1}}$. This value is in a good agreement with $\bar{H}_{\mathrm{lim}}$ (Sn) = $-47.4\,\mathrm{kJ\,mol^{-1}}$, obtained in [6]. For nickel dissolution in solid tin $\bar{H}_{\mathrm{lim}}$ (Ni) is equal to $-3 \pm 1\,\mathrm{kJ\,mol^{-1}}$. This value is significantly different from $\bar{H}_{\mathrm{lim}}$ (Ni) = $-11.6\,\mathrm{kJ\,mol^{-1}}$ reported in [6] but our value is more realistic due to practically no solubility of Ni in bct-Sn. The value of standard enthalpy of NiSn formation, $\Delta_f H^\circ(298.15)$, was reassessed and value of $\Delta_f H^\circ(298.15)$ ($NiSn_9$) compound was estimated with the help of

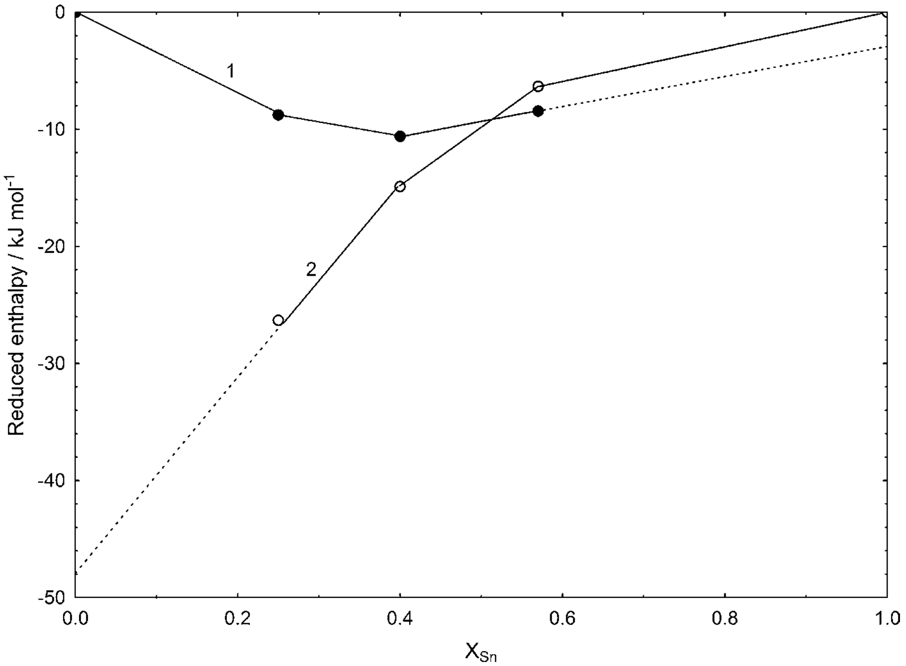

Fig. 1. Enthalpy diagram of the Ni–Sn system at 298.15 K. (1) Dependence of the enthalpies of formation of Ni–Sn alloys, referred to mole of Ni atoms, on molar fraction of Sn. (2) Dependence of the enthalpies of formation of Ni–Sn alloys, referred to mole of Sn atoms, on molar fraction of Sn.

Table 1
Thermodynamic constants of the intermetallic compounds in Ni–Sn system.

Phase	$\Delta_f H^\circ(298.15)$ (kJ mol^{-1})	$S^\circ(298.15)$ (J K^{-1} mol^{-1})	$C^\circ_{p,m}(298.15)$ (J K^{-1} mol^{-1})
fcc-Ni	0	29.87 ± 0.08 [29,39,40]	26.07 [29,39,40]
bct-Sn	0	51.55 ± 0.33 [29,39,40]	26.99 [29,39,40]
λ-Ni_3Sn	−110.1 ± 1.2 [35] −93.7 [40] −99.6 ± 1 [13,37]	131.4 [40]	99.7 [40]
η-Ni_3Sn	−91.0 ± 2.4 [38] (at 1332 K)	–	–
λ-Ni_3Sn_2	−156.9 [39,40] −158.9 ± 3.2 [35]	173.6 [39,40]	108.7 [39,40]
η-Ni_3Sn_2	−173.0 ± 1 [13,37] −155 ± 1.4 [29] −173.0 ± 5 [36]	–	–
NiSn (electrodeposit)	−58 ± 3.4 [6] −54.4 ± 1.5 [7] −57.0 ± 3.2 [12]	–	–
Ni_3Sn_4	−177.3 ± 3.9 [35,40] −205.4 [36] −168.0 ± 1 [13,37]	257.7 [40]	–

a diagram showed in Fig. 2. It represents enthalpies of formation of the metastable Ni–Sn alloys (dotted line) superimposed to the enthalpies of formation of stable Ni–Sn alloys (solid line). The solid alloys in the range of compositions of $X_{Sn} > 0.75$ could be metastable due to a restricted number of electrons transferred from Sn to Ni [41]. Higher tin concentrations do not change the number of electrons accepted by Ni. As it is seen from Fig. 2, the points for metastable $Ni_{0.5}Sn_{0.5}$ and $Ni_{0.2}Sn_{0.8}$ alloys are well fitted by the line connecting $\bar{H}_{\lim}$ (Ni) and $\bar{H}_{\lim}$ (Sn). The value of $\Delta_f H^\circ(298.15)$ ($Ni_{0.2}Sn_{0.8}$) was taken from [35]. Therefore, with the assumption that the point for $Ni_{0.1}Sn_{0.9}$ is on the same line, it is easy to find $\Delta_f H^\circ(298.15)$ ($Ni_{0.1}Sn_{0.9}$) equal to −8.5 ± 1 kJ mol^{-1}. The reassessed value of $\Delta_f H^\circ(298.15)$ for the $Ni_{0.5}Sn_{0.5}$ alloy is equal to −27 ± 2 kJ mol^{-1}; this value is in a good agreement with recent calorimetric measurement (−28.5 ± 1.6 kJ mol^{-1}) [12].

Calculations of the standard entropy of Ni_3Sn_4, NiSn и $NiSn_9$ compounds were carried out by Kireev's method [42], the modified formula of Hertz [43] and on the base of the temperature of decomposition (disproportion) of metastable $NiSn_9$. Kireev's method is based on the fact that entropy changes during reactions of the compounds formation of the same type from elements in standard state, $\Delta_f S^\circ(298.15)$, and reduced to the number of atoms in the compounds (m), is approximately constant:

$$\left(\frac{1}{m}\right)\Delta_f S^\circ(298.15) = k_1 \tag{1}$$

Then at 298.15 K,

$$S^\circ(\mathrm{Ni}_x\mathrm{Sn}_y) = xS^o(\mathrm{Ni}) + yS^o(\mathrm{Sn}) + (x+y)k_1 \tag{2}$$

The analogous correlation is also correct for the heat capacity when Ni_xSn_y compounds are formed from the elements in standard state:

$$\left(\frac{1}{m}\right)\Delta_f C^\circ_{p,m} = k_2 \tag{3}$$

$$C^\circ_{p,m}(\mathrm{Ni}_x\mathrm{Sn}_y) = xC^\circ_{p,m}(\mathrm{Ni}) + y\,C^\circ_{p,m}(\mathrm{Sn}) + (x+y)k_2 \tag{4}$$

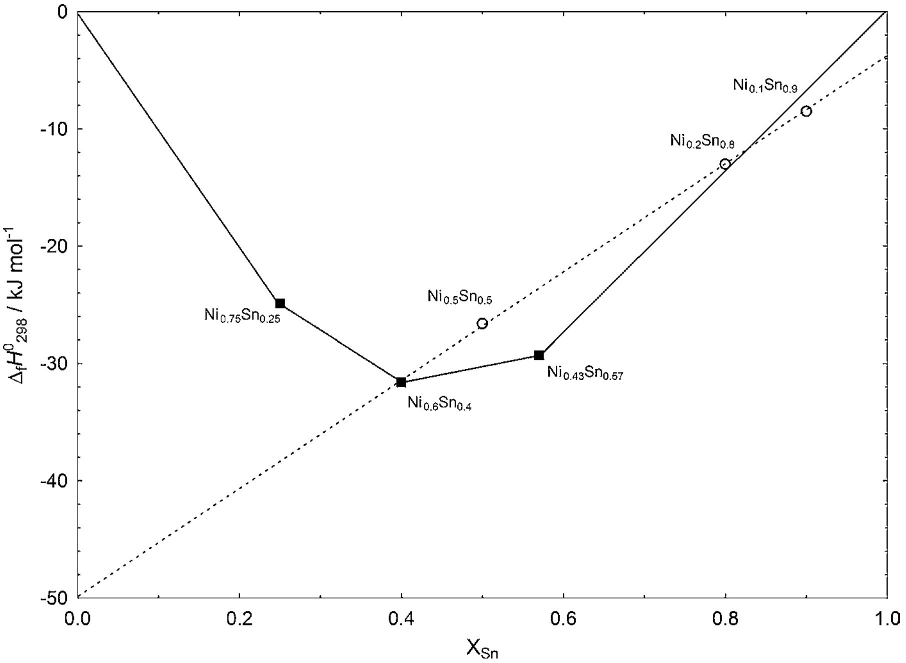

Fig. 2. Enthalpies of formation of the metastable Ni–Sn alloy (dotted line) superimposed to the enthalpies of formation of the stable Ni–Sn alloys (solid line).

Table 2
Standard molar heat capacity and standard entropy of the intermetallic compounds in Ni–Sn system.

Compound	$C^{\circ}_{p,m}(298.15)$ (J K^{-1} mol^{-1})	T_{dec} (K)	$S^{\circ}(298.15)$ (J K^{-1} mol^{-1}) Equations: (2)	(5)	(10)	Adopted value
NiSn	45.1[a]	575	72.5	70.8	–	71.7 ± 2
$NiSn_9$	228.0[a]	373	419.6	384.3	421.8	420.7 ± 5
λ-Ni_3Sn	99.60[c]	–	–	–	–	131.38[c]
λ-Ni_3Sn_2	108.67[c]	–	–	–	–	173.64[c]
Ni_3Sn_4	160.3[a]	1067[b]	260.9	251.9	–	256.4 ± 5

[a] Eq. (4).
[b] Incongruent melting.
[c] [39,40].

Hertz's formula has the following form:

$$S^{\circ}(298.15) = k_H \left(\frac{M}{C^{\circ}_{p,m}(298.15)} \right)^{1/3} m \qquad (5)$$

where k_H, M, $C^{\circ}_{p,m}(298.15)$ and m are the Hertz constant, the molar weight of a compound, the heat capacity at 298.15 K and the number of atoms in the compound, respectively.

The $NiSn_9$ compound decomposes according to the following reaction [9]:

$$3NiSn_9 = Ni_3Sn_4 + 23Sn \qquad (6)$$

At the temperature of decomposition (T_{dec} = 373 K) the change of the Gibbs energy for reaction (6) can be accepted equal to zero. Hence:

$$\Delta_r G^{\circ}(T) = \Delta_r H^{\circ}(298.15) - T\Delta_r S^{\circ}(298.15) = 0 \qquad (7)$$

and at T = 373 K

$$\Delta_r S^{\circ} = \frac{\Delta_r H^{\circ}}{T} \qquad (8)$$

In turn, the change of the entropy for reaction (6) at standard temperature is obtained using the following equation:

$$\Delta_r S^{\circ} = S^{\circ}(Ni_3Sn_4) + 23S^{\circ}(Sn) - 3S^{\circ}(NiSn_9) \qquad (9)$$

From Eq. (9) the standard entropy of $NiSn_9$ is given as:

$$S^{\circ}(NiSn_9) = 1/3[S^{\circ}(Ni_3Sn_4) + 23S^{\circ}(Sn) - \Delta_r S^{\circ}] \qquad (10)$$

Using the data from Table 1 the values of k_1, k_2 и k_H were obtained equal to −0.75, −3.00 J K^{-1} mol^{-1} and 22.56, respectively. The results for NiSn, Ni_3Sn_4 and $NiSn_9$ heat capacity and entropy calculations are presented in Table 2.

The heat capacity of NiSn, Ni_3Sn_4 and $NiSn_9$ was estimated with an error of approximately 5%. For NiSn and Ni_3Sn_4 the results of entropy calculation from the different methods are satisfactorily consistent with each other. Note that the calculated value of the Ni_3Sn_4 entropy is also in an agreement with the value 257.7 J K^{-1} mol^{-1} given in [40]. In the case of $NiSn_9$ there is no consistency between the value obtained by the Hertz's formula and those calculated by Eq. (10). It is reasonable to consider the value $S^{\circ}(298.15)$ ($NiSn_9$) = 384.3 J K^{-1} mol^{-1} as a magnitude referred to the hypothetical stable modification of $NiSn_9$ since the constants k_1, k_2 and k_H were deduced from the data for the stable phases of Ni–Sn system. An argument in favor of this suggestion is the relationship between the reduced entropy of the nickel intermetallic compounds, $(1/m)S^{\circ}(298.15)$, and the number (m) of tin atoms (Fig. 3). Fig. 3 illustrates that the value $(1/m)S^{o}(298.15)$ ($NiSn_9$), obtained by extrapolation to m = 10, practically coincides with the same value which was found with the help of Hertz's formula.

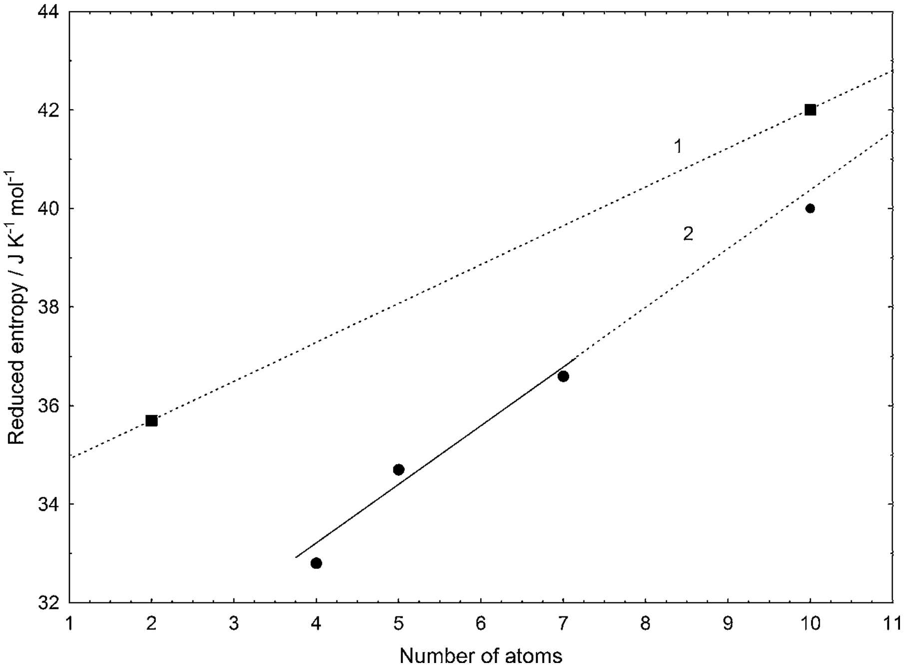

Fig. 3. Reduced standard entropy, $(1/m)$ $S^{\circ}(298.15)$, of intermetallic compounds in the Ni–Sn system versus the number of atoms (m) in the compound. (1) Metastable compounds; (2) stable compounds.

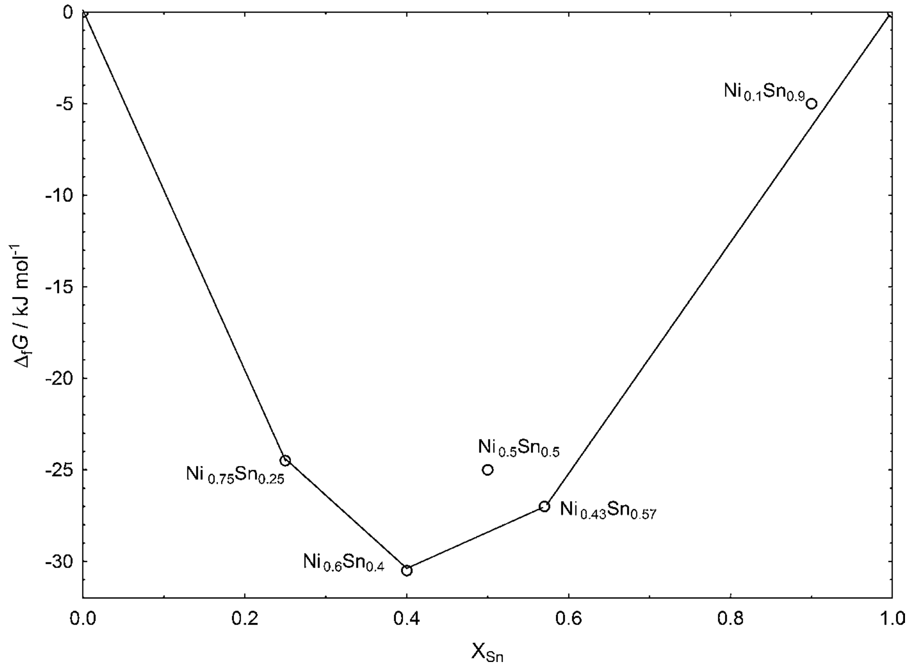

Fig. 4. Dependence of the Gibbs energy of formation of the alloys in Ni–Sn system at 298 K on tin molar fraction.

To understand the general behavior of the Ni–Sn system, the diagrams of the Gibbs energy of formation versus composition can be used. The calculations of the Gibbs energy of formation from solid Ni and Sn for intermetallic phases (per one mole of alloy) were performed using the data in Tables 1 and 2 by following well-known equation of thermodynamics:

$$\Delta_f G^\circ(T) = \Delta_f H^\circ(298.15) - T\Delta_r S^\circ(298.15) \tag{11}$$

$\Delta_f G^\circ(T)$, $\Delta_f H^\circ(298.15)$ and $\Delta_r S^\circ(298.15)$ correspond formally to the mixing quantities of stoichiometric alloys in solid state at $T = 298$ K. The dependence of the Gibbs energy of the solid alloys versus the molar fraction of Sn is shown in Fig. 4.

The phases located in the region of $X_{Sn} > 0.75$ are thermodynamically unstable, in accordance to the rule of the tangent lines [44] which describes the phase-coexistence conditions. It is obvious that such behavior could be connected with the gradually growing influence of the so-called volume (size) effect. The molar volumes of metallic nickel and tin have a large difference [45] and are equal to 6.60 and 16.30 cm^3 mol^{-1}, respectively.

3. Liquid alloys

The combined approach of the modified quasi-chemical and the Wilson–Tsuboka–Katayama models [46] was used to predict thermodynamic properties of the Ni–Sn liquid alloys in this work. There are different modifications [47–51] of the original quasi-chemical Guggenheim model [52]. Note that the CALPHAD approach has been used earlier [31–33] to develop the thermodynamic description of the liquid Ni–Sn alloys.

3.1. Modified quasi-chemical model

The modified quasi-chemical model differs from that of Guggenheim [52] by introducing the composition dependence on *effective coordination number* of atoms [48] and in accordance with the work of Blander and Pelton [49] we replace the mole fraction by *the equivalent fraction*. The latter takes into account the shift in the maximum of short range ordering from 0.5 mole fraction and this ordering is generally attributed to the formation of the most stable associates. The total excess of the entropy of mixing includes configuration and non-configuration contributions, and it depends on the degree of ordering in the melts [49–51]. However, in order to simplify the formalism, we have determined the excess entropy of mixing indirectly using the correlation between the excess enthalpy and the entropy of mixing in accordance with the work of Kubaschewski [53].

A binary system with components ‘1’ and ‘2’ in which ‘1’ and ‘2’ particles are mixed by the way of substitution in a quasi-lattice is examined by the quasi-chemical theory [47–52,54–56]. The amounts of 1–1, 2–2 and 1–2 types of pairs formed by the nearest neighbors are determined by the value of the so-called energy of interchange, associated with the formation of two 1–2 pairs from 1–1 and 2–2 pairs, according to the following quasi-chemical reaction:

$$[1\text{–}1] + [2\text{–}2] = 2[1\text{–}2] \tag{12}$$

The constant of the reaction, which corresponds to the chemical equilibrium between the pairs of the bound atoms in Eq. (12), can be written in quasi-chemical approximation as:

$$k_{(12)} = \exp\left(\frac{-\Delta_r G}{RT}\right) = 4\exp\left(\frac{2\omega}{RT}\right) \tag{13}$$

Here, $\Delta_r G$, ω, R and T are the Gibbs energy of the reaction, the interchange energy of the reaction, the universal gas constant, and the absolute temperature, respectively. The enthalpy of mixing, $\Delta_m H$, and coefficient of activity, γ_i, of the end-member components are determined by the following equations [47,52,54–56]:

$$\Delta_m H = -X^* Q = -X^* Z\omega = -\frac{2Qx_1x_2}{1+\beta} \tag{14}$$

$$\gamma_i = \left(\frac{x_i - X^*}{x_i^2}\right)^{z/2} = \left[\frac{\beta - 1 + 2x_i}{x_i(\beta+1)}\right]^{z/2} \tag{15}$$

Here, X^*, x_i, and Z are the molar fraction of the 1–2 pairs, the equivalent molar fraction of the end-member component i, and the effective coordination number; Q and β are parameters. The expression for X^* follows:

$$X^* = \frac{2x_1x_2}{1+\beta} \tag{16}$$

The equivalent fractions are defined as:

$$x_1 = \frac{b_1X_1}{b_1X_1 + b_2X_2} \tag{17}$$

$$x_2 = \frac{b_2X_1}{b_1X_1 + b_2X_2} \tag{18}$$

where X_1 and X_2 are molar fractions of the components 1 and 2; b_1 and b_2 are the numbers chosen such that $x_1 = x_2 = 0.5$ at the composition of the maximum ordering [49–51]. According to Lupis [48] it is convenient to introduce an auxiliary parameter, λ. The expression for λ is:

$$\lambda = \exp\left(\frac{-2\omega}{RT}\right) - 1 \tag{19}$$

The parameter β is given by

$$\beta = (1 + 4x_1x_2\lambda)^{1/2} \tag{20}$$

The parameter β is a measure of the tendency towards ordering in the melt. $\beta = 1$ for a perfectly random mixture, $\beta > 1$ indicates a tendency for clustering of the end-members, and $\beta < 1$ indicates a tendency towards the formation of a compound.

The equation of the partial enthalpy of mixing, $H_{i,}$, is [47,54]:

$$H_i = \Delta_m H + (1 - x_i)\frac{d(\Delta_m H)}{dx_i} \tag{21}$$

where

$$\frac{d(\Delta_m H)}{dx_i} = -2Q\left[\frac{1-2x_i}{\beta+1} + \frac{2\lambda(1-x_i)x_i(2x_i-1)}{\beta(\beta+1)^2}\right] \tag{22}$$

To calculate the coefficients of activity at the infinite dilution of all solutes, γ_i^∞, the excess Gibbs energy of mixing, $\Delta_m G^{ex}$, and the excess entropy of mixing, $\Delta_m S^{ex}$, the following expressions can be used [48]:

$$\ln \gamma_i^\infty = 0.5 Z_i^\infty \ln(1+\lambda) \tag{23}$$

$$\Delta_m G^{ex} = RT[x_1 \ln(x_1\gamma_1) + x_2 \ln(x_2\gamma_2)] \tag{24}$$

$$\Delta_m S^{ex} = \frac{(\Delta_m H - \Delta_m G^{ex})}{T} \tag{25}$$

As pointed above and following from Eqs. (13)–(15), the calculation of the thermodynamic functions of mixing in the frames of this model demands prior knowledge of the values of the energy of interchange. The energy of interchange can be calculated according to the following equation [56]:

$$\omega_{298} = k_M \Delta E^\circ \left\{1 - \exp\left[-a\left(\frac{\Delta\Phi}{\Phi_{\text{Li}}}\right)^2\right]\right\} \tag{26}$$

where k_M, ΔE°, a, Φ_{Li}, and $\Delta\Phi$ are the reduced constant of Madelung ($k_M = 1.6 \pm 0.05$), the charge transfer affinity between the unlike atoms by formation of a hypothetically pure (100%) ionic bond and referred to one mole of electrons, an empirical constant equal to 0.29, the work function of crystalline lithium, and the difference in the work functions of the alloying metals, respectively. The value of the charge transfer affinity was found in [56] on the base of the correlation between ionic contribution to the bond energy and the bond ionicity for compounds with ZnS and NaCl structures, using Pauling's method [57]; and it was found equal to 1.05 ± 0.05 eV or 101.3 ± 4.8 kJ mol^{-1}.

In accordance to the theory of the vacancy mechanism of fusion [58] we accepted that the energy of interchange at the temperature of fusion, ω_T, is correlated with that of solids at 298 K as

$$\omega_T = 0.9\omega_{298} \tag{27}$$

Further, using the common correlation between excess enthalpy, H^{ex}, and excess entropy, S^{ex}, of mixing [48,53–56],

$$H^{ex} = \tau S^{ex} \tag{28}$$

where τ is constant, gives:

$$\omega_T = 0.9\omega_{298}\left(1 - \frac{T}{\tau}\right) \tag{29}$$

The coefficient τ^{-1} for metal systems is known to be constant and equals to 4.5×10^{-5} [56].

3.2. *Application of the quasi-chemical model for calculation of the thermodynamic functions of mixing in Ni–Sn system*

The calculations were performed for 1580 K on the reason of the existence of a large set of experimental data for the thermodynamic functions of mixing at that temperature which is necessary for the testing of the fitness of the modified quasi-chemical model. With the substitution of the work function value for Li, Ni and Sn ($\Phi_{\text{Li}} = 2.85$, $\Phi_{\text{Ni}} = 5.20$ and $\Phi_{\text{Sn}} = 4.15$ eV [45]) in formula (26) we obtained $\omega_{298} = 6262$ J mol^{-1} and further we arrived by formula (29) to the following equation for the temperature dependence of the energy of interchange:

$$\omega_T(\text{J mol}^{-1}) = 5636 - 0.25T \tag{30}$$

The formula suggested in [59] was used for evaluation of the coordination number (CN) of atoms in liquids:

$$CN = \frac{36\sqrt{2}\mu}{\pi} = 16.21\mu \tag{31}$$

where μ is the density of atomic packing in liquid. In turn, the density of atomic packing in the liquid at temperature T can be found using the following formula [60]:

$$\mu = \mu_m\left(\frac{T}{T_m}\right)^{-0.18}\left(\frac{V}{V_m}\right)^{0.249} \tag{32}$$

where μ_m and V_m are the density of atomic packing and the molar volume at the temperature of fusion, T_m, respectively. Note that the dependence of the molar volume on the temperature is expressed by the well-known relationship of thermal expansion:

$$V = V_m[1 + \alpha_V(T - T_m)] \tag{33}$$

where α_V is the coefficient of the volume expansion equal to 0.87×10^{-4} cm^3 K^{-1} for tin [60]. Using $V_m^{\text{Sn}} = 17.03$ cm^3 mol^{-1} and $\mu_m^{\text{Sn}} = 0.396$ [60], the value of coordination number for tin was found to be equal to 6.4 at 1580 K. This value is in good agreement with the result of a calculation performed with help of a more complicated method ($CN = 6.9$) [61]. According to the theory of [57], the coordination number of nickel at this temperature was accepted equal to $CN = 0.9(CN_c) = 0.9 \cdot 12 = 10.8$ (CN_c is coordination number of the crystalline nickel). We assumed that in liquid alloys, there is a linear dependence of the effective coordination number, Z, varying from 10.8 to 6.0 with tin molar fraction increasing from 0 to 0.5, and this number is constant and equals to 6.0 at tin molar fraction in the region $X_{\text{Sn}} > 0.5$. The later assumption is based on the data for crystalline structure of Ni–Sn phases in which the Ni and Sn atoms have coordination numbers 6 and 7 [62]. Integral and partial enthalpies of mixing of the components calculated by Eqs. (14), (21) and (22) are given in Fig. 5. The following values for the model parameters were used in calculations: $\lambda = -0.529$; $b_{\text{Sn}} = 1$; $b_{\text{Ni}} = 2/3$;

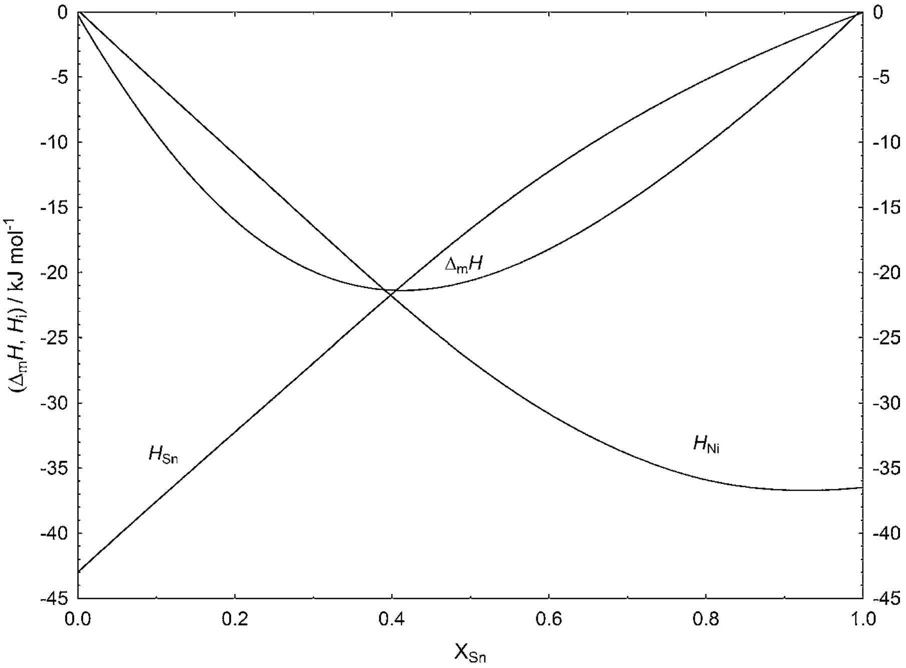

Fig. 5. The integral mixing enthalpy, $\Delta_m H$; the partial mixing enthalpies, H_{Sn}, and H_{Ni}, in the liquid Ni–Sn system at 1580 K according to the modified quasi-chemical model.

$\omega_{1580} = 5241\,\text{J mol}^{-1}$; $Q_{1580} = Z\omega_{1580} = 36{,}687\,\text{J mol}^{-1}$. The numerical values of the b_{Sn} and b_{Ni} parameters were calculated using Eqs. (17) and (18) and assuming that maximum of the short range ordering had to comply with the formation of the most thermally stable compound in the Ni–Sn system (Ni_3Sn_2). The minimum ($\Delta_m H_{min}$) at $X_{Sn} = 0.4$ coincides with the data from [13,41] and $\Delta_m H_{min}$ is equal to -21.7 ± 4 (modified quasi-chemical model) in comparison with -20.0 [13] and $-20.2 \pm 0.6\,\text{kJ mol}^{-1}$ [41]. The limiting partial enthalpies, H_i^{∞}, of Ni (referred to liquid Ni) and Sn (referred to liquid Sn) at 1580 K are equal to $-36.5 \pm 5\,\text{kJ mol}^{-1}$ and $-42.9 \pm 5\,\text{kJ mol}^{-1}$ (Fig. 5), respectively.

The value H_i^{∞} for Ni is in reasonable agreement with $H_{Ni}^{\infty} = -41.9\,\text{kJ mol}^{-1}$ at 1576 K [41]. It is difficult to make a conclusion concerning limiting partial enthalpy of mixing for Sn because as for as we are aware there is a lack of reliable experimental data in the literature. The agreement of the calculated and experimental data on the concentration dependence of tin activity is satisfactory only in the interval of compositions X_{Sn} between 0 and 0.5 (Fig. 6). It can be suggested that the volume effect begins markedly to intervene with increasing of X_{Sn}. This effect expresses the positive deviation of the experimental values for activity from Raoult's law and also from the values of tin activity predicted by the model. It is necessary to note that a better agreement between the results of the calculation and the experimental data will be observed for nickel due to the well-known rule of crystallochemistry which asserts that insertion of atoms of smaller size into a crystalline lattice demands lower energy contribution.

3.3. Application of the Tsuboka–Takayama–Wilson equations for prediction of the activity coefficients and the Gibbs energy of mixing

The Wilson's equations [64] for calculation of the coefficients of activity in two-component system are following:

$$\ln \gamma_1 = -\ln(X_1 + \Lambda_{12}X_2) + \Theta X_2 \qquad (34)$$

$$\ln \gamma_2 = -\ln(\Lambda_{21}X_1 + X_2) - \Theta X_1 \qquad (35)$$

$$\Theta = \frac{\Lambda_{12}}{X_1 + \Lambda_{12}X_2} - \frac{\Lambda_{21}}{\Lambda_{21}X_1 + X_2} \qquad (36)$$

where X_1 и X_2 are the molar fractions of components 1 and 2; Λ_{12} and Λ_{21} are parameters of the Wilson's model.

The Wilson's equations for the coefficients of activity are a pair of transcendental equations which can be solved only numerically when the experimental activity coefficients are known. The most commonly used numeric methods are the nonlinear least squares, the gradient search and the simplex pattern search [65]. In case the coefficients of activity at infinite dilution are used, the Wilson's equations are simplified to [65]:

$$\ln \gamma_1^{\infty} = -\ln \Lambda_{12} + 1 - \Lambda_{21} \qquad (37)$$

$$\ln \gamma_2^{\infty} = -\ln \Lambda_{21} + 1 - \Lambda_{12} \qquad (38)$$

Further, these equations can be reduced to the following expression of a single variable which is solved readily by the trial-and-error method:

$$\Lambda_{12} = \frac{1}{\gamma_1^{\infty}} \left\{ \exp\left[1 - \frac{1}{\gamma_2^{\infty}} \exp(1 - \Lambda_{12})\right] \right\} \qquad (39)$$

Then, we have:

$$\Lambda_{21} = 1 - \ln(\Lambda_{12}\gamma_1^{\infty}) \qquad (40)$$

Taking into account the values of the coefficients of activity ($\gamma_{Sn}^{\infty} = 0.017$ and $\gamma_{Ni}^{\infty} = 0.089$ calculated by Eq. (23)) and giving index 1 to tin, index 2 to nickel we obtained after several iterations $\Lambda_{12} = \Lambda_{SnNi} = 1.932$ and $\Lambda_{21} = \Lambda_{NiSn} = 4.428$. The dependencies of the activity on the concentration calculated by Eqs. (37)–(40) are plotted in Fig. 6. These values are in a very close agreement with the results of the modified quasi-chemical model. The Wilson's equations as well as the equations of the quasi-chemical model cannot take into account the volume effect when $X_{Sn} > 0.5$. To overcome this problem we used the Tsuboka and Katayama modification [46] of the original Wilson's equations:

$$\ln \gamma_1 = \ln \frac{(X_1 + V_{12}X_2)}{X_1 + \Lambda_{12}X_2} + (\Theta - \Theta_V)X_2 \qquad (41)$$

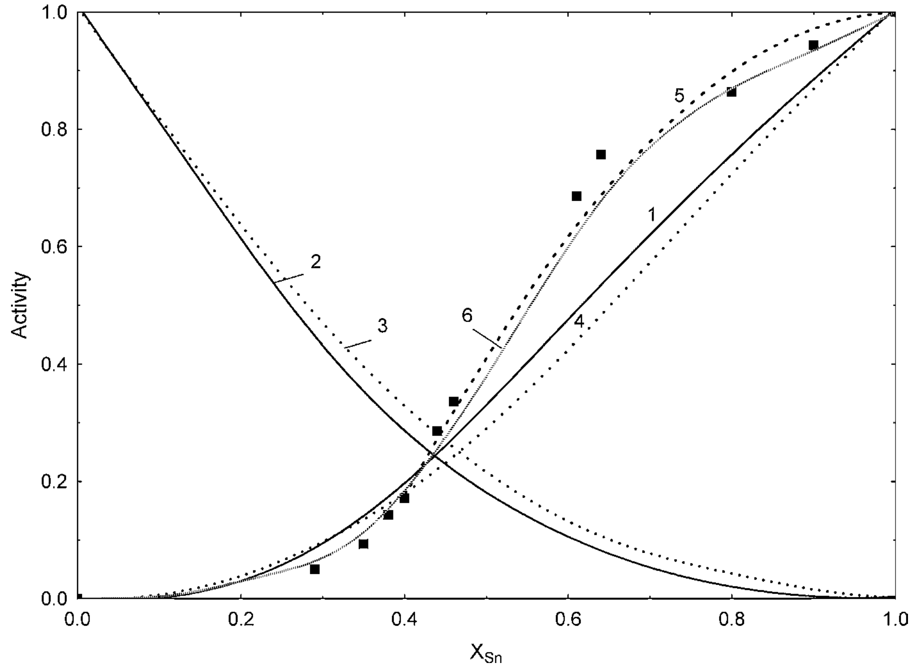

Fig. 6. Nickel and tin activities in Ni–Sn system at 1580 K. (1 and 2) Activities of Sn and Ni, respectively (modified quasi-chemical model); (3 and 4) activities of Ni and Sn, respectively (Wilson's model); (5) activities of Sn (the Tsuboka and Katayama modification of the original Wilson's model); (6) CALPHAD calculations [32,33] of Sn activities; ■– experimental data [63] on tin activities.

$$\ln \gamma_2 = \ln \frac{V_{21}X_1 + X_2}{\Lambda_{21}X_1 + X_2} - (\Theta - \Theta_V)X_1 \qquad (42)$$

$$\Theta_V = \frac{V_{12}}{X_1 + V_{12}X_2} - \frac{V_{21}}{V_{21}X_1 + X_2} \qquad (43)$$

$$\Theta = \frac{\Lambda_{12}}{X_1 + \Lambda_{12}X_2} - \frac{\Lambda_{21}}{\Lambda_{21}X_1 + X_2} \qquad (44)$$

$$V_{12} = \frac{V_2}{V_1} \qquad (45)$$

$$V_{21} = \frac{V_1}{V_2} \qquad (46)$$

where V_2 and V_1 are molar volumes and all other symbols have been indicated earlier. Note, that at $V_2 = V_1$ Eqs. (41) and (42) convert to the original Wilson's equations.

Fig. 6 illustrates the dependence of tin activity on tin molar fraction, calculated by Eq. (41) compared to the experimental data [63] and CALPHAD calculations at 1573 K [32,33].

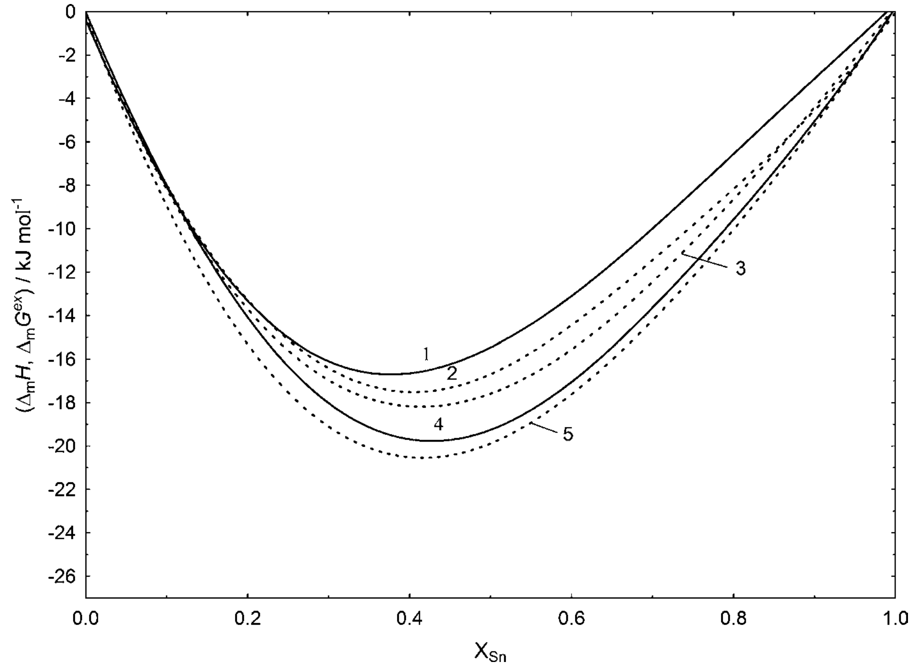

Fig. 7. The calculated excess Gibbs energy of mixing (combined approach of the modified quasi-chemical model and the Tsuboka–Takayama–Wilson equations, curve 2) and the calculated enthalpies of mixing (modified quasi-chemical model, curve 5) at 1580 K in compare with experimental data [13,41,63] and CALPHAD method calculations. (1 and 4) Experimental excess Gibbs energies and integral enthalpies of mixing, respectively; (3) calculated enthalpies of mixing according to the CALPHAD method [32,33].

The molar volumes used in calculations were $V_{\text{Sn}}^{1580} = 18.62\,\text{cm}^3\,\text{mol}^{-1}$ and $V_{\text{Ni}}^{1580} = 7.59\,\text{cm}^3\,\text{mol}^{-1}$. It can be seen that the Tsuboka–Katayama modification of the Wilson's equations seems to take into account volume effect in the range of $X_{\text{Sn}} = 0.5–1.0$ reasonably well. The activity coefficients of the end-members of Ni–Sn system, corrected by the method of Tsuboka and Katayama, were further used to derivate the concentration dependence of the excess Gibbs energy of mixing at 1580 K (Eq. (24)). The results of an application of the combined approach to the determination of the mixing quantities for liquid Ni–Sn system at 1580 K are presented in Fig. 7 (curves 2 and 5) in compare to the experimental data [13,41,63] (solid curves 1 and 4) and CALPHAD method [32,33] (curve 3).

The following cubic polynomial [31], fitting the experimental data [63],

$$\Delta_m G^{ex} = -85.3415X^3 + 188.765X^2 - 103.454X \qquad (47)$$

where X is the molar fraction of Sn, was used to construct the composition dependence of the excess Gibbs energy of mixing in Fig. 7. In turn, the following equation, representing the experimental values of the enthalpies of mixing [41]:

$$\begin{aligned}\Delta_m H = {} & X(1-X)(-46.01 - 6.788X - 209.616X^2 \\ & + 203.879X^3 - 20.145X^4)\end{aligned} \qquad (48)$$

where $X = X_{\text{Ni}}$, was used to plot the composition dependence of the enthalpies of mixing. The agreement between predicted and experimental mixing quantities for liquid Ni–Sn alloys is seen to be reasonable.

4. Conclusions

The standard enthalpy of formation, $\Delta_f H^\circ(298.15)$, of a metastable NiSn was reassessed and $\Delta_f H^\circ(298.15)$ of a new metastable NiSn_9 compound was estimated. These values were found equal to -54 ± 4 (in good agreement with calorimetric measurement of Clarke and Dutta [6]) and $-85 \pm 5\,\text{kJ}\,\text{mol}^{-1}$, respectively. The limiting partial enthalpy of Ni in solid Sn ($\bar{H}_{\text{lim}}$ (Ni) $= -3 \pm 1\,\text{kJ}\,\text{mol}^{-1}$) and Sn in solid Ni ($\bar{H}_{\text{lim}}$ (Sn) $= -49 \pm 4\,\text{kJ}\,\text{mol}^{-1}$), referred to the solid state of the solutes, were determined by a graphical method. The value of $\bar{H}_{\text{lim}}$ (Sn) agrees well with data [6].

The heat capacity of NiSn, Ni_3Sn_4 and NiSn_9 was estimated by Kireev's method with an error of approximately 5%. The calculated $C_{p,m}^\circ(298.15)$ values of these compounds are 45.1, 160.3 and $228.0\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$, respectively.

Using different approaches $S^\circ(298.15)$ $(\text{Ni}_3\text{Sn}_4) = 256.4 \pm 5$, $S^\circ(298.15)$ $(\text{NiSn}) = 71.7 \pm 2$ and $S^\circ(298.15)$ $(\text{NiSn}_9) = 420.7 \pm 5\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ were calculated. The value for Ni_3Sn_4 is very close to $(257.7\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})$ tabulated in a reference book [40]. The entropies of NiSn and NiSn_9 were estimated for the first time.

It was shown that there is no minimum in the Gibbs energy diagram for Ni–Sn system in the vicinity of NiSn and NiSn_9. Therefore, we can adopt the point of view of Augis and Bennet [7] that the equiatomic NiSn is an extension of the composition range of Ni_3Sn_2 and not a low-temperature equilibrium phase. The compound $\text{NiSn}_{9,}$ supersaturated by Sn, is also not a low-temperature equilibrium phase.

The modification of Guggenheim's quasi-chemical model including the Blander–Pelton and the Lupis approaches was developed for liquid binary systems. Methods for the determination of the model parameters were presented. These methods were based on prior knowledge of the available values of the work function of the constituents and the structural data of the constituents and the intermetallic compounds. It was shown that the modified quasi-chemical model as well as Wilson's model can predict the integral and partial enthalpies of mixing in good agreement with experimental values. The limiting partial enthalpies, H_i^∞, of Ni (referred to liquid Ni) and Sn (referred to liquid Sn) at 1580 K are equal to -36.5 ± 5 and $-42.9 \pm 5\,\text{kJ}\,\text{mol}^{-1}$, respectively. The model takes into consideration the effects of the temperature and the short range ordering on thermodynamic functions of mixing, and has the advantage that prior knowledge of the experimental mixing quantities is not required. The values of the limiting coefficients of activity for Ni and Sn at 1580 K are: $\gamma_{\text{Sn}}^\infty = 0.017$ and $\gamma_{\text{Ni}}^\infty = 0.089$. The field of application of this model for the coefficients activity and Gibbs energy of mixing seems to be limited to the systems where the volume effect does not intervene.

The combined approach on the base of the modified quasi-chemical model and Tsuboka–Katayama–Wilson's equations reproduces in a good approximation the experimental data on the coefficients activity and the Gibbs energy of mixing for Ni–Sn system. Finally, the extension of this approach to the binary systems, where the volume effect is inherent, is motivated.

Acknowledgements

The authors would like to thank Dr. Iryna Bashtan-Kandybovich and Ph.D candidate Kalin Penev (University of Western Ontario, Canada) for technical assistance.

References

[1] T. Watanabe, Nano-Plating, Elsevier, Amsterdam, 2004.
[2] O.V. Reva, T.N. Vorobyova, V.V. Sviridov, Russ. J. Electrochem. 35 (9) (1999) 1070 (in Russian).
[3] B.V. Kuznetsov, Ph.D. Thesis, Belarusian State University, Minsk, 2007.
[4] V.V. Sviridov, T.V. Gaevskaya, L.I. Stepanova, T.N. Vorobyova, Chemical problems of the development of new materials and technologies, in: T.N. Vorobyova (Ed.), Collection of Papers, Belarusian State University Publishing, Minsk, 2003, pp. 9–59.
[5] B.V. Kuznetsov, T.N. Vorobyova, Trans. Inst. Metal Finish. 84 (3) (2006) 159.
[6] M. Clarke, P.K. Dutta, J. Phys. D.: Appl. Phys. 4 (1971) 1652.
[7] J.A. Augis, J.E. Bennet, J. Electrochem. Soc. 125 (2) (1978) 335.
[8] G. Schwitzgebel, R. Mildenberger, Ber. Bunsenges. Phys. Chem. 101 (11) (1997) 1742.
[9] W. Riesenkampf, T. Biestek, J. Morgiel, W. Lasocha, J. Mater. Sci. 36 (19) (2001) 4633.
[10] P.L. Cavallotti, L. Nobili, A. Vicenzo, Electrochim. Acta 50 (2005) 4557.
[11] V.P. Glibin, B.V. Kuznetsov, T.N. Vorobyova, J. Alloys Compd. 386 (2005) 139.
[12] B.V. Kuznetsov, T.N. Vorobyova, Bull. Belarusian State University 2 (1) (2006) 17 (in Russian).
[13] H. Ipser, H. Flandorfer, Ch. Luef, C. Schmetterer, J. Mater. Sci.: Mater. Electron. 18 (2007) 3.
[14] U.R. Kattner, JOM 54 (2) (2002) 45.
[15] R.E. Watson, L.H. Bennett, CALPHAD 5 (1981) 25, 8 (1984) 307.
[16] C. Colinet, A. Pasturel, P. Hicter, CALPHAD 9 (1985) 71.
[17] F. Ducastelle, Cohesion and structure, in: F.R. de Boer, D.G. Pettifor (Eds.), Order and Phase Stability in Alloys, vol. 3, Elsevier, Amsterdam, 1991.
[18] D. de Fontaine, Solid State Phys. 47 (1994) 33.
[19] J.W. Connolly, A.R. Williams, Phys. Rev. B 27 (1983) 5169.
[20] R. Agarwal, H. Feufel, F. Sommer, J. Alloys Compd. 217 (1995) 59.
[21] I. Arpshofen, M.J. Pool, U. Gerling, F. Sommer, E. Schultheiû, B. Predel, Z. Metallkd. 72 (1981) 776.
[22] I. Arpshofen, M.J. Pool, U. Gerling, F. Sommer, E. Schultheiû, B. Predel, Z. Metallkd. 72 (1981) 842.
[23] R. Castanet, R. Chastel, Z. Metallkd. 78 (1987) 97.
[24] H. Feufel, F. Sommer, J. Alloys Compd. 224 (1995) 42.
[25] R. LuÈck, J. Tomiska, B. Predel, Z. Metallkd. 82 (1991) 944.
[26] K. Nagarajan, F. Sommer, J. Less-Common Met. 142 (1988) 319.
[27] K. Nagarajan, F. Sommer, J. Less-Common Met. 146 (1989) 89.
[28] H. Wang, R. LuÈck, B. Predel, Z. Metallkd. 83 (1992) 528–532.
[29] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelly, Selected Values of the Thermodynamic Properties of Binary Alloys, ASM Metal Park, OH, 1973, pp. 1237–1239.
[30] P. Nash, A. Nash, Bull. Alloy Phase Diagrams 6 (1985) 350.
[31] P. Nash, H. Choo, R.B. Schwartz, J. Mater. Sci. 33 (1998) 4929.
[32] G. Ghosh, Metall. Mater. Trans. A 30 (6) (1999) 1481.
[33] H.S. Liu, J. Wang, Z.P. Jin, CALPHAD 28 (2004) 363.
[34] T. Heumann, Z. Metallkd. 35 (1943) 206–211.
[35] B. Predel, W. Vogelbein, Thermochim. Acta 30 (1979) 201.
[36] A.N. Torgersen, H. Bros, R. Castanet, A. Kjekshus, J. Alloys Compd. 307 (2000) 167.

[37] H. Flandorfer, U. Saeed, C. Luef, A. Sabbar, H. Ipser, Thermochim. Acta 459 (2007) 34.
[38] G.P. Vassilev, K.I. Lilova, J.C. Gachon, Thermochim. Acta 447 (2006) 106.
[39] I. Barin, Thermochemical Data of Pure Substances/Ihsan Barin. In collab. with Fried Sauert [Transl.: F. Hampson], Part II. La–Zr, VCH, Weinheim-Basel (Switzerland)/Cambridge/New York, 1992.
[40] M. Binnewies, E. Milke, Thermochemical Data of Elements and Compounds, Second revised and extended edition, Wiley–VCH, 2002.
[41] R. Haddad, M. Gasune-Escard, J.P. Bros, A. Ranniger-Helvicek, E. Hayer, K.L. Komarek, J. Alloys Compd. 247 (1997) 82.
[42] V.A. Kireev, Thermodynamics of Chemical Reactions: Methods of Calculations, Khimia, Moscow, 1970 (in Russian).
[43] A.G. Moratchevski, I.B. Sladkov, Thermodynamic Calculations in Metallurgy, Metallurgia Publishing, Moscow, 1985 (in Russian).
[44] F. Weinhold, Classical and Geometrical Theory of Chemical and Phase Thermodynamics, Wiley, Hoboken/New Jersey, 2009, pp. 269–270.
[45] F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Nissen, Cohesion in Metals: Transition Metal Alloys, North-Holland Physics Publishing, Amsterdam/Oxford/New York/Tokyo, 1988.
[46] T. Tsuboka, T. Katayama, J. Chem. Eng. Japan 8 (1975) 181.
[47] B.A. Kogeurov, Statistical Thermodynamics, Metallurgia Publishing, Moscow, 1975 (in Russian).
[48] C.H. Lupis, Chemical Thermodynamics of Materials, Elsevier Science Publishing Co., New York, 1983.
[49] M. Blander, A.D. Pelton, Geochim. Cosmochim. Acta 51 (1987) 85.
[50] A.D. Pelton, M. Blander, Metall. Trans. B 17 (1986) 805.
[51] G. Eriksson, A.D. Pelton, Metall. Trans. B 24 (1993) 807.
[52] E.A. Guggenheim, Mixtures, Claredon Press, Oxford, 1952.
[53] O. Kubaschewski, High. Temp. High. Press 3 (1981) 435.
[54] V.A. Grigorian, A.Ya. Stomakhin, A.G. Ponomarenko, L.N. Belianchikov, Yu.I. Utotchkin, G.I. Kotelnikov, O.I. Ostrovski, Physico-chemical Calculations of the Metallurgical Processes, Metallurgia Publishing, Moscow, 1989 (in Russian).
[55] N.A. Svidunovich, V.P. Glibin, L.K. Svirko, Thermodynamics of the Interactions in Alloys, Metallurgia Publishing, Moscow, 1989 (in Russian).
[56] V.P. Glibin, Doctoral Thesis, Belarusian State University, Minsk, 2001.
[57] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca/New York, 1939.
[58] T. Gorečki, Z. Metallkd. 70 (1979) 121.
[59] V.P. Scripov, A.E. Galashev, Russian Chem. Rev. (Uspekhi Khimii) 2 (1983) 117 (in Russian).
[60] E.I. Har'kov, V.I. Lisov, V.E. Fedorov, Physics of Liquid Metals, Vischa Shkola Publishing, Kiev, 1979 (in Russian).
[61] D.P Tao, Metal. Mater. Trans. B 33 (6) (2002) 502.
[62] Structure Reports: Vol. 32A (1967)/General Editor W.B. Pearson; Vol. 39A (1973)/General Editor J. Trotter, International Union of Crystallography, Utrecht.
[63] V.N. Eremenko, G.M. Lukashenko, V.L. Pritula, Russian J. Phys. Chem. 45 (1971) 1993 (in Russian).
[64] G.M. Wilson, J. Am. Chem. Soc. 86 (1964) 127.
[65] S.M. Walas, Phase Equilibria in Chemical Engineering, Butterworth Publishers, Boston/London/Toronto, 1985.