

A THERMODYNAMIC EVALUATION OF THE Ag–Sn SYSTEM

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ABSTRACT

All the different solution phases and compounds of the Ag–Sn system have been analyzed in terms of thermodynamic models based on selected and agreed values for the lattice stabilities of the pure elements.

A set of new self consistent parameters has been obtained by using the well-known optimization procedure developed by Lukas et al., *Calphad*, 1 (1977) 225, which takes into account all the available experimental information with its accuracy concerning both thermodynamic properties and phase equilibria data.

Phase diagram and characteristic thermodynamic functions have been calculated and compared to the experimental values with the THERMODATA software. A satisfactory agreement has been obtained by using nineteen optimized coefficients for more than five hundred experimental points, with a simple substitutional model for solution phases and a linear approximation for the temperature dependency of the Gibbs energy of the compound Ag_3Sn ; the short range order of that phase has not been modelled in a first step.

The remaining difficulties concerning the invariant reaction between the liquid phase and the two solid solution phases, fcc and hcp in the rich silver region are discussed.

INTRODUCTION

This work is a part of a more important project which has been performed within the framework of one of the aims of the SGTE (Scientific Group Thermodata Europ), which exists to produce data for selected systems and to supply specialized data banks.

Details of several other systems are soon to be published [2] (Au–Sn, Au–Bi, Ag–Ge, Ag–Si, Bi–Ge), and the remaining systems presented at *Calphad XVI* [3] will also be published very soon.

A very great effort has been made to produce self-consistent data. It means that the proposed parameters are not only self consistent inside the system itself, but also together with the other systems which are collected in a data base.

For this purpose, it has been necessary to adopt common values for the lattice stabilities of the pure elements, and common standards for modelling the different phases.

For the first point, a set of data has been established for both the stable [4] and metastable [5] forms. These values have been taken in this work, but if new values are available, for example if a lattice stability has to be modified, new parameters can easily be obtained after only a new run with the optimization procedure.

SHORT PRESENTATION OF THE DIFFERENT PHASES

The assessed phase diagram, reported by Karakaya and Thompson [6], is quite similar to the one reported by Hansen and Anderko [7]. The different solution phases or compounds are listed below, with the symbols currently used.

Solution phases

- (1) Liquid phase (L)
- (2) Terminal rich silver solid solution, with a face-centred cubic (A1) prototype structure: (fcc)
- (3) Terminal rich tin solid solution, with a body-cubic tetragonal (A5) prototype structure: (bct or β Sn)
- (4) Intermediate disordered solid solution, with an Mg-type hcp (A3) structure: (hcp or ζ)

Compounds

- (5) Orthorhombic short-range Ag_3Sn (ϵ). The composition range of that phase is 23.5–25 atm% Sn at $T = 463$ K.
- (6) Pure tin, with fcc (A4) structure isotypic with diamond: (Sn_{dia} or αSn) below $T = 286$ K.

EXPERIMENTAL INFORMATION

Phase diagram

Phase equilibria of the Ag–Sn system have been experimentally determined using conventional techniques by:

Heycock and Neville [8–10]: liquidus, invariant; thermal.

Petrenko [11]: liquidus, invariant; thermal.

Murphy [12]: liquidus, invariant, solidus, solvus; thermal, micrographic studies.

Hume Rothery et al. [13]: solidus, solvus; micrographic studies.

Hanson et al. [14]: liquidus, invariant, solidus; thermal.

Hume Rothery and Reynolds [15]: liquidus, thermal.

Jenckel and Roth [16]: solid solubility of Ag in Sn, reported by Owen and Roberts [17].

Owen and Roberts [17]: solidus, solvus; X-ray analysis.

Homer and Plummer [18]: solid solubility of Ag in Sn, reported by Owen and Roberts [17].

Umanskiy [19]: solidus, solvus, X-ray analysis.

Fahri et al. [20,21]: liquidus; e.m.f. measurements.

Vnuk et al. [22]: solvus; hardness measurements.

The eutectic point has been located at $T = 494.15$ K, $x_{\text{Sn}}^{(\text{L})} = 0.962$ [8,11,12,14].

The assessed values for the two peritectic reactions [7] are

equilibrium $\text{L} + \text{hcp} \rightleftharpoons \epsilon$

$T = 753$ K; $x_{\text{Sn}}^{\text{hcp}} = 0.2285$, $x_{\text{Sn}}^{\epsilon} = 0.25$, $x_{\text{Sn}}^{\text{L}} = 0.496$

equilibrium $\text{L} + \text{fcc} \rightleftharpoons \text{hcp}$

$T = 997$ K; $x_{\text{Sn}}^{\text{fcc}} = 0.115$, $x_{\text{Sn}}^{\text{hcp}} = 0.135$, $x_{\text{Sn}}^{\text{L}} = 0.195$

The experimental values given for the solubility of Ag in βSn are rather scattered: less than 0.09 atm% [12], 0.055 atm% at $T = 483$ K [14], 0.036 atm% at $T = 493$ K [18], and approximately 0.1 atm% at $T = 473$ K [16].

The most recent work of Vnuk et al. [22] has been selected. The solubility curve is given in the range 298–494 K ($x_{\text{Ag}}^{(\beta\text{Sn})}$ (atm%): $T(\text{K}) = 0.0045 : 333$; $0.0073 : 393$; $0.011 : 413$; $0.018 : 433$; $0.025 : 443$; $0.04 : 453$; $0.062 : 463$; $0.075 : 473$; $0.0795 : 483$; 0.08 (maximal): 494 K).

Thermodynamic properties

Bibliographic research on the thermodynamic properties of the Ag–Sn system has been carried out by means of the “Thermdoc bibliographic data base” integrated in the THERMODYATA system [23].

Liquid alloys

Values of the partial Gibbs energy of Sn in the liquid phase have been measured by e.m.f. method by Yanko et al. [25] ($T = 606, 623, 653, 663, 685$ K; $x_{\text{Sn}} = 0.86\text{--}0.994$), Frantik and McDonald [24] ($T = 1073$ K; $x_{\text{Sn}} = 0.3\text{--}1$), Laurie et al. [26] ($T = 900$ K; $x_{\text{Sn}} = 0.33\text{--}1$), Nozaki et al. [27] ($T = 1100$ K; $x_{\text{Sn}} = 0\text{--}1$), Elliott and Lemons [28] ($T = 807$ K; $x_{\text{Sn}} = 0.966\text{--}1$), Roy Chowdury and Ghosh [29] ($T = 900, 1100$ K; $x_{\text{Sn}} = 0\text{--}1$), Kubaschewski and Alcock [30] ($T = 1180$ K; $x_{\text{Sn}} = 0.07\text{--}0.293$), Okajima and Sakao [31] ($T = 773, 893$ K; $x_{\text{Sn}} = 0.3\text{--}1$, a_{Ag} , a_{Sn}), Iwase et al. [32]

($T = 1073, 1173$ K; $x_{\text{Sn}} = 0-1$), Kameda et al. [33] ($T = 636-983$ K; $x_{\text{Sn}} = 0.27-0.80$), and by mass spectrometry by Yamaji and Kato [34] ($T = 1423$ K; $x_{\text{Sn}} = 0-1$, a_{Ag} , a_{Sn}).

Calorimetric studies of heats of solution of metals in liquid tin have been made by Kotchi et al. [42], Boom [35], Tichnor and Bever [36], and of enthalpy of mixing by Kawakami [37], Kleppa [38] ($T = 723$ K; $x_{\text{Sn}} = 0.64-0.99$), Wittig and Gehring [39] ($T = 1248$ K; $x_{\text{Sn}} = 0-1$), Castanet et al. [40] ($T = 1280$ K; $x_{\text{Sn}} = 0-1$), Itagaki and Yazawa [41] ($T = 1243$ K; $x_{\text{Sn}} = 0-1$), and Rakotomavo et al. [43] ($T = 1373$ K; $x_{\text{Sn}} = 0-1$).

Solid alloys

Solid solutions (fcc) and (hcp or ζ)

The activity of tin has been measured by the e.m.f. method by Laurie et al. [26] and taken from a figure on the original paper, for $T = 900$ K $x_{\text{Sn}} = 0-0.178$ and for $T = 650$ K $x_{\text{Sn}} = 0.24-0.25$.

Enthalpies of formation of the solid solutions have been determined by liquid tin solution calorimetry by Kleppa [38]: at $T = 723$ K $x_{\text{Sn}} = 0.065-0.25$.

The thermodynamic values selected by Hultgren et al. [44] agree (± 628 J per gram atom) with those of Laurie et al. [26] and (± 418 J per gram atom) with those of Kleppa [38].

Nearly stoichiometric phase Ag_3Sn

The heat of formation of two alloy samples of very nearly the same composition was measured by calorimetry at $T = 723$ K by Kleppa [38] as -6.06 ± 0.23 and -6.19 ± 0.23 KJ per gram atom respectively. Taking into account the value of the Gibbs energy of the transformation $\text{Sn}(\text{bct}) \rightleftharpoons \text{Sn}(\text{liq}) (+6973 \text{ J})$ the heat of formation referred to the pure solid elements was calculated as -4317 and -4447 J per gram atom at $T = 723$ K.

Heat capacities have been determined by differential scanning calorimetry by Wallbrecht et al. [45] for temperatures between 235 and 780 K; the $C_p(T)$ relationship for the temperature interval 298–600 K is given by

$$C_p = 23.18 + 7.18 \times 10^{-3}T - 8779(T)^{-2}$$

EVALUATION METHOD

The Gibbs energy of the different solution phases has been described by using a simple substitutional model. Excess Gibbs energy has been developed by a Redlich–Kister polynomial equation of the form

$$\Delta^E G = x_{\text{Ag}} x_{\text{Sn}} \sum_{\nu=0}^n (x_{\text{Ag}} - x_{\text{Sn}}) L_{\text{Ag,Sn}}^{(\nu)}(T) \quad (1)$$

where

$$L_{\text{Ag,Sn}}^{(\nu)}(T) = a_{\text{Ag,Sn}}^{(\nu)} + b_{\text{Ag,Sn}}^{(\nu)} T \quad (2)$$

The coefficients $L_{\text{Ag,Sn}}^{(\nu)}$ are linear functions of the temperature, i.e. $a_{\text{Ag,Sn}}^{(\nu)}$ and $b_{\text{Ag,Sn}}^{(\nu)}$ correspond to the temperature-independent values of the enthalpy and the excess entropy of mixing. This assumption is justified because no sensible variation of the enthalpy of mixing has been experimentally determined.

For the short range ordered phase Ag_3Sn , the Gibbs energy of formation has been represented by a linear dependency with temperature, and without taking into account the non-stoichiometric range in a first step.

$$\Delta G = a + bT \quad (3)$$

The calculated values for ΔCp (by using the S.G.T.E. values for pure Ag and Sn) are equal to a mean value of -0.48 J per gram atom in the range 300–600 K. This value could be fixed in the optimization procedure by taking a three terms expression for the Gibbs energy

$$\Delta G = a + bT + cT \ln T \quad (4)$$

with $c = -\Delta Cp = +0.48$ J per gram atom.

In a first step, the mean value of ΔCp has been considered as negligible. The values used for the lattice stabilities of the pure components come from the SGTE assessment [46] for the stable solid and liquid phases and from the assessment of Saunders [47] for the metastable phases (required to express the excess properties of mixing of the different solid solution phases), except for the bct structure of silver, which has been estimated arbitrarily as 4184 J.

The following values have been used [46,47]

$$\begin{aligned} {}^\circ G_{\text{Ag}}^{\text{L}} - {}^\circ G_{\text{Ag}}^{\text{fcc}} &= 11025.293 - 8.890146 T - 103219.980 E - 25 T^7 \\ &\quad 298.15 < T < 1235.08 \\ &= 11507.972 - 9.300494 T - 1412186.248 E + 23 T^{-9} \\ &\quad 1235.08 < T < 3000.00 \end{aligned} \quad (5)$$

$${}^\circ G_{\text{Ag}}^{\text{hcp}} - {}^\circ G_{\text{Ag}}^{\text{fcc}} = 300.0 + 0.30 T \quad (6)$$

$${}^\circ G_{\text{Ag}}^{\text{bct}} - {}^\circ G_{\text{Ag}}^{\text{fcc}} = 4184 \quad (\text{estimation}) \quad (7)$$

$$\begin{aligned} {}^\circ G_{\text{Sn}}^{\text{L}} - {}^\circ G_{\text{Sn}}^{\text{bct}} &= 7104.380 - 14.089569 T + 14950281.636 E - 25 T^7 \\ &\quad 298.15 < T < 505.12 \\ &= 6970.585 - 13.811447 T + 125.305 E + 23 T^{-9} \\ &\quad 505.12 < T < 3000.00 \end{aligned} \quad (8)$$

$${}^\circ G_{\text{Sn}}^{\text{fcc}} - {}^\circ G_{\text{Sn}}^{\text{bct}} = 4150 - 5.2 T \quad (9)$$

$${}^\circ G_{\text{Sn}}^{\text{hcp}} - {}^\circ G_{\text{Sn}}^{\text{bct}} = 3900 - 4.4 T \quad (10)$$

The different parameters of the various solution phases $a_{\text{Ag,Sn}}^{(\nu)}(\phi)$ and $b_{\text{Ag,Sn}}^{(\nu)}(\phi)$, and of the stoichiometric compound Ag_3Sn , a and b , have been optimized by using a program developed by Lukas et al. [1] that takes into account all the available experimental information and accuracy, after having discarded by a primary criticism some values either for experimental reasons or because they were too indirectly measured.

RESULTS AND DISCUSSION

Table 1 shows the optimized parameters of the excess Gibbs energy for the various solution phases referred to the pure elements having the same structure as the corresponding phase, and of the Gibbs energy of formation of the nearly stoichiometric compound Ag_3Sn referred to Ag (fcc) and Sn (bct).

The phase diagram has been calculated with the optimized coefficients and compared to the experimental one in Fig. 1.

Table 2 shows experimental and calculated temperature and composition for the invariant equilibria and temperatures of fusion or decomposition of stoichiometric compounds.

A quite satisfactory agreement is observed except for the invariant reaction $\text{fcc} + \text{L} \rightleftharpoons \text{hcp}$, which is calculated to be 22 K lower than the experi-

TABLE 1

Excess Gibbs energy, $\Delta^E G$, coefficients for the liquid, fcc, hcp (ζ), bct phases, and Gibbs energy, ΔG , coefficients for the stoichiometric compound, referred to Ag(fcc) and Sn(bct).

$$\Delta^E G = x_{\text{Ag}} x_{\text{Sn}} \sum_{\nu=0}^n (x_{\text{Ag}} - x_{\text{Sn}}) L_{\text{Ag,Sn}}^{(\nu)}(T)$$

$$L_{\text{Ag,Sn}}^{(\nu)}(T) = a_{\text{Ag,Sn}}^{(\nu)} + b_{\text{Ag,Sn}}^{(\nu)} T \quad (\nu = 0, 1, 2, 3)$$

and

$$\Delta G = a + bT$$

Phase	ν	$a_{\text{Ag,Sn}} \text{ (J)}$	$b_{\text{Ag,Sn}} \text{ (J K}^{-1}\text{)}$
Liquid	0	-3902.15	-4.96927
	1	-16974.05	7.424515
	2	-14299.05	10.67712
	3	-5979.25	6.497125
fcc	0	-11196.6	18.50995
	1	-24806.9	0
hcp or ζ	0	-5738.3	13.80747
	1	-36079.4	2.99534
bct	0	27218.3	-18.85109
Compound	x_{Sn}	a	b
$\text{Ag}_3\text{Sn}(\epsilon)$	0.25	-4382.0	-1.22005

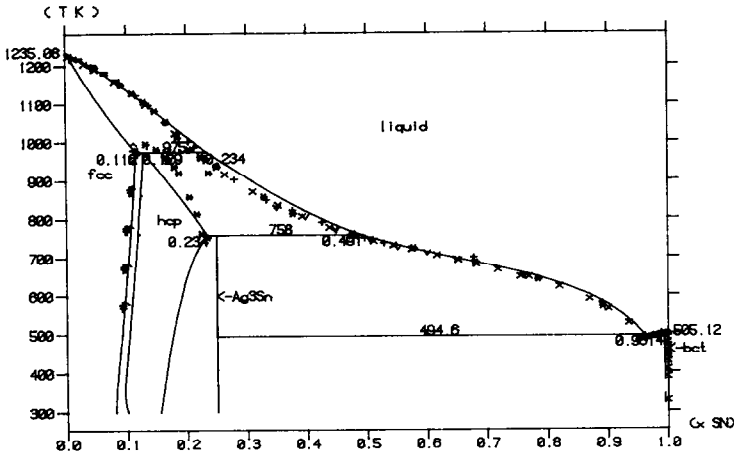


Fig. 1. Comparison between the calculated Ag-Sn phase diagram and selected experimental data. \circ , Heycock and Neville [8]; \times , Heycock and Neville [10]; $+$, Petrenko [11]; $*$, Murphy [12]; $\#$, Hume-Rothery et al. [13]; $=$, Hume-Rothery and Reynolds [15]; \wedge , Owen and Roberts [17]; \cdot , Umanskiy [19]; ∇ , Fahri et al. [20]; k , Vnuk et al. [22].

mental value reported [6,7]. Moreover, the shape of the liquidus deviates from the experimental one between the two calculated invariant temperatures 758 and 975 K, which corresponds to the diphasic equilibrium hcp + L. From a thermodynamic point of view, this can be explained by the difficulty of representing the shape of the Gibbs energy of the hcp solid solution for the following reasons: (a) the selected lattice stabilities for Ag(hcp) and Sn(hcp) are not far from the stable structures Ag(fcc) and Sn(bct); (b) it is not possible to add more coefficients for the hcp solid solution because there is not enough experimental information in this field.

TABLE 2

Three phase equilibria and congruent transformations in the Ag-Sn system

Transformation	Calculated		Experimental		Reference
	$T(K)$	$x = x_{Sn}$	$T(K)$	$x = x_{Sn}$	
Ag(fcc) \rightleftharpoons Ag(liq)	1235.08	0	1235.08	0	6
Sn(bct) \rightleftharpoons Sn(liq)	505.12	1	505.12	1	6
L \rightleftharpoons Ag ₃ Sn + bct	494.6	$x^L = 0.961$ $x^\epsilon = 0.250$ $x^{bct} = 0.9992$	494.15	$x^L = 0.962$ $x^\epsilon = 0.250$ $x^{bct} = 0.9992$	6,7 22
hcp + L \rightleftharpoons Ag ₃ Sn	758	$x^{hcp} = 0.234$ $x^\epsilon = 0.250$ $x^L = 0.491$	753.15	$x^{hcp} = 0.228$ $x^\epsilon = 0.250$ $x^L = 0.496$	6,7
fcc + L \rightleftharpoons hcp	975	$x^{fcc} = 0.116$ $x^L = 0.234$ $x^{hcp} = 0.129$	997.15	$x^{fcc} = 0.115$ $x^L = 0.195$ $x^{hcp} = 0.130$	6,7

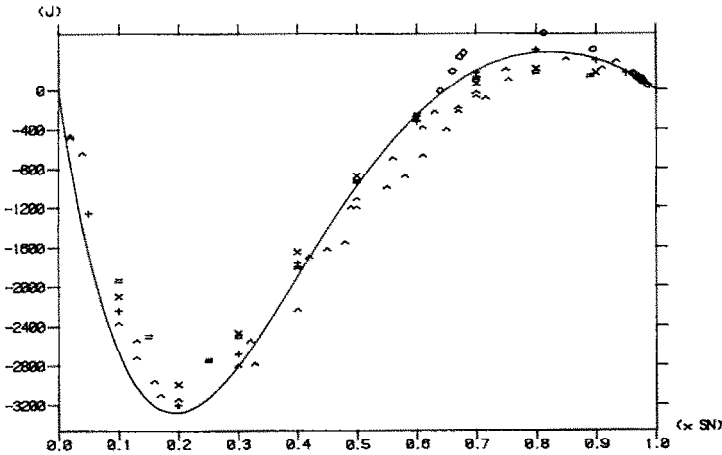


Fig. 2. Comparison between the calculated enthalpy of mixing (temperature independent) of the liquid phase and selected experimental data: —, HI; \circ , Kleppa [38]; \times , Wittig and Gehring [39]; +, Castanet et al. [40]; =, Itagaki and Yazawa [41]; \wedge , Rakotomavo et al. [43].

Figure 2 shows the good agreement obtained between the calculated enthalpy of mixing of the liquid without variation of the temperature and the available experimental information resulting from calorimetry measurements.

In Fig. 3, the partial Gibbs energy of Sn in the liquid phase calculated at $T = 823$ K has been compared with the selected data of Fahri [21]. The agreement is excellent. The agreement is also quite satisfactory with the other authors.

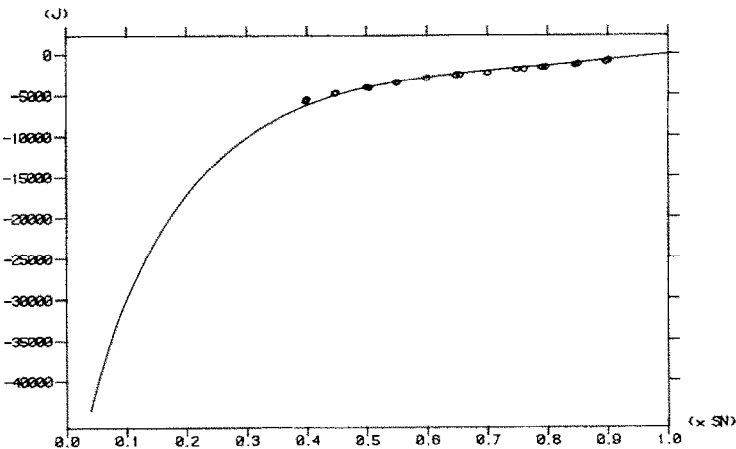


Fig. 3. Comparison between the calculated partial Gibbs energy of Sn in the liquid phase at $T = 823$ K and selected experimental data: —, GP Sn; \circ , Fahri [21].

SUMMARY

A complete thermodynamic evaluation of the Ag–Sn system is presented. A set of self-consistent parameters for the various phases has been obtained. Comparison between all the available experimental information and the calculated values is satisfactory, except for the invariant reaction $\text{fcc} + \text{L} \rightleftharpoons \text{hcp}$ which is calculated at a lower temperature than the experimental one. The possible reasons for this disagreement have been discussed.

This set of parameters can be used for tabulation of standard thermodynamic functions or calculation in multicomponent systems. It can easily be updated if new experimental data become available.

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