

# Thermodynamic Reoptimization of the Ag-Sn System

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(Submitted November 22, 1995)

The Ag-Sn binary system is reoptimized because of the increasing interest in lead-free solder development. The ordered semistoichiometric  $\text{Ag}_3\text{Sn}$  phase is described as a line compound while the other phases are represented by Redlich-Kister expressions. Results are compared with previous efforts, and the agreement between the calculated phase diagram and the assessed phase boundary data has been significantly improved while reproduction of experimental data for thermodynamic properties remains excellent.

## 1. Introduction

Recently there has been great interest by material scientists in the development of lead (Pb)-free solders. Ag-Sn alloys are very promising as Pb-free substitutes for Pb-Sn alloys, espe-

cially when ternary or quaternary alloying elements are considered [94McC]. Therefore, knowledge of the thermodynamic properties and phase diagrams of the Ag-Sn binary and Ag-Sn based multicomponent alloys is very useful. In this paper, thermodynamic optimization of the Ag-Sn binary system and comparison of current results with the previous evaluations

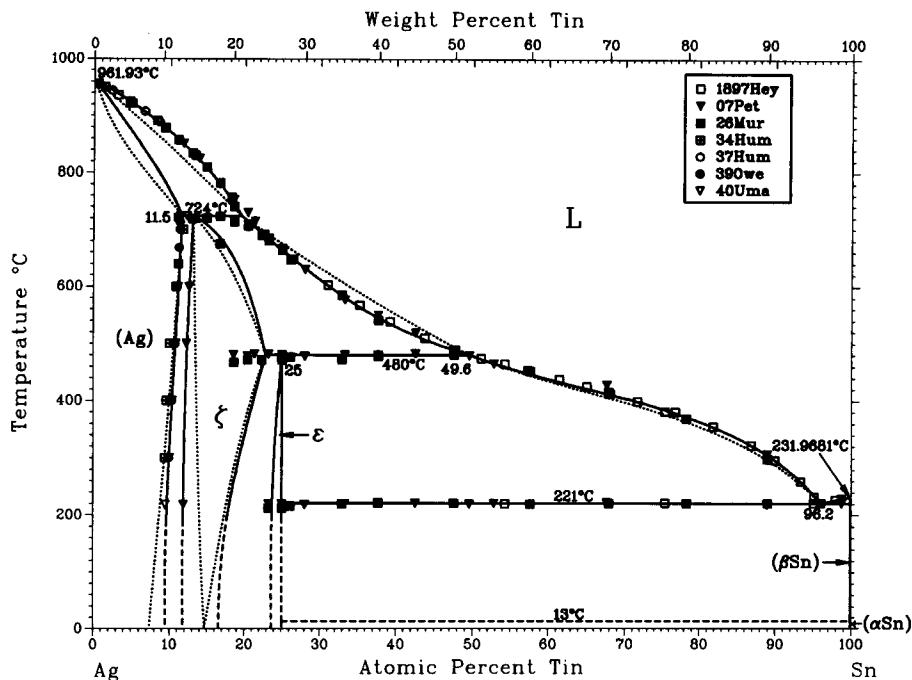


Fig. 1 Assessed phase diagram presented by Karakaya and Thompson [87Kar].

presented by Karakaya and Thompson [87Kar] and Chevalier [88Che] are carried out carefully.

Phase relationships of the Ag-Sn system are not very complicated. Solution phases include liquid, face-centered cubic (fcc) (Ag) and body-centered tetragonal (bct) (Sn) terminal solid solution, intermediate disordered solid solution close-packed hexagonal (cph) ( $\zeta$ ), a semistoichiometric ordered compound  $\epsilon\text{Ag}_3\text{Sn}$  with a narrow range of solubility in the Ag-rich band, and pure cubic Sn below 13 °C. There are three temperature-invariant equilibria: a eutectic equilibrium  $L \leftrightarrow \text{bct}(\text{Sn}) + \epsilon$  at 494 K and two peritectic equilibria  $L + \text{cph} \leftrightarrow \epsilon$  and  $L + \text{fcc}(\text{Ag}) \leftrightarrow \text{cph}$  at 753 and 997 K, respectively.

Thermodynamic and phase equilibrium data were assessed by Karakaya and Thompson [87Kar], and a set of parameters was proposed. Chevalier [88Che] optimized this system thermodynamically and presented a thermodynamic self-consistent description for this system. But agreement between the studies and available experimental data is not as good as it should be. This is discussed in the "Thermodynamic" section.

The objective of this study was to choose proper thermodynamic models to describe the phases and to develop more precise parameters so that the calculated phase diagram would agree very well with experimental data. This is important in forecasting the thermodynamic properties and phase diagrams of the higher-order systems, which include the Ag-Sn binary system as an important ingredient.

## 2. Experimental Information

### 2.1 Phase Diagram Data

As mentioned, there are six phases in the Ag-Sn system: liquid, fcc (Ag), bct (Sn), cph  $\zeta$ , orthorhombic short-ranged  $\epsilon\text{Ag}_3\text{Sn}$ , and pure Sn with fcc structure isotypic with diamond below 13 °C. The present authors are interested in the temperature range above 25 °C, so pure Sn below 13 °C is not considered here.

The liquidus curves were determined by several investigations [1890Hey, 1894Hey, 1897Hey, 07Pet, 26Mur, 34Han, 37Hum] and all the reports are similar.

**Table 1 Phase Diagram Data Used in This Optimization**

Equilibrium phases	Reference	Temperature, K	Concentration of phases, at. % Sn	
Liquid + bct (Sn).....	[87Kar]	505.12	100.0	100.0
Liquid + fcc (Ag) .....	[87Kar]	1235.08	0.0	0.0
		1223.15	1.7	0.9
		1173.15	7.1	3.3
		1123.15	11.8	6.0
		1073.15	15.3	8.5
		1023.15	18.3	10.6
Liquid + cph + fcc (Ag).....	[87Kar]	997.15	19.5	13.0
Liquid + cph.....	[87Kar]	973.15	21.7	15.6
		873.15	31.2	20.2
		773.15	45.2	22.5
Liquid + cph + $\text{Ag}_3\text{Sn}$ .....	[87Kar]	753.15	49.6	22.8
Liquid + $\text{Ag}_3\text{Sn}$ .....	[87Kar]	673.15	71.4	25.0
		573.15	89.7	25.0
Liquid + $\text{Ag}_3\text{Sn}$ + bct (Sn).	[87Kar]	494.15	96.2	25.0
cph + fcc (Ag) .....	[87Kar]	973.15	12.7	11.3
		873.15	12.5	11.0
		773.15	12.2	10.7
		673.15	12.0	10.3
		573.15	11.9	9.9
		494.15	11.8	9.5
cph + $\text{Ag}_3\text{Sn}$ .....	[87Kar]	673.15	21.2	24.5
		573.15	19.2	24.0
		494.15	18.0	23.7
bct (Sn) + $\text{Ag}_3\text{Sn}$ .....	[81Vnu]	491.15	99.922	25.0
		473.15	99.928	25.0
		463.15	99.941	25.0
		453.15	99.960	25.0
		443.15	99.976	25.0
		433.15	99.982	25.0
		413.15	99.988	25.0
		393.15	99.992	25.0
		333.15	99.996	25.0

**Table 2** Lattice Stability Parameters Used in This Optimization

$$G_{Ag}^{0,L} - G_{Ag}^{fcc} = 11\,025.293 - 8.890146T - 1.0321998 \times 10^{-20}T^7 \quad 298.15 < T < 1235.08$$

$$= 11\,507.972 - 9.300494T - 1.412186248 \times 10^{29}T^{-9} \quad 1235.08 < T < 3000.00$$

$$G_{Ag}^{0,\epsilon\text{ph}} - G_{Ag}^{0,fcc} = 300.0 + 0.30T$$

$$G_{Ag}^{0,bct} - G_{Ag}^{0,fcc} = 4184 \quad (\text{estimation})$$

$$G_{Sn}^{0,L} - G_{Sn}^{0,bct} = 7104.380 - 14.089569T + 1.4950281636 \times 10^{-18}T^7 \quad 298.15 < T < 505.12$$

$$= 6970.585 - 13.811447T + 1.25305 \times 10^{25}T^{-9} \quad 505.12 < T < 3000.00$$

$$G_{Sn}^{0,fcc} - G_{Sn}^{0,bct} = 4150 - 5.2T$$

$$G_{Sn}^{0,\epsilon\text{ph}} - G_{Sn}^{0,bct} = 3900 - 4.4T$$

**Note:** Units are J/mol of atoms.  $T$  is in K.

Many experimental data of the solidus and solvus are available [26Mur, 34Hum, 39Owe, 40Uma, 81Vnu]. Maximum Sn solubility of 11.3 and 12.3 at.% in fcc (Ag) was determined by [39Owe] and [26Mur], respectively. The solubility of Ag in bct (Sn) was determined [26Mur, 34Hum, 38Jen, 39Hom, 81Vnu] and found to be quite small.

The existence of cph  $\zeta$  was reported [08Pus, 26Mur, 26Wes, 31Nia, 40Uma]. The existence of  $\epsilon\text{Ag}_3\text{Sn}$  was determined [07Pet, 26Mur, 26Pre, 31Nia, 40Uma, 52Mic], and the phase was reported to be homogeneous between 23.7 and 25 at.%.

The assessed phase diagram proposed by Karakaya and Thompson [87Kar] is shown in Fig. 1. The experimental phase boundary data measured by different authors agree well with each other, and the assessed boundaries (solid line) can represent most of the experimental data. Therefore, reassessment of the experimental data is not very meaningful. So the assessed phase diagram data are adopted directly in this optimization. Experimental data of the solubility of Ag in bct (Sn) are from the measurement by Vnuk et al., [81Vnu], which was not used in the Karakaya [87Kar] optimization. All the phase diagram data used in this evaluation are listed in Table 1.

## 2.2 Thermodynamic Properties

Partial Gibbs energies of Sn in the liquid phase have been measured by the electromotive force (emf) method [45Fra, 46Yan, 66Lau, 66Noz, 67Ell, 71Roy, 72Kub, 74Oka, 78Iwa, 80Kam] and by mass spectrometry [72Yam]. Calorimetric measurements of solution enthalpies of metals in liquid Sn were carried out [52Tic, 74Boo, 79Kot], and the mixing en-

thalpies of liquid alloys were measured calorimetrically [30Kaw, 55Kle, 63Wit, 68Ita, 69Cas, 84Rak].

The activity of Sn in solid solution (fcc and cph) was determined by emf [66Lau]. Enthalpies of formation of the solid solutions was measured by a liquid Sn solution calorimeter [55Kle].

The enthalpy of formation of the  $\text{Ag}_3\text{Sn}$  phase was measured by calorimetry at  $T = 723$  K [55Kle], and the heat capacities were determined by differential scanning calorimetry [81Wal].

## 3. Thermodynamic Model and Optimization

### 3.1 Lattice Stability Parameters

Lattice stability parameters for pure elements were described by the formula:

$$G_i^{0,\phi}(T) - G_i^{\text{ref}}(T) = A + BT + CT \ln T + DT^2 + ET^{-1} + FT^3 + IT^7 + JT^{-9} \quad (\text{Eq 1})$$

where  $G_i^{\text{ref}}(T)$  denotes the Gibbs energy of the pure element  $i$  at the temperature of  $T$  in its stable state. In this study,  $G_{Ag}^{\text{fcc}}(T)$  and  $G_{Sn}^{\text{bct}}(T)$  were chosen as  $G_i^{\text{ref}}(T)$  for pure Ag and Sn, respectively. The coefficients  $A$  through  $J$  for stable solid and liquid phases are from the SGTE data file [91Din], and those for the metastable phases are from Chevalier [88Che] to make the comparison with his work more reasonable. All the coefficients are summarized in Table 2.

### 3.2 Models for Binary Phases

The concentration dependencies of the Gibbs energy of the phases were represented by the Redlich-Kister polynomial and the stoichiometric compound model.

#### 3.2.1 Redlich-Kister Polynomial

The liquid, fcc (Ag), disordered cph, and solid solution, bct (Sn) are described by this model with the bct (Sn) phase simplified to the regular solution model. The expression of Gibbs energy is:

$$G^\phi - G^{\text{SER}} = G^{\text{ref}} + G^{\text{id},\phi} + G^{\text{ex},\phi} \quad (\text{Eq 2})$$

where

$$G^{\text{ref}} = [G_{Ag}^{0,\text{ref}1}(T) - G_{Ag}^{\text{fcc}}(T)]X_{Ag} + [G_{Sn}^{0,\text{ref}2}(T) - G_{Sn}^{\text{bct}}(T)]X_{Sn} \quad (\text{Eq 3})$$

$$G^{\text{id},\phi} = RT[X_{Ag} \ln(X_{Ag}) + X_{Sn} \ln(X_{Sn})] \quad (\text{Eq 4})$$

$$G^{\text{ex},\phi} = X_{Ag}X_{Sn}[K_0 + K_1(X_{Ag} - X_{Sn}) + K_2(X_{Ag} - X_{Sn})^2 + \dots] \quad (\text{Eq 5})$$

The variables in Eq 2 to 5 are:

**Table 3 Comparison of Model Parameters from Different Authors**

Reference	Phase	Parameters, J/mol	Reference	Phase	Parameters, J/mol
[87Kar] .....	Liquid	$G^{ex} = X_{Sn}X_{Ag}[K_0 + K_1(X_{Ag} - X_{Sn}) + K_2(X_{Ag} - X_{Sn}) + K_3(X_{Ag} - X_{Sn})]$ $K_0 = -36\,796 + 12.097T$ $K_1 = 101\,919 - 34.596T$ $K_2 = -79\,864 - 3.432T$ $K_3 = 16\,634 + 26.51T$	[88Che] .....	bct (Sn)	$G^{ex} = K_0 X_{Sn} X_{Ag}$ $K_0 = 27\,218.3 - 18.851097T$
	fcc (Ag)	$G^{ex} = K_0 X_{Sn} X_{Ag}$ $K_0 = -28\,750 - 1.350T$		Ag <sub>3</sub> Sn compound	$\Delta_f G = -4\,382.0 - 1.22005T$
	cph	$G^{ex} = K_0 X_{Sn} X_{Ag}$ $K_0 = 81\,116 + 8.764T$	Present work.....	Liquid	$G^{ex} = X_{Sn}X_{Ag}[K_0 + K_1(X_{Ag} - X_{Sn}) + K_2(X_{Ag} - X_{Sn}) + K_3(X_{Ag} - X_{Sn})]$ $K_0 = -3\,559.18 + 8.33230T$ $K_1 = -13\,952.39 + 7.22841T$ $K_2 = -14\,792.38 + 10.61305T$ $K_3 = -8\,188.78 + 1.77201T$
	Ag <sub>3</sub> Sn	$G^{ex} = K_0 X_{Sn} X_{Ag}$ $K_0 = -309150 + 17.407T$		fcc (Ag)	$G^{ex} = X_{Sn}X_{Ag}[K_0 + K_1(X_{Ag} - X_{Sn})]$ $K_0 = 22\,229.49 - 13.67161T$ $K_1 = -9\,694.12 - 1.86628T$
	bct (Sn)	$G^{ex} = K_0 X_{Sn} X_{Ag}$ $K_0 = 25\,125$		cph	$G^{ex} = X_{Sn}X_{Ag}[K_0 + K_1(X_{Ag} - X_{Sn}) + K_2(X_{Ag} - X_{Sn})]$ $K_0 = 12\,632.78 - 16.56063T$ $K_1 = 11\,987.53 + 7.58574T$ $K_2 = -16\,981.11 - 7.25931T$
[88Che].....	Liquid	$G^{ex} = X_{Sn}X_{Ag}[K_0 + K_1(X_{Ag} - X_{Sn}) + K_2(X_{Ag} - X_{Sn}) + K_3(X_{Ag} - X_{Sn})]$ $K_0 = -3\,902.15 - 4.96927T$ $K_1 = -16\,974.05 + 7.424515T$ $K_2 = -14\,299.05 + 10.67712T$ $K_3 = -5\,979.25 + 6.497125T$		bct (Sn)	$G^{ex} = K_0 X_{Sn} X_{Ag}$ $K_0 = 34\,052.67 - 18.73441T$
	fcc (Ag)	$G^{ex} = X_{Sn}X_{Ag}[K_0 + K_1(X_{Ag} - X_{Sn})]$ $K_0 = -11\,196.6 + 18.50995T$ $K_1 = -24\,806.9$		Ag <sub>3</sub> Sn	$\Delta_f G = 3\,848.52 - 8.22311T$
	cph	$G^{ex} = X_{Sn}X_{Ag}[K_0 + K_1(X_{Ag} - X_{Sn})]$ $K_0 = -5\,738.3 + 13.80747T$ $K_1 = -36079.4 + 2.99534T$			

$G^\phi$  Gibbs energy of 1 mol atoms of phase  $\phi$

$X_{Ag}, X_{Sn}$  Mole fraction of Ag and Sn in the phase, respectively

$G_{Ag}^{0,ref1}(T)$  Gibbs energy of pure Ag at temperature  $T$  in the state of phase "ref1"

$G_{Sn}^{0,ref2}(T)$  Gibbs energy of pure Sn at temperature  $T$  in the state of phase "ref2"

$G^{SER}$  Abbreviation of  $G_{Ag}^{SER}(T)X_{Ag} + G_{Sn}^{SER}(T)X_{Sn}$

### 3.2.2 Stoichiometric Compound Model

Ag<sub>3</sub>Sn is a semistoichiometric ordered compound with a narrow range of solubility in the Ag-rich side. This phase is described as a regular solution by Karakaya and Thompson [87Kar] and as a line compound by Chevalier [88Che], respectively. Because the solubility range is very narrow, it is not worth using a complicated model to describe it. Therefore in this optimization, the Ag<sub>3</sub>Sn phase is treated as a stoichiometric compound the same as in the Chevalier evaluation. The expression of Gibbs energy is:

$$G^\phi(T) - H^{SER} = G^{ref} + \Delta_f G^\phi$$

where  $\Delta_f G^\phi$  is Gibbs energy of formation of the compound.

### 3.3 Optimization Procedure

All the values of the model parameters for the phases in this system are optimized from the experimental thermodynamic data and phase equilibrium data listed in Table 1. The optimization was carried out using the software developed by Lukas et al. [95Luk], which can accept different types of experimental data in the same operation. This program is based on the principle of the least square method and works by minimizing an error sum where each selected experimental value has been given a weight taken from literature or estimated by personal judgment. The weight can be changed to achieve a satisfactory description of most of the experimental data. The results of this work are listed in Table 3.

### 4. Comparison with Previous Works

This system was assessed and calculated by Karakaya and Thompson [87Kar], and the results are shown in Fig. 1, in which the solid lines are from the assessed phase diagram and the dashed lines are calculated from the thermodynamic model. Chevalier [88Che] optimized this system again. The present optimization and previous works are compared.

## Section I: Basic and Applied Research

**Table 4** Three-Phase Equilibrium Data from Different Authors

Equilibria phases	Reference	Composition, at. % Sn			Temperature, K	Reaction type
Liquid, fcc (Ag), cph.....	Assessed	19.5	11.5	13.0	997.15	Peritectic
	[87Kar]	19.5	11.5	13.0	997.15	Peritectic
	[88Che]	23.4	11.6	12.9	975.0	Peritectic
	Present	20.8	10.7	12.9	993.82	Peritectic
Liquid, cph, Ag <sub>3</sub> Sn .....	Assessed	49.6	22.8	25.0	753.15	Peritectic
	[87Kar]	49.6	22.8	25.0	753.15	Peritectic
	[88Che]	49.1	23.4	25.0	758.00	Peritectic
	Present	50.6	23.1	25.0	753.25	Peritectic
Liquid, Ag <sub>3</sub> Sn, bct (Sn).....	Assessed	96.2	25.0	99.91	494.15	Eutectic
	[87Kar]	96.2	25.0	99.91	494.15	Eutectic
	[88Che]	96.1	25.0	99.2	494.6	Eutectic
	Present	95.8	25.0	99.91	496.5	Eutectic

Parameters of all three works are listed in Table 3. The parameters proposed by Karakaya and Thompson [87Kar] are the simplest, and the present parameter is a little complicated concerning the number of coefficients. Considering the consistency of the calculated phase diagram with the assessed one, the increase in coefficient number is acceptable.

All three-phase equilibrium data are listed in Table 4. Agreement of the current calculated results with the assessed three-phase equilibrium data is better than that of Chevalier [88Che], especially at the equilibrium among liquid, fcc (Ag), and cph phases. While the parameters proposed by Karakaya and Thompson [87Kar] were converted to the form suitable for the Lukas program in order to calculate a phase diagram, they were unsuccessful in reproducing the assessed phase diagram, though the calculated thermodynamic properties can agree well with the experimental data as shown in Fig. 3(c). So the present authors assume that the three-phase equilibrium data of the [87Kar] calculation are the same as the assessed data according to the calculated phase diagram presented by Karakaya and Thompson [87Kar] (dashed line shown in Fig. 1).

As shown in Fig. 1, the deviation of the calculated phase diagram from the assessed boundaries is significant despite the assumption that the three-phase equilibrium data are the same as the assessed data. Figure 2 compares the phase diagrams calculated by Chevalier [88Che] and the present authors with the assessed diagram, respectively. Obviously the present diagram agrees better than the Chevalier [88Che] diagram with the assessed phase diagram.

Although the Chevalier [88Che] optimization can reproduce the phase diagram generally, the deviation of the three-phase equilibrium temperature of L + fcc ↔ cph and deviations of liquidus and solidus between 975 and 758 K from the experimental data are unsolved problems in the [88Che] optimization. As mentioned in [88Che], these problems are attributed to the following reasons. First, the selected lattice stabilities for cph (Ag) and cph (Sn) are not far from the stable structure fcc (Ag) and bct (Sn). Second, it is not possible to add more coefficients for the cph solid solution because there is not enough experimental information. But according to Okamoto and

Massalski [91Oka], a different selection of lattice stability parameters is not necessary to make the calculated phase diagram inconsistent with experimental data. On the other hand, the calculated phase diagram with the stability parameters chosen arbitrarily can also agree well with the experimental diagram. The necessary thermodynamic data for the cph (Ag) region can be predicted by the phase equilibrium laws because enough experimental data exist for its coexisting phases.

The present authors increased the number of terms in the *R-K* polynomial series for the cph disordered solution phase and re-optimized this system using all the experimental data available. As mentioned, the previous unsolved problems are then solved very well, and it may be concluded that the mismatch of the calculated phase diagram by Chevalier with the assessed data is due to the different treatment of the cph phase instead of the reasons stated previously.

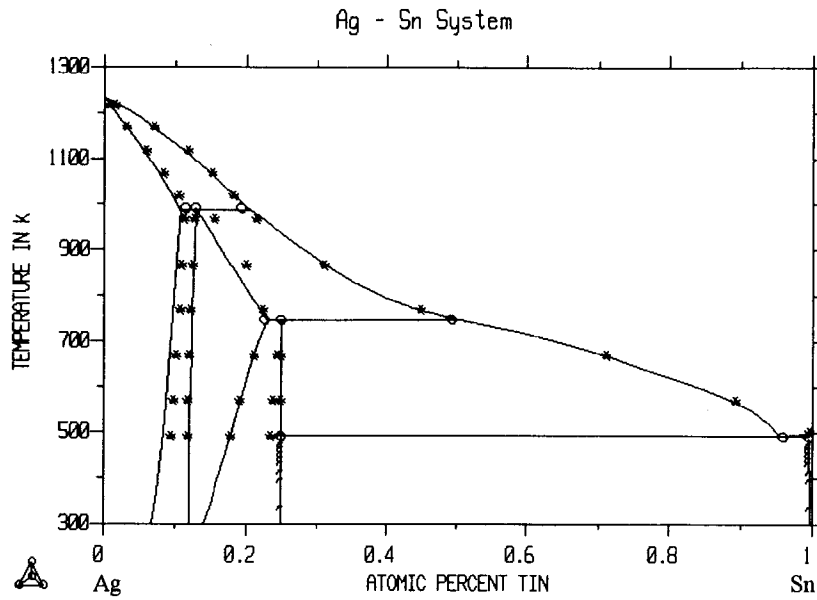
Figure 3 compares thermodynamic properties calculated by different authors with experimental data. Obviously, agreement between calculated partial Gibbs energies of Sn in the liquid phase at 900 K and calculated enthalpy of mixing with measured values of the present work remains fairly good, as shown in Fig. 3(a).

## 5. Conclusions

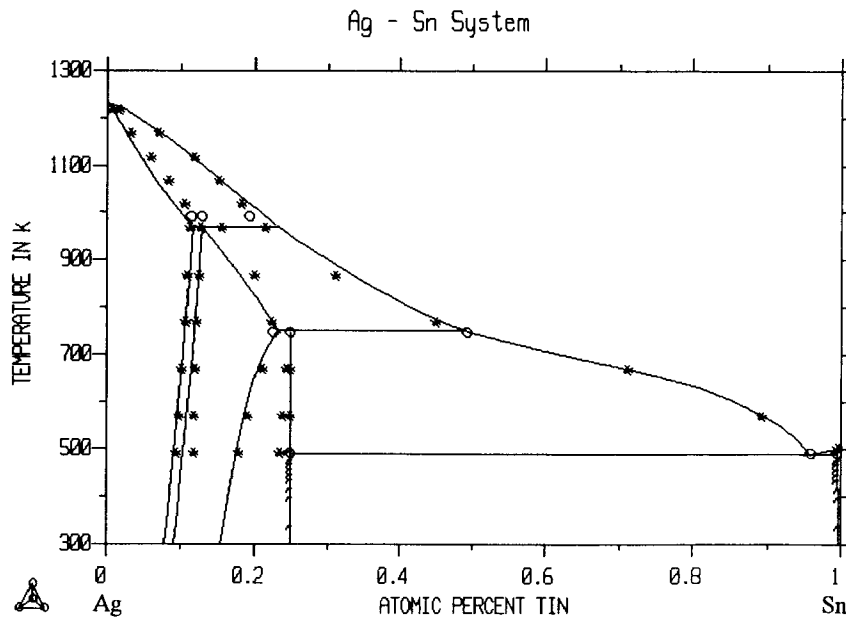
The Ag<sub>3</sub>Sn phase was simplified as a line compound in this optimization. The parameters of formation of the Ag<sub>3</sub>Sn phase and solution model parameters for other phases in the Ag-Sn system were optimized to reproduce the assessed phase diagram presented by Karakaya and Thompson [87Kar]. The results were compared with those of previous works by Karakaya and Thompson [87Kar] and Chevalier [88Che]. Agreement between the present optimized phase diagram and the assessed experimental diagram is the best, and this has been attributed mainly to the proper treatment of the cph disordered solution phase.

## Acknowledgment

The authors express great thanks to Dr. H.L. Lukas of Max-Planck Institut für Metallforschung, Stuttgart, Germany for

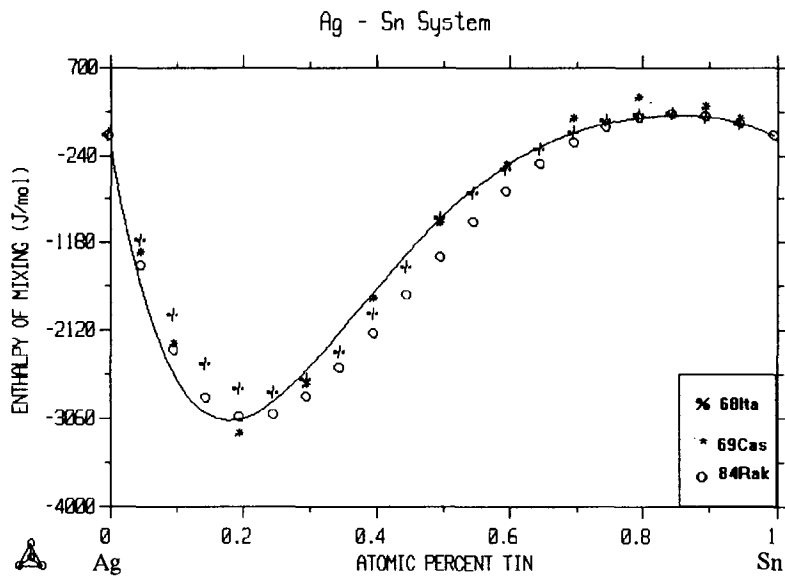
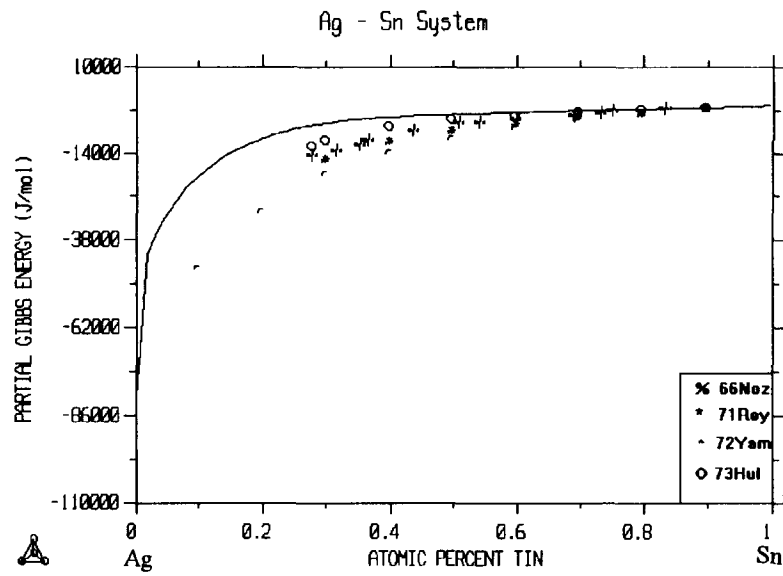


(a)



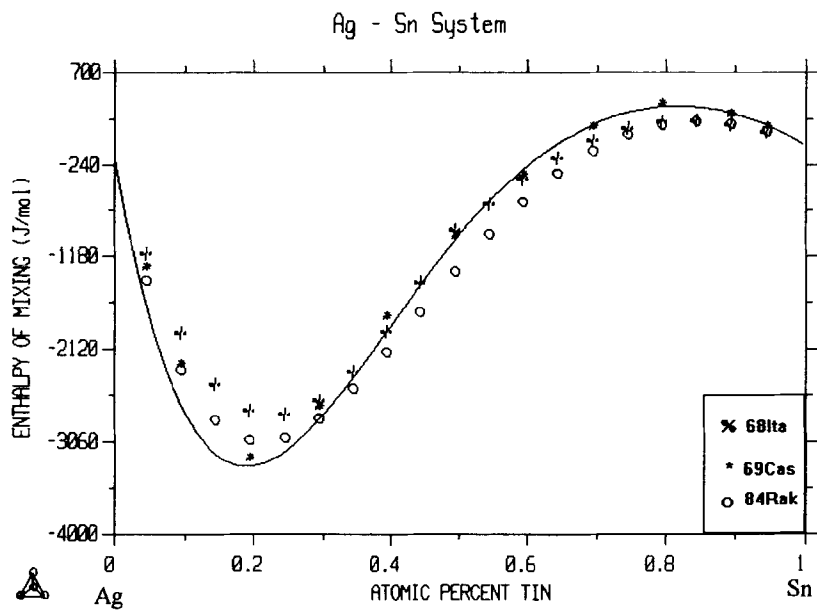
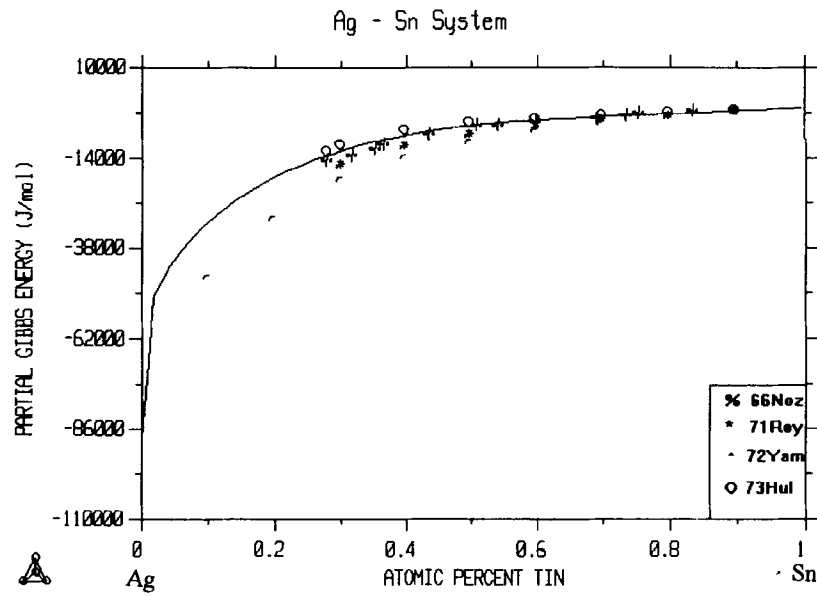
(b)

**Fig. 2** Comparison of calculated phase diagrams with assessed phase boundary: (a) this work and (b) Chevalier [88Che]. Asterisks (\*) are assessed phase boundary data [87Kar]. Open circles (o) are assessed three-phase equilibrium data [87Kar]. Carets (^) are experimental data from [81Vnu].



(a) Present work

Fig. 3a Comparison of calculated partial Gibbs energies with experimental data ( $T = 900$  K) and of calculated integral enthalpies of mixing with experimental data.



(b) Chevalier's work

Fig. 3b Comparison of calculated partial Gibbs energies with experimental data ( $T = 900$  K) and of calculated integral enthalpies of mixing with experimental data.



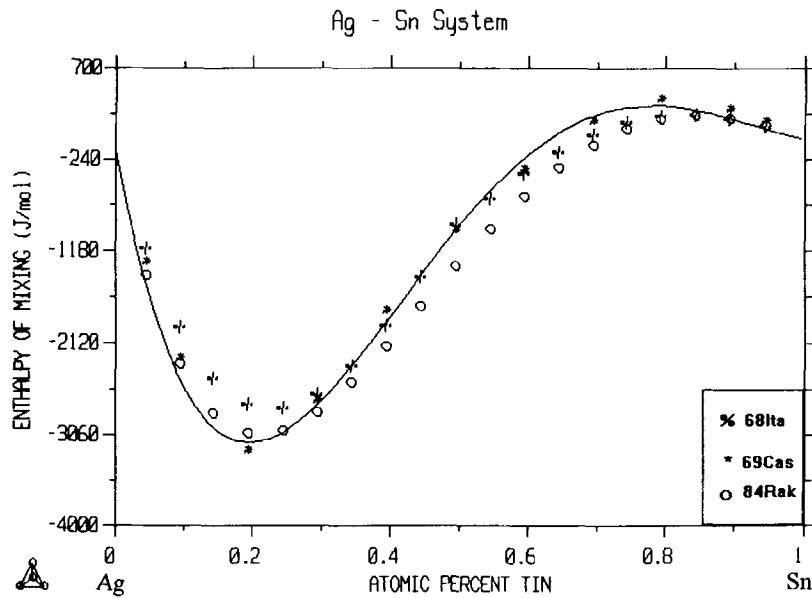
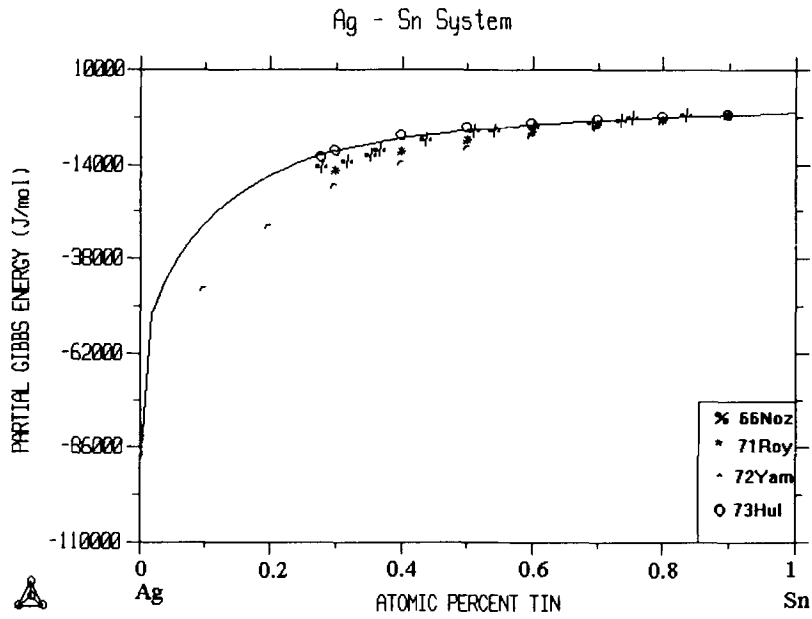


Fig. 3c Comparison of calculated partial Gibbs energies with experimental data ( $T = 900$  K) and of calculated integral enthalpies of mixing with experimental data.

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