

# Thermodynamic Assessment of the Sn–Ti System

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**Summary.** The knowledge of phase equilibria and thermodynamic properties in the ternary Cu–Sn–Ti system is of technical importance for active brazing filler metals. Thermodynamic descriptions of the binary systems Cu–Ti and Cu–Sn are well established. In this work a self-consistent thermodynamic description of the Sn–Ti binary system has been obtained by fitting critically reviewed thermochemical and phase diagram data. The newest and most consistent lattice stability has been used, and all the intermetallic phases and recent experimental information have been taken into account. The equilibrium measurement on the Sn-rich side and more experimental thermodynamic properties are required for a better thermodynamic description of this system. The evaluated thermodynamic description of the Sn–Ti binary system will serve as part of the thermodynamic database for Cu–Sn–Ti brazing alloys.

**Keywords.** Thermodynamics; Phase diagrams; Sn–Ti binary system; Tin compounds; Phase transformations.

## Introduction

The Cu–Sn–Ti system is of technical importance for active brazing filler metals [1], but no complete phase diagram can be found in literatures up to now. However, this would be necessary for technical applications. Thermodynamic descriptions of the binary systems Cu–Ti and Cu–Sn have already been established [2–4]. For the Sn–Ti binary system, *Murray* [5] made a comprehensive review and assessment in 1987. However, a stable phase,  $\text{Sn}_3\text{Ti}_2$ , was found and recently confirmed in the Sn–Ti binary system [6, 7]. Furthermore, the lattice stability of Sn was recently updated by the Scientific Group Thermodata Europe (SGTE). Therefore, in the present work a thermodynamic reassessment of the Sn–Ti system has been conducted based on available experimental data in literature.

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## Assessment of Experimental Data

### *Phase Equilibrium and Crystallographic Data*

Although the Ti-rich side is studied by different techniques [8–12], it can be concluded that  $\beta$ -Ti transforms congruently into  $\alpha$ -Ti at about 6.7 at.% Sn and 1115 K [10]. Concerning the peritectoid reaction  $\beta$ -Ti + SnTi<sub>3</sub>  $\rightleftharpoons$   $\alpha$ -Ti, the reported invariant reaction temperatures range from 1137 to 1213 K [8, 12, 13]. The value 1163 K, obtained from the thermal analysis and the metallographic studies [12], is preferred and used in the present work. In Refs. [10, 11] the incoherent precipitation of SnTi<sub>3</sub> in  $\alpha$ -Ti was probably suppressed, so that the metastable extension of the  $\alpha$ -Ti/ $\beta$ -Ti boundary may have been measured. Most of them agreed in placing the homogeneity range of SnTi<sub>3</sub> at about 23 to 25 at.% Sn [8, 10–12].

The reactions in the range 25–50 at.% Sn were first investigated by incipient melting studies [14]. The congruent melting temperatures of SnTi<sub>3</sub> and Sn<sub>5</sub>Ti<sub>6</sub> were determined to be  $1936 \pm 20$  K and  $1767 \pm 20$  K, respectively [14]. Similarly, the eutectic reaction  $L \rightleftharpoons \beta$ -Ti + SnTi<sub>3</sub> was located at  $1880 \pm 20$  K [14], which complies with the 1863 K from the metallographic studies [10]. The reaction  $\text{SnTi}_3 + L \rightleftharpoons \text{SnTi}_2$  was located at 1825 K in Ref. [14]. However, the reactions  $\text{SnTi}_2 + L \rightleftharpoons \text{Sn}_3\text{Ti}_5$  and  $L \rightleftharpoons \text{Sn}_3\text{Ti}_5 + \beta\text{-Sn}_5\text{Ti}_6$  were investigated using as-cast and slowly-cooled specimens [14], the temperatures of these reactions are thus only rough estimates.

*Eremenko* [15] determined the Sn-rich liquidus and the types of the invariant reactions at the Sn-rich side using the differential thermal analysis (DTA) method. It appeared that the crystallization of all Sn–Ti alloys is completely generated by an eutectic transformation 1–2 K below the melting temperature of pure Sn. Furthermore, the solubility of Ti in solid Sn was found to be extremely low. Though its nature has not yet been established, an invariant reaction taking place at  $\sim 1063$  K in alloys containing 61.7–81.7 at.% Sn was also found in Ref. [15]. Another equilibrium method was used to measure the solubility of Ti in liquid Sn in Ref. [16]. The intermetallic phase Sn<sub>5</sub>Ti<sub>6</sub> was brought in equilibrium with liquid Sn, annealed at different temperatures, and the solubility of Ti in liquid Sn was measured at each temperature. The determined solubility of Ti was significantly lower than the data in Ref. [15]. It is obvious that the measurement at a fixed composition is more suitable for flat phase boundaries, whereas the one at a fixed temperature applies better for steep phase boundaries. Therefore, the liquidus data of Ref. [16] may be more reliable than the data measured in Ref. [15]. This is also confirmed by a third set of data from Refs. [17, 18], during the process of optimization there were continual conflicts between the liquidus data [15] and thermodynamic data measured by authors of Refs. [17, 18]. Therefore, only *Darby's* liquidus data [16] have been used in the present optimization.

Recently, the phase equilibria of the Sn–Ti system were studied with isothermal annealing of powder and melted alloy samples in the range of 29–88 at.% Sn and 623–1373 K [6]. The experiments show that there is a new intermetallic phase Sn<sub>3</sub>Ti<sub>2</sub>, stable up to at least 973 K and probably not more than 1043 K. Its space group and lattice constants have been investigated by X-ray diffraction and *Mössbauer* spectroscopy [7]. The hexagonal  $\beta$ -Sn<sub>5</sub>Ti<sub>6</sub> phase was observed in the samples annealed at 943 K and higher temperatures [6, 19]. Hence, the temperature

**Table 1.** Crystal Structures of the stable phases of the Sn–Ti system

Phase	Strukturbericht designation	Composition Sn at. %	Prototype	Space group	References
$\beta$ -Ti	A2	0–7.5	W	<i>Im3m</i>	[5]
$\alpha$ -Ti	A3	0–17	Mg	<i>P6<sub>3</sub>/mmc</i>	[5]
SnTi <sub>3</sub>	D0 <sub>19</sub>	23–25	Ni <sub>3</sub> Sn	<i>P6<sub>3</sub>/mmc</i>	[31]
SnTi <sub>2</sub>	B8 <sub>2</sub>	32.7–35.9	InNi <sub>2</sub>	<i>P6<sub>3</sub>/mmc</i>	[14]
Sn <sub>3</sub> Ti <sub>5</sub>	D8 <sub>8</sub>	37.5	Mn <sub>5</sub> Si <sub>3</sub>	<i>P6<sub>3</sub>/mcm</i>	[32]
$\beta$ -Sn <sub>5</sub> Ti <sub>6</sub>	–	45.5	–	<i>P6<sub>3</sub>/mmc</i>	[19]
$\alpha$ -Sn <sub>5</sub> Ti <sub>6</sub>	–	45.5	Nb <sub>6</sub> Sn <sub>5</sub>	<i>Immm</i>	[19]
Sn <sub>3</sub> Ti <sub>2</sub>	–	60	–	<i>Cmca</i>	[6, 7]
(Sn)	A5	99.98–100	$\beta$ -Sn	<i>I4<sub>1</sub>/amd</i>	[5]

of the polymorphic transformation in Sn<sub>5</sub>Ti<sub>6</sub> should be lower than 943 K. Therefore, the exothermic reaction at 1063 K tentatively identified in Ref. [15] was proposed as the invariant reaction of  $L + \beta\text{-Sn}_5\text{Ti}_6 \rightleftharpoons \text{Sn}_3\text{Ti}_2$ .

There are four solution phases and six stable intermetallic compounds in the Sn–Ti system, liquid,  $\alpha$ -Ti,  $\beta$ -Ti,  $\beta$ -Sn, Sn<sub>3</sub>Ti<sub>2</sub>,  $\alpha$ -Sn<sub>5</sub>Ti<sub>6</sub>,  $\beta$ -Sn<sub>5</sub>Ti<sub>6</sub>, Sn<sub>3</sub>Ti<sub>5</sub>, SnTi<sub>2</sub>, and SnTi<sub>3</sub>. The crystallographic data of all these phases are summarized in Table 1.

### Thermodynamic Data

Enthalpies of mixing in the liquid state at 2000 K were measured over the composition range 50–100 at.% Sn [20]. The enthalpies of dissolution of Ti in Sn–Ti melts of composition 91–100 at.% Sn were measured at 1240–1687 K directly in a high-temperature isoperibolic calorimeter [17]. The partial enthalpies of Ti in liquid Sn measured at 1173 K in high dilution [21] provide strongly positive values, which is contrary to other data [17, 20]. Therefore, the data of Ref. [21] were not included in this assessment.

Ti activities in liquid Sn were measured by using nitrogen-nitride phase equilibria [22] and an EMF cell technique [18]. As for the heat formation of intermetallic compounds, there is a discrepancy between predicted and experimental data, which can be seen in Table 2. The first measurements were performed by calorimetric methods [23] and it was stated that the data need to be regarded as estimates. Later, the enthalpies of formation of intermetallic compounds were calculated using the semi-empirical model of *Miedema* [24], which did not reproduce the former experimental data [23]. Recently, the standard enthalpies of  $\alpha$ -Sn<sub>5</sub>Ti<sub>6</sub> formation

**Table 2.** Comparison between enthalpies of formation of intermetallic phases

Refs.	Technique	$\Delta H_f^\theta$ (kJ/mol of atoms)				
		Sn <sub>3</sub> Ti <sub>2</sub>	Sn <sub>5</sub> Ti <sub>6</sub> -L	Sn <sub>3</sub> Ti <sub>5</sub>	SnTi <sub>2</sub>	SnTi <sub>3</sub>
[23]	Experiment		–115	–94	–92	–50
[24]	Theoretical prediction		–52	–50	–47	–38
[25]	Experiment		–43.4 ± 1.4			
This work	Calculation	–36.8	–40.3	–37.8	–36.9	–35.2

were measured by direct synthesis calorimetry [25]. This data is closer to the predicted data of Ref. [24]. So, both of them were used. Enthalpies of formation were also determined again recently in Ref. [26]. However, they are very different from all other data [23–25], therefore, they were not included in the present optimization.

### Thermodynamic Modeling

In order to match the pre-existing database and their crystal structures, the detailed expressions for the phases' *Gibbs* energy are proposed below.

#### *Solution Phases: liquid, bcc, hcp, and bct*

The liquid, bcc, hcp, and bct phases are treated as substitutional solutions as (Sn,Ti):(Va)<sub>n</sub> with assumption that Sn and Ti can completely substitute each other in the model, Va means vacancies, and *n* is a constant dependent on the crystal structure. The *Gibbs* energy (in J/mol) is expressed by Eq. (1) where <sup>0</sup>G<sub>*i*</sub><sup>φ</sup> is the molar *Gibbs* energy of the pure element *i* with the structure φ, which is taken from SGTE Pure elements database V.4., which is based on the original unary database established by *Dinsdale* [27].

$$G_m^\phi = x_{Sn} {}^0G_{Sn}^\phi + x_{Ti} {}^0G_{Ti}^\phi + RT(x_{Sn} \ln x_{Sn} + x_{Ti} \ln x_{Ti}) + {}^{ex}G_m^\phi \quad (1)$$

It should be mentioned that the new stability of Sn in hcp was used in the present work as consistent with other solder alloy systems, such as the Sn–Ag–Cu system [28]. Here, *x<sub>i</sub>* is the molar fraction of element *i* in the φ phase. <sup>ex</sup>G<sub>*m*</sub><sup>φ</sup> is the excess *Gibbs* energy, expressed in *Redlich-Kister* polynomials (Eq. (2)), where <sup>j</sup>L<sub>Sn,Ti</sub><sup>φ</sup> is the *j*<sup>th</sup> binary interaction parameter expressed as *a* + *bT*, and *a* and *b* are model parameters to be evaluated from experimental data.

$${}^{ex}G_m^\phi = x_{Sn}x_{Ti} \sum_{j=0}^n {}^jL_{Sn,Ti}^\phi (x_{Sn} - x_{Ti})^j \quad (2)$$

They have different values for different phases, although the same letters are used throughout the text.

#### *Intermetallic Phases*

Due to their narrow solubility range and limited experimental data, the compounds Sn<sub>3</sub>Ti<sub>2</sub>, α-Sn<sub>5</sub>Ti<sub>6</sub>, β-Sn<sub>5</sub>Ti<sub>6</sub>, Sn<sub>3</sub>Ti<sub>5</sub>, and SnTi<sub>2</sub> are described as stoichiometric phases. Because no data of the heat capacities of the compounds are available, the *Gibbs* energies (in J/mol) of the different phases are approximated on the base of the *Neumann-Kopp* rule (Eq. (3)), where G<sub>Sn</sub><sup>SER</sup> and G<sub>Ti</sub><sup>SER</sup> are the *Gibbs* energies of pure Sn and Ti at 298.15 K and 101325 Pa, *i.e.* the so-called Standard Element Reference (SER).

$$G_m^{Sn_mTi_n} = a + bT + mG_{Sn}^{SER} + nG_{Ti}^{SER} \quad (3)$$

According to the model of other phases with the same crystal structure, for example Ni<sub>3</sub>Sn in Ref. [29], the compound energy formalism (CEF) with two

sublattices, (Sn%,Ti):(Sn,Ti%)<sub>3</sub>, is used to describe the compound D0<sub>19</sub>–SnTi<sub>3</sub>, in which % means the main element in the sublattice. Ti can substitute part of Sn in the first sublattice and in the second sublattice *vice versa*. The *Gibbs* energy (in J/mol) is expressed as shown by Eq. (4) where  $y_{Sn/Ti}^{1/2}$  is the molar fraction of Sn or Ti in the first or the second sublattice, respectively.

$$G_m^{SnTi_3} = y_{Sn}^1 y_{Sn}^2 G_{SnSn_3}^0 + y_{Sn}^1 y_{Ti}^2 G_{SnTi_3}^0 + y_{Ti}^1 y_{Sn}^2 G_{TiSn_3}^0 + y_{Ti}^1 y_{Ti}^2 G_{TiTi_3}^0 + RT[(y_{Sn}^1 \ln y_{Sn}^1 + y_{Ti}^1 \ln y_{Ti}^1) + 3(y_{Sn}^2 \ln y_{Sn}^2 + y_{Ti}^2 \ln y_{Ti}^2)] + G^{ex} \quad (4)$$

$G_{SnSn_3}^0$  and  $G_{TiTi_3}^0$  are assumed identical with the *Gibbs* energies of 4 mole of pure Sn or Ti occupying all the lattice sites of the compound SnTi<sub>3</sub>,  $G_{TiSn_3}^0$  is the *Gibbs* energy of the hypothetical stoichiometric phase TiSn<sub>3</sub>, and  $G^{ex}$  is the excess *Gibbs* energy term (Eq. (5)).

$$G^{ex} = y_{Sn}^1 y_{Ti}^1 (y_{Sn}^2 L_{Sn,Ti:Sn} + y_{Ti}^2 L_{Sn,Ti:Ti}) + y_{Sn}^2 y_{Ti}^2 (y_{Sn}^1 L_{Sn:Sn,Ti} + y_{Ti}^1 L_{Ti:Sn,Ti}) \quad (5)$$

The parameters  $L_{i,j:k}$  and  $L_{k:i,k}$  account for interaction energies between the atoms on one sublattice for a given occupancy of the other, and can be described by the *Redlich-Kister* polynomial with temperature dependent coefficients as shown by Eq. (6).

$$L_{i,j:k} = \sum_{n=0,1,\dots}^z (a_n + b_n T)(Y_i - Y_j)^n \quad (6)$$

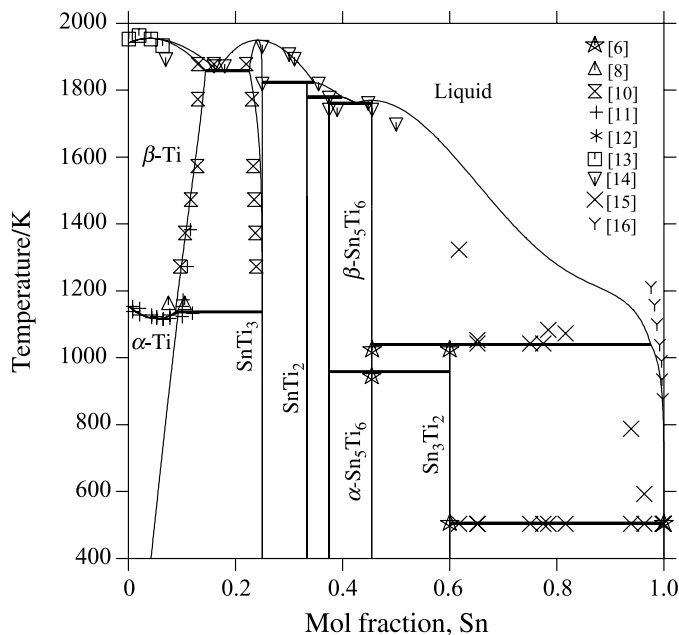
The coefficients  $a$  and  $b$  in Eqs. (2), (3), and (6) were derived in the present optimization.

## Optimization and Discussion

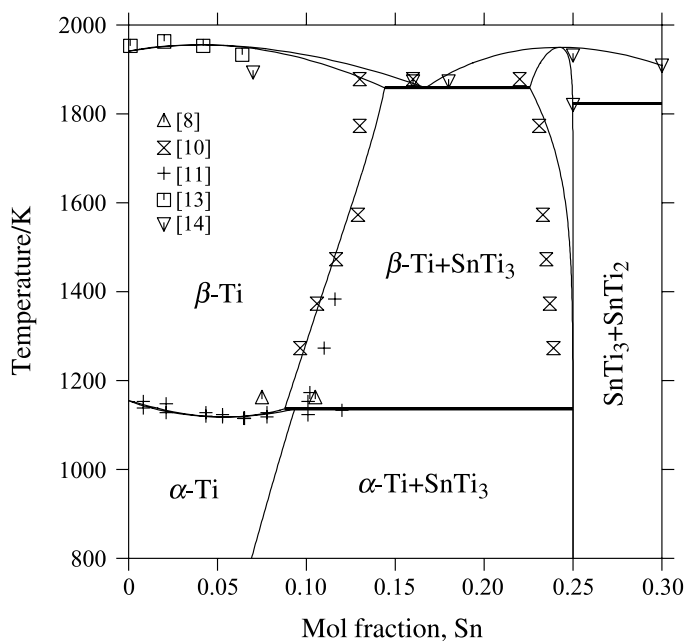
The model parameters were evaluated using the *Parrot* module of the Thermo-Calc software [30], which is able to deal with various kinds of experimental data in one operation. It works by minimizing the square sum of the differences between experimental data and computed values. During the assessment procedure, all the experimental data were first critically reviewed and selected as described above. Each data point was then assigned a certain weight. These weights were chosen and adjusted systematically according to data uncertainties from the original publications plus the modeler's judgment, until most of the experimental data were accounted for within the estimated uncertainty limits.

Two steps were taken to optimize the parameters. At first, all the compounds were treated as line compounds in constructing the framework of the phase diagram. The input data for optimization calculations were: (i) the heat of mixing data for the liquid [20], (ii) the  $\alpha$ -Ti/ $\beta$ -Ti phase boundaries [11], (iii) the Sn-rich liquidus [16], (iv) the enthalpies of formation of intermetallic compounds [24, 25], and (v) the three-phase invariant reactions and congruent transformation points [6, 8, 11, 14]. Then, in combination with the solubility data of SnTi<sub>3</sub> [10], the CEF model was used to describe the solubility range of the SnTi<sub>3</sub> phase.  $G_{SnSn_3}^0$  and  $G_{TiTi_3}^0$  are defined as  $G_{SnSn_3}^0 = 4G_{Sn}^{SER} + 10$  and  $G_{TiTi_3}^0 = 4G_{Ti}^{SER} + 5000$ .  $G_{SnTi_3}^0$  is the *Gibbs* energy of the ideal stoichiometric compound SnTi<sub>3</sub>, whose initial value is

taken from the first step of optimization where  $\text{D0}_{19}\text{-SnTi}_3$  was treated as a stoichiometric compound.  $G_{\text{TiSn}_3}^0$  takes  $G_{\text{SnSn}_3}^0 + G_{\text{TiTi}_3}^0 - G_{\text{SnTi}_3}^0$  as its initial value. After the final optimization with all the parameters and all the experimental data, a complete and self-consistent thermodynamic description of the Sn–Ti binary system was thus obtained, which is listed in Appendix 1.

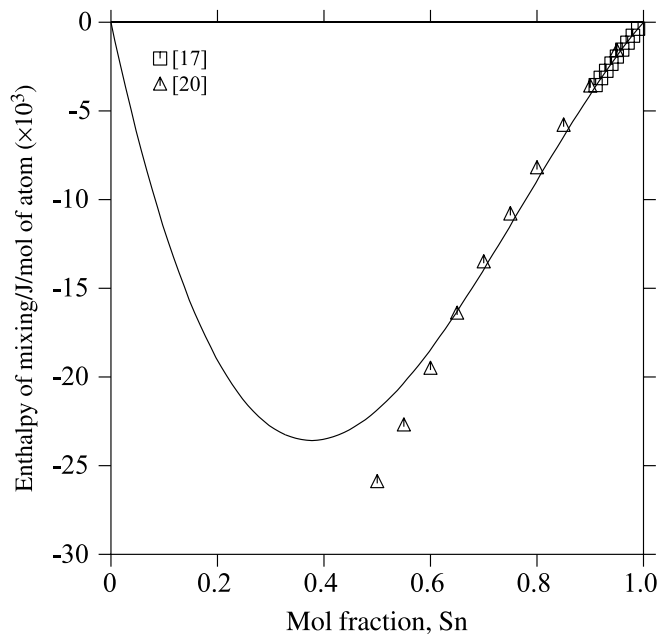


**Fig. 1.** Comparison between the calculated Sn–Ti phase diagram and the experimental observations

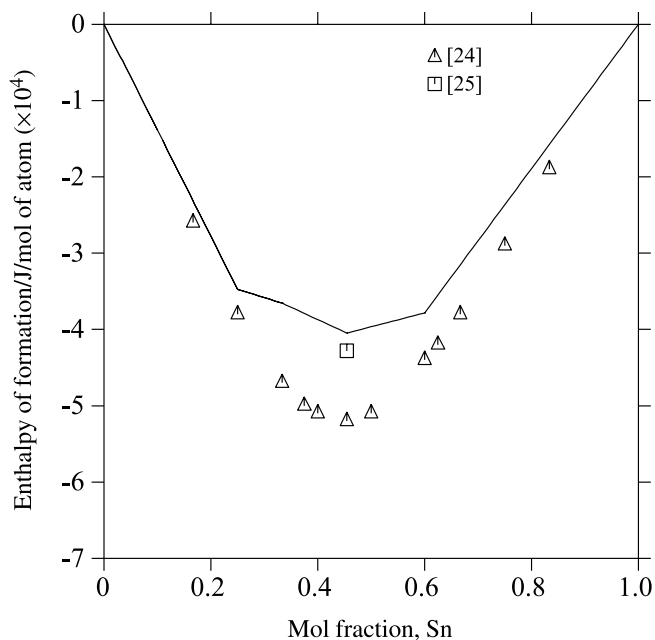


**Fig. 2.** Comparison between the Ti-rich calculated phase diagram and experimental data

Comparisons between the calculated phase diagram and the experimental observations are shown in Figs. 1 and 2. Most of the experimental data agree well with the calculations, and the congruent transformation  $\beta\text{-Ti} \leftrightarrow \alpha\text{-Ti}$  and peritectoid



**Fig. 3.** Comparison between the calculated heat of mixing of the liquid at 2000 K and the experimental data of Refs. [17] and [20]



**Fig. 4.** Comparison between the calculated standard enthalpy of formation with the theoretical prediction using the *Miedema* model [24] and experimental data of Ref. [25]

reaction  $\beta\text{-Ti} + \text{SnTi}_3 \Leftrightarrow \alpha\text{-Ti}$  were also successfully reproduced in this work. In Fig. 3, the calculated heat of mixing in the liquid at 2000 K from the present work is compared with the experimental data measured by *Esin* [20] in the range 50–100 at.% Sn and *Nikolaenko* [17] in the range 91–100 at.% Sn. The diagram for heat of mixing also confirms that the minimum integral enthalpies of formation of liquid binary Sn–Ti alloys are not in the experimental range of composition of 50–100 at.% Sn as mentioned by *Esin* [20]. As shown in Fig. 4, the enthalpy of formation calculated from the present work is not only in good agreement with the experimental data of *Meschel et al.* [25], but it also reproduces the tendency of the theoretical prediction from *de Boer et al.* [24].

Further experimental data are needed for a complete description of the Sn–Ti system. This work should focus on the determination of the liquidus line on the Sn-rich side. Also the homogeneity ranges of the intermetallic phases  $\text{SnTi}_3$  and  $\text{SnTi}_2$  should be determined with higher accuracy as a basis for a better thermodynamic description of the system. This is especially important to model the solubility of a third element, such as Cu, so that the binary assessment can serve as part of the thermodynamic database for Cu–Sn–Ti brazing alloys.

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### Appendix. Thermodynamic description of the Sn–Ti binary system (all values are in J/mol)

Liquid constituents: (Sn,Ti)

$${}^0L_{\text{Sn,Ti}}^{\text{liq}} = -88774.03 + 6.5228 T$$

$${}^1L_{\text{Sn,Ti}}^{\text{liq}} = 54178.12 - 2.4780 T$$

BCC\_A2  $\beta$ -Ti constituents: (Sn,Ti)<sub>1</sub>(Va)<sub>3</sub>

$${}^0L_{\text{Sn,Ti:Va}}^{\text{bcc}} = 90236.81 + 10.3708 T$$

$${}^1L_{\text{Sn,Ti:Va}}^{\text{bcc}} = +73071.57$$

HCP\_A3  $\alpha$ -Ti constituents: (Sn,Ti)<sub>1</sub>(Va)<sub>0.5</sub>

$${}^0L_{\text{Sn,Ti:Va}}^{\text{hcp}} = -101017.53 + 6.81 T$$

$${}^1L_{\text{Sn,Ti:Va}}^{\text{hcp}} = +50749.95 + 0.1021 T$$

BCT\_A5  $\beta$ -Sn constituents: (Sn,Ti)

$${}^0L_{\text{Sn,Ti}}^{\text{bct}} = 50000$$

$\text{Sn}_3\text{Ti}_2$  constituents: (Sn)<sub>3</sub>(Ti)<sub>2</sub>

$${}^0G_{\text{Sn,Ti}}^{\text{Sn}_3\text{Ti}_2} - 3 * G_{\text{Sn}}^{\text{SER}} - 2 * G_{\text{Ti}}^{\text{SER}} = -183828.39 + 37.2757 T$$



$\beta$ -Sn<sub>5</sub>Ti<sub>6</sub> constituents: (Sn)<sub>5</sub>(Ti)<sub>6</sub>

$${}^0G_{Sn,Ti}^{Sn_5Ti_6} - 5 * G_{Sn}^{SER} - 6 * G_{Ti}^{SER} = -383214.29 - 23.0885 T$$

$\alpha$ -Sn<sub>5</sub>Ti<sub>6</sub> constituents: (Sn)<sub>5</sub>(Ti)<sub>6</sub>

$${}^0G_{Sn,Ti}^{Sn_5Ti_6-L} - 5 * G_{Sn}^{SER} - 6 * G_{Ti}^{SER} = -442750.46 + 39.4484 T$$

D8<sub>8</sub>-Sn<sub>3</sub>Ti<sub>5</sub> constituents: (Sn)<sub>3</sub>(Ti)<sub>5</sub>

$${}^0G_{Sn,Ti}^{D8-Sn_3Ti_5} - 3 * G_{Sn}^{SER} - 5 * G_{Ti}^{SER} = -302460.91 + 0.7762 T$$

B8<sub>2</sub>-SnTi<sub>2</sub> constituents: (Sn)(Ti)<sub>2</sub>

$${}^0G_{Sn,Ti}^{B82-SnTi_2} - G_{Sn}^{SER} - 2 * G_{Ti}^{SER} = -110610.33$$

D0<sub>19</sub>-SnTi<sub>3</sub> constituents: (Sn,Ti)(Sn,Ti)<sub>3</sub>

$${}^0G_{Sn:Sn}^{D019-SnTi_3} = 4 * G_{Sn}^{SER} + 10$$

$${}^0G_{Ti:Ti}^{D019-SnTi_3} = 4 * G_{Ti}^{SER} + 5000$$

$${}^0G_{Sn:Ti}^{D019-SnTi_3} - G_{Sn}^{SER} - 3 * G_{Ti}^{SER} = -140665.42 + 2.3555 T$$

$${}^0G_{Ti:Sn}^{D019-SnTi_3} - G_{Ti}^{SER} - 3 * G_{Sn}^{SER} = +150416.86 - 2.0225 T$$

$${}^0L_{Sn,Ti:Sn}^{D019-SnTi_3} = 117921.13 - 70.7927 T$$

$$\begin{aligned} G_{Sn}^{SER} = & 250.00 \text{ K} < T < 505.08 \text{ K} : -5855.135 + 65.443315 T \\ & - 15.961 T \ln(T) - 0.0188702 T^2 + 3.121167 \times 10^{-6} T^3 - 61960 T^{-1} \\ & 505.08 \text{ K} < T < 800.00 \text{ K} : +2524.724 + 4.005269 T - 8.2590486 T \ln(T) \\ & - 0.016814429 T^2 + 2.623131 \times 10^6 T^3 - 1081244 T^{-1} - 1.2307 \times 10^{25} T^{-9} \\ & 800.00 \text{ K} < T < 3000.00 \text{ K} : -8256.959 + 138.99688 T \\ & - 28.4512 T \ln(T) - 1.2307 \times 10^{25} T^{-9} \end{aligned}$$

$$\begin{aligned} G_{Sn}^{Liquid} = & 100.00 \text{ K} < T < 505.08 \text{ K} : +7103.092 - 14.087767 T + G_{Sn}^{SER} + 1.47031 \times 10^{-18} T^7 \\ & 505.08 \text{ K} < T < 800.00 \text{ K} : +6971.586 - 13.814383 T + G_{Sn}^{SER} + 1.2307 \times 10^{25} T^{-9} \\ & 800.00 \text{ K} < T < 3000.00 \text{ K} : -1285.372 + 125.182498 T - 28.4512 T \ln(T) \end{aligned}$$

$$G_{Sn}^{bcc} = 4400.0 - 6.00 T + G_{Sn}^{SER}$$

$$G_{Sn}^{hcp} = 3900 - 7.646 T + G_{Sn}^{SER}$$

$$\begin{aligned} G_{Ti}^{SER} = & 298.15 \text{ K} < T < 900.00 \text{ K} : -8059.921 + 133.615208 T - 23.9933 T \ln(T) \\ & - 0.004777975 T^2 + 1.06716 \times 10^{-7} T^3 + 72636 T^{-1} \\ & 900.00 \text{ K} < T < 1155.00 \text{ K} : -7811.815 + 132.988068 T - 23.9887 T \ln(T) \\ & - 0.0042033 T^2 - 9.0876 \times 10^{-8} T^3 + 42680 T^{-1} \\ & 1155.00 \text{ K} < T < 1941.00 \text{ K} : +908.837 + 66.976538 T - 14.9466 T \ln(T) \\ & - 0.0081465 T^2 + 2.02715 \times 10^{-7} T^3 - 1477660 T^{-1} \\ & 1941.00 \text{ K} < T < 4000.00 \text{ K} : -124526.786 + 638.806871 T - 87.2182461 T \ln(T) \\ & + 0.008204849 T^2 - 3.04747 \times 10^{-7} T^3 + 36699805 T^{-1} \end{aligned}$$

$$\begin{aligned} G_{Ti}^{Liquid} = & 298.15 \text{ K} < T < 1300.00 \text{ K} : +12194.415 - 6.980938 T + G_{Ti}^{SER} \\ & 1300.00 \text{ K} < T < 1941.00 \text{ K} : +368610.36 - 2620.99904 T + 357.005867 T \ln(T) \\ & - 0.155262855 T^2 + 1.2254402 \times 10^{-5} T^3 - 65556856 T^{-1} + G_{Ti}^{SER} \\ & 1941.00 \text{ K} < T < 6000.00 \text{ K} : +104639.72 - 340.070171 T + 40.9282461 T \ln(T) \\ & - 0.02200832 T^2 + 1.228863 \times 10^{-6} T^3 + 1400501 T^{-1} \end{aligned}$$

$$\begin{aligned}
 G_{Ti}^{bcc} = & 298.15 \text{ K} < T < 1155.00 \text{ K} : -1272.064 + 134.71418 T - 25.5768 T \ln(T) \\
 & - 6.63845 \times 10^{-4} T^2 - 2.78803 \times 10^{-7} T^3 + 7208 T^{-1} \\
 & 1155.00 \text{ K} < T < 1941.00 \text{ K} : +6667.385 + 105.366379 T - 22.3771 T \ln(T) \\
 & + 0.00121707 T^2 - 8.4534 \times 10^{-7} T^3 - 2002750 T^{-1} \\
 & 1941.00 \text{ K} < T < 4000.00 \text{ K} : +26483.26 - 182.426471 T + 19.0900905 T \ln(T) \\
 & - 0.02200832 T^2 + 1.228863 \times 10^{-6} T^3 + 1400501 T^{-1}
 \end{aligned}$$

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