New thermodynamic investigation of some solid phases of Sn-Ti phase diagram

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Abstract. Thermodynamic description of the part of Sn-Ti phase diagram is presented using the CALPHAD approach. The thermodynamic parameters of the some phases of system modifying according new experimental phase equilibrium and thermodynamic data. Some phases described as stoichiometric, but another with sublattice models. Ti₃Sn, Ti₅Sn₃, Ti₆Sn₅ are modelled with three sublattice modes. Better agreement is obtained by the present optimization. Calculated results are compared with the original experimental data to demonstrate the successfulness of this assessment. The enthalpies of formation of solid phases are calculated and compared by two methods.

1. Introduction

Electronic industry production relies to a great extent on the soldering process. Nevertheless, it is well known that the classical solders (lead-tin based alloys) represent a serious health and environmental risk. For this reason, the use of lead-containing solders was recently restricted [1]. Sn based alloys were appropriate to change the lead-containing ones. Binary Sn-Ti phase diagram was investigated experimentally several times [2, 3]. Pietrokowsky et al. [4] investigated the binary system by metallographic, X-ray and thermal analysis. They found four intermetallic phases: Ti₃Sn, Ti₆Sn₅, Ti₂Sn, Ti₅Sn₃. Ti₅Sn and Ti₆Sn₃ are congruently melted. Ti₃Sn and Ti₆Sn₅ are formed by peritectic reaction and found a eutectoid reaction, (β-Ti) →(α-Ti) + Ti₃Sn at 864 °C. Using X-ray diffraction, they found that alloys containing more than 45 at.% Sn are mixtures of Ti₆Sn₅ and (β-Sn). Eremenko et al. [5] determined the Sn-rich liquidus and (β-Sn) eutectic temperature by differential thermal analysis. They also identified an exothermic reaction at 790 °C with a polymorphic transformation in Ti₆Sn₅. According McQuillan [6] (β-Ti) transforms congruently to (α-Ti) at 6.7 at.% Sn and 842 °C. McQuillan et al. [7] and Glazova et al. [8] confirmed congruent transformation of (α-Ti) to (β-Ti), but they not found evidence for a two-phase (α-Ti) + Ti₃Sn field. The start temperature of the martensitic (β-Ti) ⇔ (α-Ti) transformation was measured by Sato et al. [9]. In the range 2 to 9 at.% Sn, it is 740 °C to 760 °C, apparently independent of composition.

Enthalpies of formation of the binary compound phases Ti₃Sn, Ti₂Sn, Ti₅Sn₃ and Ti₆Sn₅ in the system Sn-Ti by differential scanning calorimetry were measured by Pondarevkaya et al. [10]. Meschel et al. [11] determined enthalpy of formation of phase Ti₆Sn₅ by high-temperature direct synthesis calorimetry. First optimization of the system the Sn-Ti is given by Hayes [12]. Liu et al. [13] assessed the system using a two sublattice model (Sn,Ti)(Sn,Ti)₃ for phase Ti₅Sn. They treated phase
Ti₃Sn as phase with homogeneity range and all the other compounds as stoichiometric phases. Some thermodynamic investigations of system by calculations were done using TC AB software [14].

The main objective in these studies is to investigated and described some solid phases in the Sn-Ti phase diagram.

In Table 1 are presented crystal structures of binary system and ternary system Sn-Ti.

### Table 1. Crystal structures of pure components, binary and ternary phases in system Sn-Ti

| Phase name | Pearson symbol | Prototype | Space group | Struktur-berich designation | Wyckoff positions | Referens |
|------------|----------------|-----------|-------------|----------------------------|-------------------|----------|
| (βSn)      | hP4            | Sn        | I4/mmd      | A5                         | b                 | [2]      |
| (αTi)      | hP2            | Mg        | P6/mmc      | A3                         | c                 | [2]      |
| (βTi)      | cL2           | W         | Im3n        | A2                         | a                 | [2]      |
| Ti₃Sn      | cP4           | Ni₁Sn₂    | Pn3m        | D0₁₉                       | ac                | [2]      |
| Ti₃Sn₂    | hP6           | InNi₂₅    | P6/mmc      | B8₂                        | acd               | [2]      |
| Ti₃Sn₃    | αS40          | ...       | Cmca        | ...                        | e₂f³              | [3]      |
| Ti₃Sn₄    | hP16          | Mn₅Sn₃    | P6/mmc      | D8₄                        | d₂g²              | [2]      |
| Ti₃Sn₅    | hP22          | Ti₅Sn₅    | P6/mmc      | ...                        | aecgh²            | [2]      |

### 2. Method and modeling

The Gibbs energy ($^{0}G_{A,B}^{\phi}$) of pure component i in phase φ was expressed relative to the enthalpy of the component in its stable phase at 298.15 K. $L^{i,j}_{k}$ was a binary parameter describing the interaction between components i and j in phase φ. For these parameters, $^{0}G_{A}$, was a function of temperature and $L^{i,j}_{k}$ can be functions of temperature and composition. Gibbs energy of formation of the binary compounds was expressed as:

$$^{0}G_{A,B}^{\phi} = a^{0}G_{A}^{\phi} + b^{0}G_{B}^{\phi} + A + B^{*}T$$

The solid binary phases belonging to the Sn-Ti binary system were described with the respective sublattice models. Three phases were remodelled Ti₃Sn, Ti₃Sn₂, Ti₃Sn₃ with three sublattice modes.

### 3. Results and discussion

The thermodynamic description of the binary systems and Sn-Ti system is presented in Table 2.

### Table 2. The optimized parameters and models describing the phase relations of the Sn-Ti system

| Phase   | Model                   | Thermodynamic parameter                   |
|---------|-------------------------|-------------------------------------------|
| Liquid  | (Sn,Ti)                 | $^{0}L^{Sn,Ti}_{Sn,Ti}=-91598.9-0.9416T$  |
|         |                         | $^{1}L^{Sn,Ti}_{Sn,Ti}=45862.64-12.1045T$ |
| Bct     | (Sn,Ti)                 | $^{0}L^{Sn,Ti}_{Sn,Ti}=50000$             |
| Ti₃Sn   | (Sn,Vi)(Ti,Vi)          | $^{0}G_{Ti₂Sn₃}_{Sn,Ti}+2^{0}G_{Hcp,Ti}^{Tr}+^{0}G_{Bct,Ti}^{Sl}=-122644.77+6.0034T$ |
|         |                         | $^{0}G_{Ti₂Sn₃}_{Sn,Va}+2^{0}G_{Hcp,Va}^{Tr}+^{0}G_{Bct,Va}^{Sl}=10000$ |
|         |                         | $^{0}G_{Ti₂Sn₃}_{Sn,Va}+^{0}G_{Bct}^{Tr}+^{0}G_{Bct}^{Sl}=-5000$ |
|         |                         | $^{0}G_{Ti₂Sn₃}_{Sn,Va}+^{0}G_{Bct}^{Tr}+^{0}G_{Bct}^{Sl}=300000$ |
|         |                         | $^{0}L^{Sn,Ti}_{Sn,Ti}=-33085.17$        |
|         |                         | $^{0}L^{Sn,Ti}_{Sn,Ti}=49803.91+24.471T$ |
| Ti₃Sn₂  | (Sn)(Ti)                | $^{0}G_{Ti₂Sn₃}_{Sn,Ti}+^{0}G_{Hcp,Ti}^{Tr}+^{0}G_{Bct,Ti}^{Sl}=-173931.75+7.82593T$ |
| Ti₃Sn   | (Ti)(Ti,Ti)(Ti,Sn)      | $^{0}G_{Ti₂Sn₃}_{Ti,Ti}+^{0}G_{Hcp,Ti}^{Tr}+^{0}G_{Bct,Ti}^{Sl}=-122644.77+6.0034T$ |
Fig. 1 presented Sn-Ti phase diagram calculated with parameters obtained in this work. The phases Ti₅Sn₃, Ti₅Sn₅ and Ti₅Sn₇ are treated as stoichiometric compounds. The sublattice models of (Sn,Va)(Ti,Va)₂ and (Sn,Va)(Ti)₃ are used to describe the homogeneity ranges of Ti₅Sn and Ti₅Sn, respectively.

The Sn-Ti system contains five intermetallic compounds. Ti₅Sn₃, Ti₆Sn₅ and Ti₇Sn₇ are used to describe the homogeneity ranges of Ti₅Sn and Ti₅Sn, respectively.

Fig. 1 presented Sn-Ti phase diagram calculated with parameters obtained in this work. The phases Ti₅Sn₃, Ti₅Sn₅, Ti₆Sn₅ are modeled with three sublattice modes (Table 2).

### Table 2

| Compound | Ti-Sn | Ti-Va | 0G(Ti₅Sn₃) | Hcp(Ti)| 0G(Ti₅Sn₅) | Bct(Ti) |
|----------|-------|-------|------------|-------|------------|--------|
| Ti₅Sn₃   |       |       | 0G(Ti₅Sn₃) | Hcp(Ti)| 0G(Ti₅Sn₅) | Bct(Ti) |
| Ti₅Sn₅   |       |       | 0G(Ti₅Sn₅) | Hcp(Ti)| 0G(Ti₅Sn₅) | Bct(Ti) |
| Ti₆Sn₅   |       |       | 0G(Ti₆Sn₅) | Hcp(Ti)| 0G(Ti₆Sn₅) | Bct(Ti) |
| Ti₇Sn₇   |       |       | 0G(Ti₇Sn₇) | Hcp(Ti)| 0G(Ti₇Sn₇) | Bct(Ti) |

**Figure 1.** Calculated Sn-Ti phase diagram with parameters obtained in this work.
In Fig. 2 seen diagram compared with another results calculated and experimental found in literature. In the figure good correlation was observed in equilibrium point in diagram. Comparative revue in Fig. 3 was done between enthalpies of formation of all solid phases in the binary system with AB-initio calculations and Thermocalc calculations. Good agreement was observed in obtained results.

Table 3 shows the calculated invariant points for the binary Sn-Ti system in this work. The calculated invariants were compared by another taken from literature. All obtained temperatures appeared in close results.

**Table 3.** Calculated invariant points from this work of the binary Ni-Sn, Sn-Ti system. \( \phi_i \) – equilibrium phase

| \( \phi_1 - \phi_2 - \phi_3 \) | Temp \(^\circ\)C | \( C_{B_i}^{\phi_1} \) (at%) | \( C_{B_i}^{\phi_2} \) (at%) | \( C_{B_i}^{\phi_3} \) (at%) | Ref. |
|-----------------------------|-------------|----------------|----------------|----------------|------|
| L=(\( \beta Ti \)+\( Ti_3Sn \)) | 1571        | 16.2           | 13.5           | 24.2           | This work |
|                             | 1574        | 15.9           | 13.6           | 22.8           | [15]  |
|                             | 1606        | 23.0           | 19.5           | 25.0           | [4]   |
| L= \( Ti_3Sn \)             | 1668        | 25.0           | 25.0           | -              | This work |
|                             | 1670        | 25.3           | 25.3           | -              | [15]  |
|                             | 1670        | 25.0           | 25.0           | -              | [4]   |
| L+\( Ti_3Sn=Ti_5Sn \)       | 1552        | 34.7           | 22.8           | 32.6           | This work |
|                             | 1548        | 35.0           | 23.2           | 32.7           | [15]  |
|                             | 1550        | 33.0           | 25.0           | -              | [4]   |
| L+\( Ti_3Sn=Ti_5Sn_3 \)    | 1517        | 42.3           | 34.7           | 37.3           | This work |
|                             | 1511        | 40.1           | 35.7           | 37.5           | [15]  |
|                             | 1490        | 37.5           | -              | -              | [4]   |
Figure 3. Comparative review of enthalpies of formation in solid phases of the binary Sn-Ti system calculated with AB - initio method and with Calphad method.

4. Conclusions
In this work three binary phases Ti$_3$Sn, Ti$_5$Sn$_3$, Ti$_6$Sn$_5$ are remodelled. It was found transition reaction between \( \alpha \) and \( \beta \)-Sn. New topological and thermochemical data are available for the Sn-Ti systems. The good agreement in binary system is obtained between calculated and experimental phase equilibria data.

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