

An Investigation of Phase Equilibria of the Bi-Sb-Sn System

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The liquidus surface and invariant reactions involving the liquid phase are calculated to determine the solidification behavior of Bi-Sb-Sn alloys. Only two U-type invariant reactions $\text{Liq.} + \text{Sb}_2\text{Sn}_3 = \text{SbSn} + (\text{Sn})$ at 517.9K and $\text{Liq.} + \text{SbSn} = (\text{Sn}) + (\text{Sb})$ at 411.8K are found. Thermodynamic calculation does not predict the presence of a ternary eutectic reaction in this system. The calculated solidification behavior of ternary alloys are found to be consistent with the experimental data as determined by differential scanning calorimetry. An isothermal section of the Bi-Sb-Sn system at 398K is also established. The equilibrium composition of the solid phases are determined by analytical electron microscopy. In contrast to an earlier report, the Bi-content in the SbSn phase is found to be about 5 wt.%.

Key words: Bi-Sb-Sn isothermal section, Bi-Sb-Sn liquidus surface, solder alloys

INTRODUCTION

In electronic devices, the solder joints provide electrical contact and mechanical strength to establish and maintain the integrity of the soldered assembly. Although many solder alloys are available, lead-tin solders are most commonly used in electronic packaging due to their unique combination of chemical, physical, and mechanical properties. However, lead-base solders pose environmental and health hazards, and such solders have been banned in many non-electronic applications due to various anti-lead legislations. For this reason, substantial effort is being made to design Sn-base solders that may be capable of replacing lead-base solders. The criteria for selecting Sn-base solders from electronic and automotive industry perspective and progress of designing such solders have recently been reported by several researchers.¹⁻⁵

This study originates from our effort to design and test a hierarchy of lead-free solders for applications in (Received November 30, 1993; revised March 7, 1994)

the electronic industries. As a part of this effort, we are currently engaged in developing a thermodynamic database for designing lead-free solders. Another important application of such a thermodynamic database is that it will help us understand the interfacial reaction between the solder and the substrate. The Bi-Sb-Sn ternary is an important system in the development of lead-free solders, both Bi and Sb are added to impart desirable properties. In this study, we have performed thermodynamic calculation of the phase equilibria in the Bi-Sb-Sn system. This includes calculation of liquidus and solidus surfaces, isothermal sections and isopleths. Our calculations were supplemented and verified by some experimental results.

THERMODYNAMIC CALCULATIONS

The basis for the calculation of phase equilibria of the ternary Bi-Sb-Sn is the thermodynamic description of individual phases in the binary systems Bi-Sb, Bi-Sn, and Sb-Sn. The binary system Bi-Sb is isomorphous in the solid state, and a thermodynamic de-

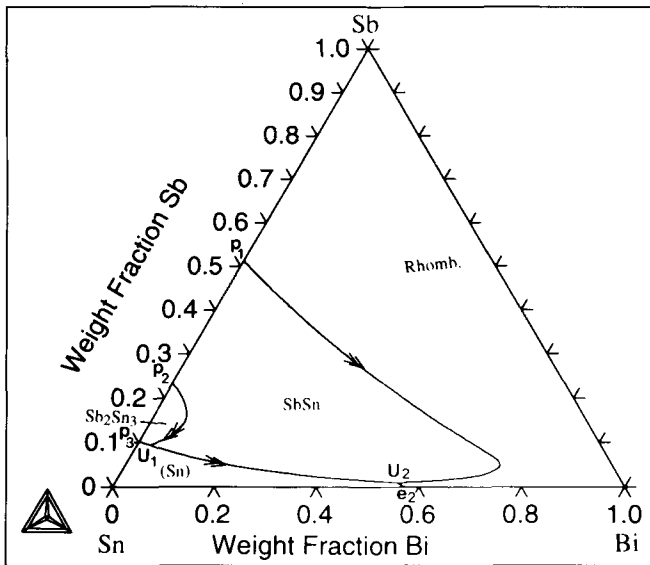


Fig. 1. Calculated liquidus surface of the Bi-Sb-Sn system.

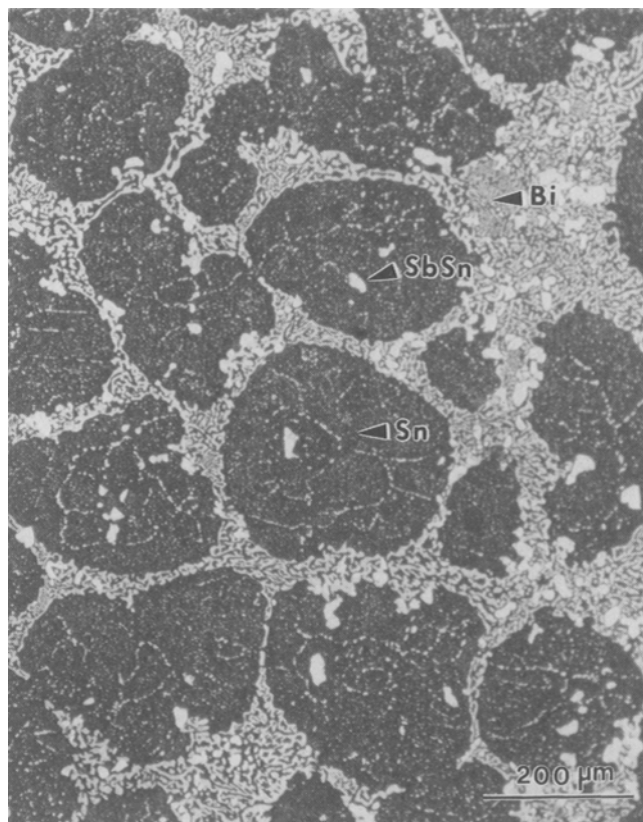


Fig. 2. Optical micrograph of a Sn-45Bi-3Sb alloy after annealing at 398K for 25 days.

scription of this phase has recently been provided by Feutelais et al.⁶ The Sb-Sn system was modeled by Jönsson and Ågren⁷ and a part of it is remodeled in this work. There are four solid phases in Sb-Sn system: Sb-rich terminal solution, Sn-rich terminal solution, SbSn, and Sb₂Sn₃. The thermodynamic parameters of the Bi-Sn system have been evaluated in this work. The thermodynamic models used in the present work are described below.

Liquid and Solid Solution Phases

The liquid and solid solution phases are treated with a substitutional solution model in which the molar Gibbs energy (G_m^ϕ) of a phase ϕ is expressed as

$$G_m^\phi = \sum_{i=1}^n X_i {}^\circ G_m^\phi + RT \left(\sum_{i=1}^n X_i \ln X_i \right) + {}^{xs} G_m^\phi \quad (1)$$

where ${}^\circ G_i^\phi$ is the Gibbs energy of pure element i in the phase ϕ . The excess Gibbs energy, ${}^{xs} G_m^\phi$, is described by using a Redlich-Kister polynomial

$${}^{xs} G_m^\phi = \sum_{i \neq j}^n X_i X_j \left[L_{0,ij}^\phi + L_{1,ij}^\phi (X_i - X_j) + L_{2,ij}^\phi (X_i - X_j)^2 + \dots \right] \quad (2)$$

where $L_{0,ij}^\phi$, $L_{1,ij}^\phi$, and $L_{2,ij}^\phi$ are the regular, subregular and sub-subregular interaction parameters and may vary with temperature.

Intermediate Phase SbSn

The SbSn phase has rhombohedral structure, but can be considered as a slightly distorted NaCl structure.⁸ At the ideal stoichiometry, the structure consists of one sublattice being occupied by Sb atoms and the other sublattice by Sn atoms. However, at the nonstoichiometric compositions, the ordering cannot be perfect and intermixing of the atoms in the sublattices is essential. The homogeneity range of this phase was described by an ordering model.⁷ However, it was found that by adopting such an ordering model, it is difficult to derive all the parameters in the ternary regime from limited experimental data.

Therefore, in this work, a defect model is used to describe this phase. In this model, one sublattice is occupied by Sb and Sn and the other sublattice is occupied by Sb and vacancies (Va). A previous study⁹ as well as our results indicate that some amount of Bi also dissolves in SbSn. The homogeneity range of SbSn in the ternary regime is represented by the formula (Sb, Sn)_{0.5}(Bi, Sb, Va)_{0.5}. The molar Gibbs energy of this phase is expressed as

$$\begin{aligned} G_m^{\text{SbSn}} = & Y_{\text{Sb}}^I Y_{\text{Bi}}^{II} {}^\circ G_{\text{Sb}_{0.5}\text{Bi}_{0.5}} + Y_{\text{Sn}}^I Y_{\text{Bi}}^{II} {}^\circ G_{\text{Sn}_{0.5}\text{Bi}_{0.5}} \\ & + Y_{\text{Sn}}^I Y_{\text{Sb}}^{II} {}^\circ G_{\text{Sb}_{0.5}\text{Sn}_{0.5}} + Y_{\text{Sb}}^I Y_{\text{Va}}^{II} {}^\circ G_{\text{Sb}_{0.5}\text{Va}_{0.5}} \\ & + Y_{\text{Sn}}^I Y_{\text{Va}}^{II} {}^\circ G_{\text{Sn}_{0.5}\text{Va}_{0.5}} + Y_{\text{Sb}}^I Y_{\text{Sb}}^{II} {}^\circ G_{\text{Sb}_{0.5}\text{Sb}_{0.5}} \\ & + 0.5RT(Y_{\text{Sb}}^I \ln Y_{\text{Sb}}^I + Y_{\text{Sn}}^I \ln Y_{\text{Sn}}^I \\ & + Y_{\text{Bi}}^{II} \ln Y_{\text{Bi}}^{II} + Y_{\text{Sb}}^{II} \ln Y_{\text{Sb}}^{II} + Y_{\text{Va}}^{II} \ln Y_{\text{Va}}^{II}) \end{aligned} \quad (3)$$

where Y_i are the site fractions of each kind of species on the two sublattices. The parameters ${}^\circ G_{\text{Sb}_{0.5}\text{Bi}_{0.5}}$, ${}^\circ G_{\text{Sn}_{0.5}\text{Bi}_{0.5}}$, and ${}^\circ G_{\text{Sb}_{0.5}\text{Sn}_{0.5}}$ represent the Gibbs energy of formation of the stoichiometric compounds Sb_{0.5}Bi_{0.5}, Sn_{0.5}Bi_{0.5}, and Sb_{0.5}Sn_{0.5}, respectively, from the pure elements in their reference states. ${}^\circ G_{\text{Sb}_{0.5}\text{Va}_{0.5}}$ and ${}^\circ G_{\text{Sn}_{0.5}\text{Va}_{0.5}}$ are the Gibbs energies of formation of two hypothetical compounds formed by two sublattices: one is fully occupied by either Sb or Sn

atoms and the second is fully occupied by vacancies. The parameter ${}^{\circ}G_{\text{Sb}_2\text{Sn}_3}^{\text{Sb}_2\text{Sn}_3}$ represents the Gibbs energy of transformation of rhombohedral-Sb to the structure of SbSn. The site fractions are related to the atomic fractions

$$\begin{aligned} X_{\text{Bi}} &= \frac{Y_{\text{Bi}}^{\text{II}}}{(Y_{\text{Sb}}^{\text{I}} + Y_{\text{Sn}}^{\text{I}} + Y_{\text{Bi}}^{\text{II}} + Y_{\text{Sb}}^{\text{II}})} \\ X_{\text{Sb}} &= \frac{(Y_{\text{Sb}}^{\text{I}} + Y_{\text{Sb}}^{\text{II}})}{(Y_{\text{Sb}}^{\text{I}} + Y_{\text{Sn}}^{\text{I}} + Y_{\text{Bi}}^{\text{II}} + Y_{\text{Sb}}^{\text{II}})} \\ X_{\text{Sn}} &= \frac{Y_{\text{Sn}}^{\text{I}}}{(Y_{\text{Sb}}^{\text{I}} + Y_{\text{Sn}}^{\text{I}} + Y_{\text{Bi}}^{\text{II}} + Y_{\text{Sb}}^{\text{II}})} \end{aligned} \quad (4)$$

Also, the following relations hold

$$\begin{aligned} Y_{\text{Sb}}^{\text{I}} + Y_{\text{Sn}}^{\text{I}} &= 1 \\ Y_{\text{Bi}}^{\text{II}} + Y_{\text{Sb}}^{\text{II}} + Y_{\text{Va}}^{\text{II}} &= 1 \end{aligned} \quad (5)$$

Intermediate Phase Sb_2Sn_3

This phase is treated as stoichiometric, as there is no information available on the composition range of stability. Then the molar Gibbs energy, relative to the

reference states of the pure elements, can be expressed as

$$G_{\text{m}}^{\text{Sb}_2\text{Sn}_3} = H_{\text{f}}^{\text{Sb}_2\text{Sn}_3} - TS_{\text{f}}^{\text{Sb}_2\text{Sn}_3} \quad (6)$$

where $H_{\text{f}}^{\text{Sb}_2\text{Sn}_3}$ and $S_{\text{f}}^{\text{Sb}_2\text{Sn}_3}$ are the enthalpy and entropy of formation of Sb_2Sn_3 . Since the thermodynamic description for the SbSn phase used here is slightly different from that used by Jönsson and Ågren,⁷ the parameters for SbSn, Sb_2Sn_3 , and the rhombohedral phases are assessed in this work while those for the liquid and (Sn) phases are taken from Jönsson and Ågren.⁷ All thermodynamic calculations are performed using THERMO-CALC¹⁰ software.

EXPERIMENTAL

Two ternary alloys Sn-10Bi-5Sb and Sn-45Bi-3Sb were made from pure elements (99.999 wt.%) and samples were held at 1073K for 5 h in evacuated and sealed quartz tubes and furnace cooled to room temperature. Then they were annealed at 398K for 29 to 33 days. Melting and solidification behavior of the alloys were studied by differential scanning calorimetry (DSC). Phase identification and microstructural characterization were done by optical metallography,

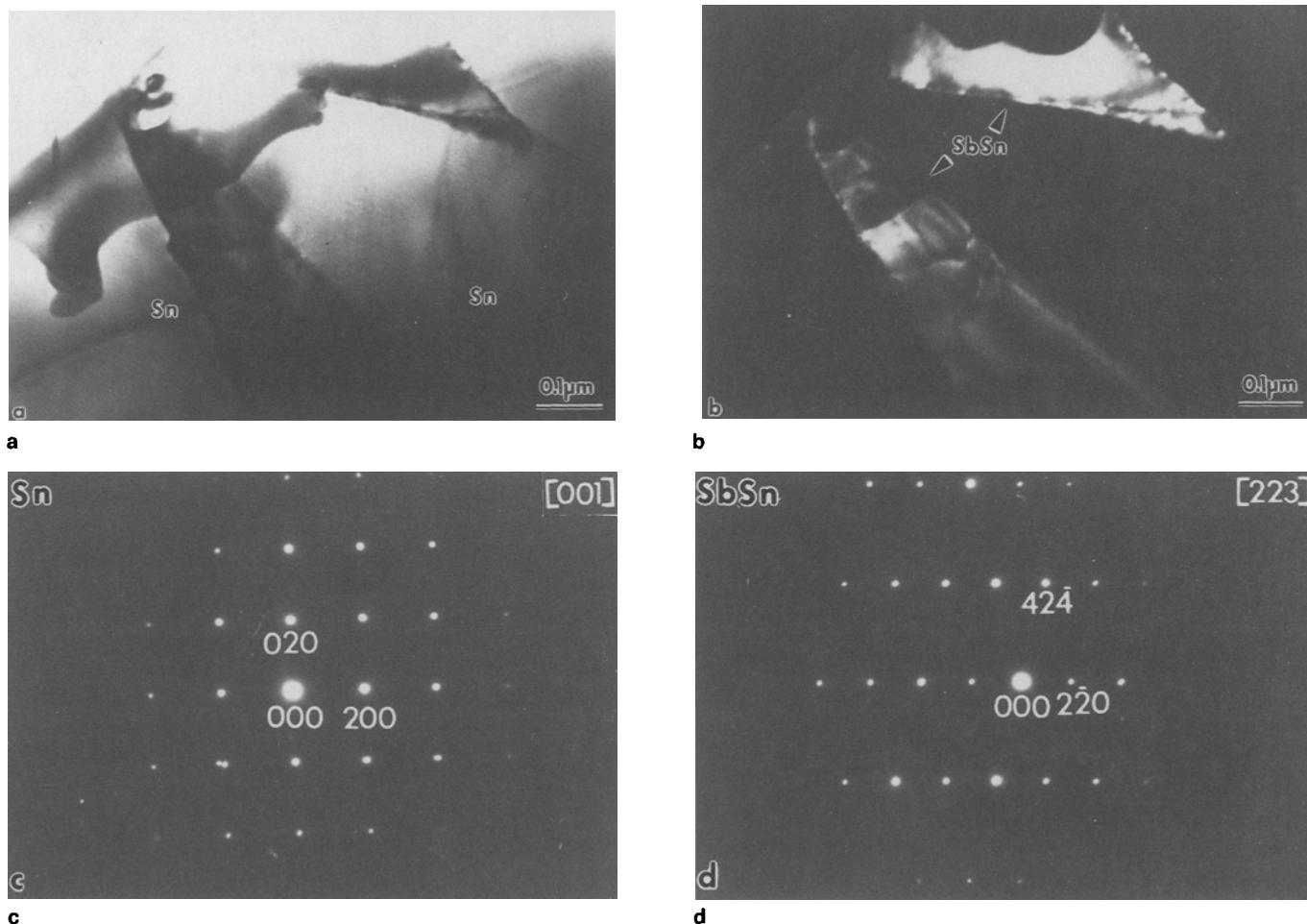


Fig. 3. Transmission electron micrographs of the Sn-45Bi-3Sb alloy: (a) bright field, and (b) centered dark field with $(\bar{2}20)_{\text{SbSn}}$ reflection, (c) SADP from (Sn) in [001] orientation, and (d) SADP from SbSn in [223] orientation.

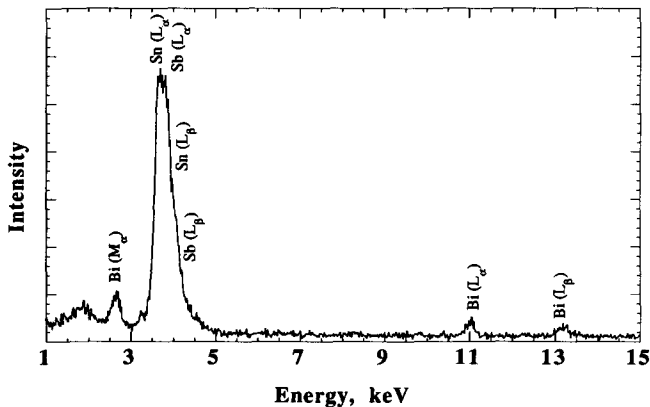


Fig. 4. A typical x-ray fluorescence spectra from the SbSn phase.

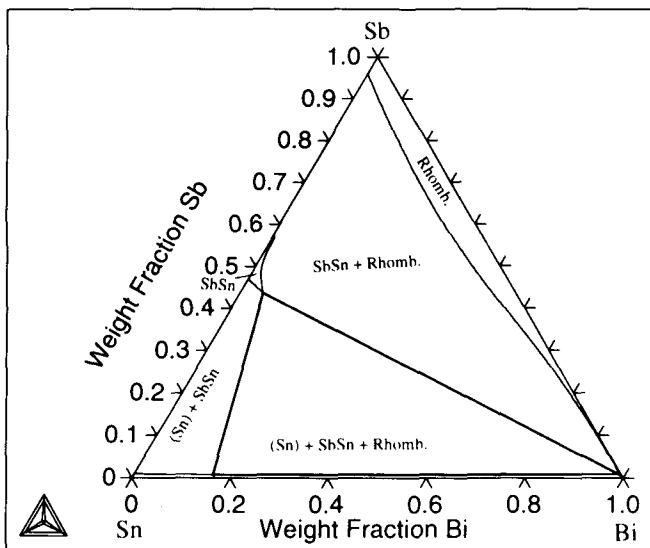


Fig. 5. Calculated isothermal section of the Bi-Sb-Sn system at 398K.

scanning electron microscopy (SEM), transmission electron microscopy (TEM), and analytical electron microscopy (AEM). Specimens for TEM and AEM were prepared by ion-milling.

RESULTS AND DISCUSSION

Figure 1 shows the calculated liquidus surface. There are two ternary U-type invariant reactions, designated U_1 ($\text{Liq.} + \text{Sb}_2\text{Sn}_3 = \text{SbSn} + (\text{Sn})$) and U_2 ($\text{Liq.} + \text{SbSn} = (\text{Sn}) + (\text{Sb})$), occurring at 517.9 and 411.8K, respectively. There are four melting grooves with (Sn), SbSn, Sb_2Sn_3 and the rhombohedral phase as the primary crystallization product. The binary invariant reaction p_1 and one set of reaction products ($\text{Liq.} + (\text{Sn}) + \text{SbSn}$) from U_1 feed the transition reaction U_2 . The other set of reaction products ($(\text{Sn}) + \text{SbSn} + \text{Sb}_2\text{Sn}_3$) feeds the binary eutectoid reaction $\text{Sb}_2\text{Sn}_3 = \text{SbSn} + (\text{Sn})$. Vogel and Apel⁹ reported the liquidus surface of the Bi-Sb-Sn system. The calculated invariant reaction U_2 is consistent with their liquidus surface. However, Vogel and Apel⁹ did not report the participation of Sb_2Sn_3 phase in the solidification process, and, therefore, their liquidus surface is inconsistent with the presently accepted binary Sb-Sn phase diagram.

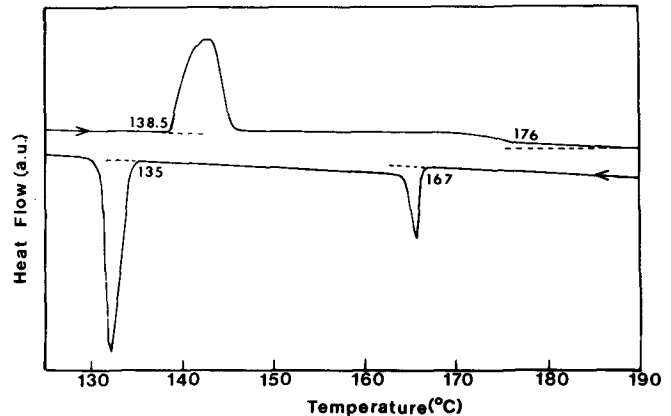


Fig. 6. Differential scanning calorimetry thermogram of the Sn-45Bi-3Sb alloy at a heating (and cooling) rate of 5°C/min.

Figure 2 shows an optical micrograph of Sn-45Bi-3Sb alloy after annealing. By means of secondary electron and backscattered electron imaging and x-ray mapping, the phases were identified to be: (Sn) being dark, SbSn being bright, and rhombohedral phase being slightly gray. Figure 3 shows transmission electron micrographs containing (Sn) and SbSn phases and the corresponding selected area diffraction patterns (SADP). A typical x-ray fluorescence spectra from SbSn phase, as obtained by AEM, is shown in Fig. 4. Using standards of Bi-Sb, Sb-Sn, and Bi-Sn alloys of known compositions, the Bi-content the SbSn phase was determined to be about 5.0 wt.%. This is substantially lower than that reported by Vogel and Apel.¹⁰ The composition of the SbSn phase, as determined by AEM, was used to evaluate the interaction parameters ${}^{\circ}G_{\text{Sb}_0.5\text{Bi}_0.5}$ and ${}^{\circ}G_{\text{Sn}_0.5\text{Bi}_0.5}$ described in Eq. (3).

Figure 5 shows the calculated isothermal section at 398K. Vogel and Apel⁹ reported an isothermal section at 298K. The solid solubility of Sb in (Sn) reported by Vogel and Apel⁹ at 298K is significantly higher than that in the presently accepted Sb-Sn phase diagram. Also, a vertical section reported by Vogel and Apel⁹ at 30 wt.% Bi is not consistent with the binary phase diagram. Due to all these inconsistencies, many of our calculated results cannot be compared with the experimental results of Vogel and Apel.⁹

Figure 6 shows the DSC thermogram of the Sn-45Bi-3Sb alloy at a heating (and cooling) rate of 5°C/min. The liquidus and solidus temperatures for this alloy were predicted to be 188.5 and 138.8°C, respectively. As shown in Fig. 6, the corresponding experimental values are 176 and 138.5°C. During heating, the alloy starts melting around 138.5°C and the melting continues until the rest of the alloy containing mostly SbSn melts. Substantial undercooling, typical of Sn-base alloys, in the cooling run may be noticed in Fig. 6. Similarly, in the Sn-10Bi-5Sb alloy, the liquidus and solidus temperatures were 232 and 192°C, respectively, and the corresponding predicted values are 226 and 173°C. Considering the fact that the predicted values of liquidus temperatures and solidification ranges are based only on the binary

phase diagrams, the overall agreement is considered to be good.

CONCLUSIONS

Using the CALPHAD approach, the solidification behavior of Bi-Sb-Sn alloys has been modeled. The present calculation does not take into account any ternary interaction. Also, the present calculation does not predict any ternary eutectic reaction in the Bi-Sb-Sn system. Limited results obtained by differential scanning calorimetry are consistent with the predicted solidification behavior.

The Bi-content in the SbSn phase at 398K, determined by analytical electron microscopy, is found to be about 5 wt.%. Using this information, the necessary thermodynamic parameters are derived in order to describe the homogeneity range of SbSn phase in the ternary regime. An isothermal section at 398K is also established.

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