Phase Equilibria of Sn-In Based Micro-Soldering Alloys

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The phase equilibria of Sn-In-X (X = Ag, Bi, Sb, Zn), the most basic information necessary for the development of Pb-free micro-soldering alloys, were studied using the *CALPHAD* method. Thermodynamic analyses for describing the Gibbs energies of the constituent phases were made by optimizing the obtained data on the experimental phase diagrams, and such data in the literature, including data on thermochemical properties. The present results combined with the thermodynamic database which was recently developed by our group [I. Ohnuma et al., *J. Electron. Mater.* 28, 1164 (1999)] provide various information on phase equilibria such as liquidus and solidus surfaces, isothermal and vertical section diagrams, mole fractions of the phase constitutions, etc., and thermodynamic properties such as activity, heat of mixing, surface energy, viscosity, etc., in multi-component soldering alloy systems including the elements of Pb, Bi, Sn, Sb, Cu, Ag, Zn, and In. Typical examples for the phase diagrams and thermodynamic properties of Sn-In-X ternary systems are shown. The application of the database to the alloy design for Pb-free solders is also presented.

Key words: Phase equilibria, thermodynamics, database, Sn-In base alloys, Pb-free solders

INTRODUCTION

Although Pb-Sn solders are widely used in electronic interconnections of packing technologies, further development of Pb-free solders is urgently required due to potential legislation which would ban or restrict the use of Pb in view of the environmental and health issues concerning its toxicity. We recently developed a thermodynamic database for the calculation of phase diagrams in micro-soldering alloy systems by the *CALPHAD* (CALculation of PHAse Diagrams) method; this database consists of the elements Pb, Bi, Sn, Sb, Cu, Ag, and Zn.[1,2] The database provides various information on not only phase equilibria such as liquidus, solidus, equilibrium composition, volume fractions of constituent phases, etc., but also on thermochemical properties such as activity, heat of mixing, enthalpy of formation, surface energy, viscosity, etc. Furthermore, the equilibrium and non-equilibrium solidification processes can be simulated. However, the important element In was not available at that time. In order to include In in this database, experimental and thermodynamic analyses of some Sn-In-base ternary alloys were carried out. The present paper shows the phase equilibria of Sn-In-X (X: Ag, Bi, Sb, Zn) ternary systems, which are practically important for the development of the Pb-free solders. Some examples for the application of the thermodynamic database are also shown.

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THERMODYNAMIC DATABASE

The database for calculating phase diagrams and thermodynamic properties has been constructed by use of the CALPHAD method.[3–5] The thermodynamic parameters for describing the Gibbs energy of the liquid and solid phases are evaluated by optimizing the experimental data on phase boundaries and thermochemical properties such as activity, heat of mix-

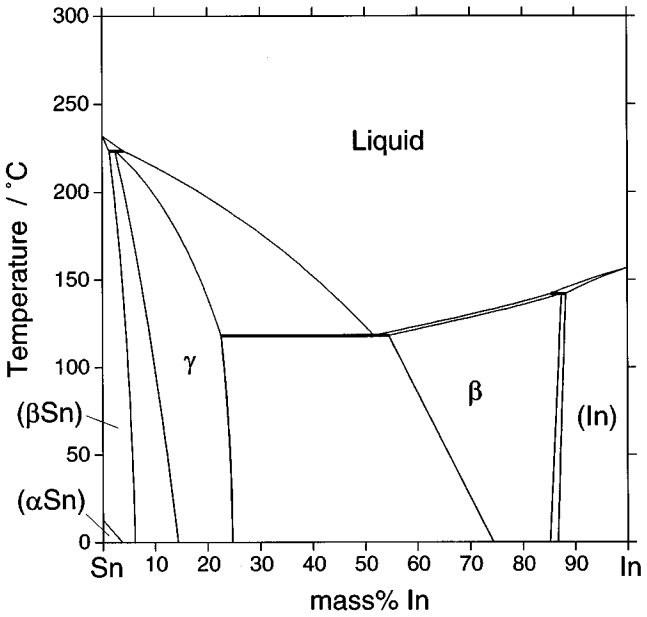

Fig. 1. Phase diagram of the Sn-In binary system.

ing and enthalpy of formation. The Gibbs energies of the liquid and solid solution phases are approximated by the regular solution model, while those of intermetallic phases with some solubility range are described by the sublattice model.[1,6,7]

For some important alloy systems for which there are few data on phase boundaries, experimental determinations of phase equilibria were conducted using differential scanning calorimetry (DSC), energy dispersion x-ray spectroscopy (EDS), x-ray diffraction, and metallographic techniques. Moreover, additional experimental work was undertaken in some binary and ternary systems to check the reliability of the previous data reported before the 1950s. This reconfirmation of the agreement between the calculated and the observed phase equilibria was required to obtain a better estimation of the thermodynamic parameters.

Table I. Survey of Thermodynamic Assessments of Binary Systems

System	Reference
Ag-In	8
Ag-Sn	9, 10
Bi-In	11
Bi-Sn	7
In-Sb	12, 13
In-Sn	14
In-Zn	15
Sb-Sn	7
Sn-Zn	10

Table I shows a survey of thermodynamic assessments of binary systems consisting of Sn-In-X (X: Ag, Bi, Sb, Zn) alloys that were carried out by our group[7,8,10,11,13] and also those previously reported.[9,12,14,15] Figure 1 shows the calculated phase diagram of the Sn-In binary system,[14] where the β phase with the bct-In type crystal structure and the hexagonal γ phase are formed. It should be noted that the assessment of the Ag-In binary system was made based on not only the previous data but also on new experimental results[8] on the phase boundaries of the hexagonal ζ phase, where the homogeneous range of the ζ phase is more limited than that shown by the previous assessment.[16]

The thermodynamic assessments of ternaries are based on the results of the Sn-In-Ag,[8] Sn-In-Bi,[11] Sn-In-Sb,[13] and Sn-In-Zn[17] systems, where the thermodynamic parameters evaluated were arranged within the framework of the *Thermo-Calc* software.[18]

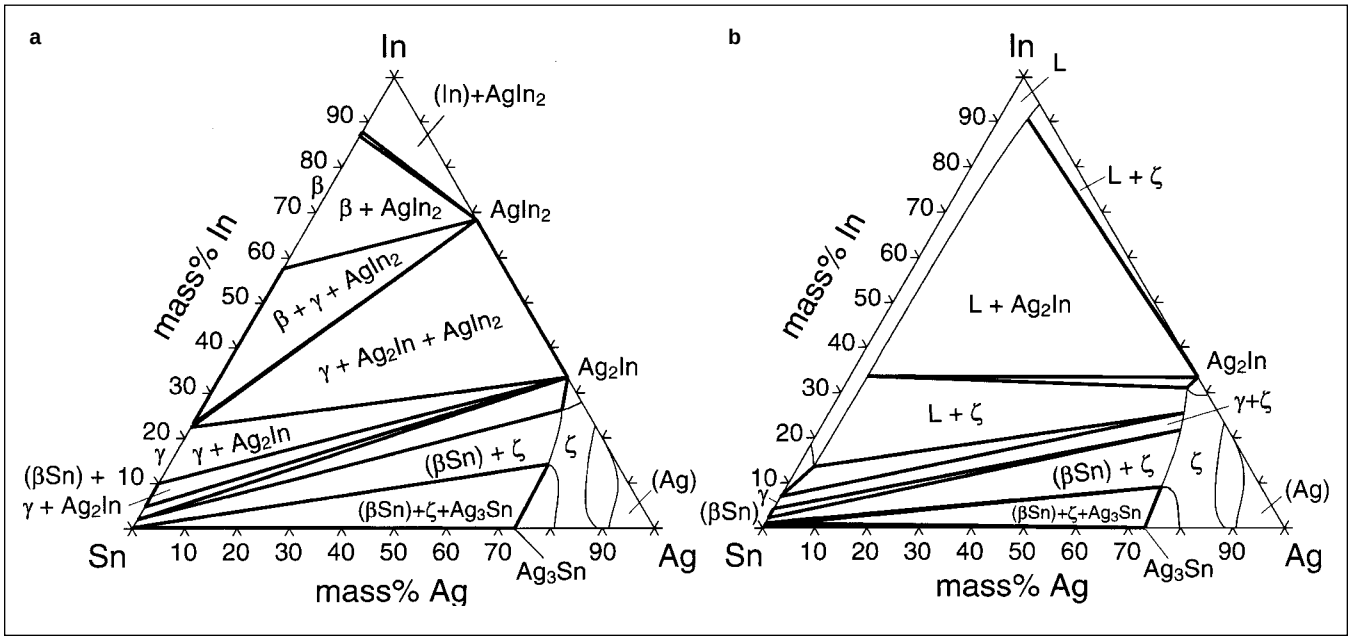

Fig. 2. Isothermal section diagrams of the Sn-In-Ag system at (a) 100°C and (b) 200°C.

PHASE DIAGRAMS

Isothermal Sections

Figures 2 to 5 show the calculated isothermal section diagrams of the Sn-In-Ag, Sn-In-Bi, Sn-In-Sb, and Sn-In-Zn systems at 100°C and 200°C. It is shown that Ag and Zn have little solubility in the Sn-rich solid solution, while Bi exhibits a wide range of solubility. The greater solubility of Bi as well as In in the solid solution of the Sn-rich phase as shown in Fig. 1 is one of the reasons why the liquid phase remains at lower temperatures in the non-equilibrium solidification process[2] 11b.

Vertical Sections

Extensive effort has been made to develop lead-free solders, Sn-20mass%In-X (X: Ag, Bi, Zn) alloys being suggested as possible alternatives to Pb-Sn solders.[19] Figure 6 shows the effect of the addition of Ag, Bi, Sb, or Zn on the phase constitution of Sn-20mass%In alloys.

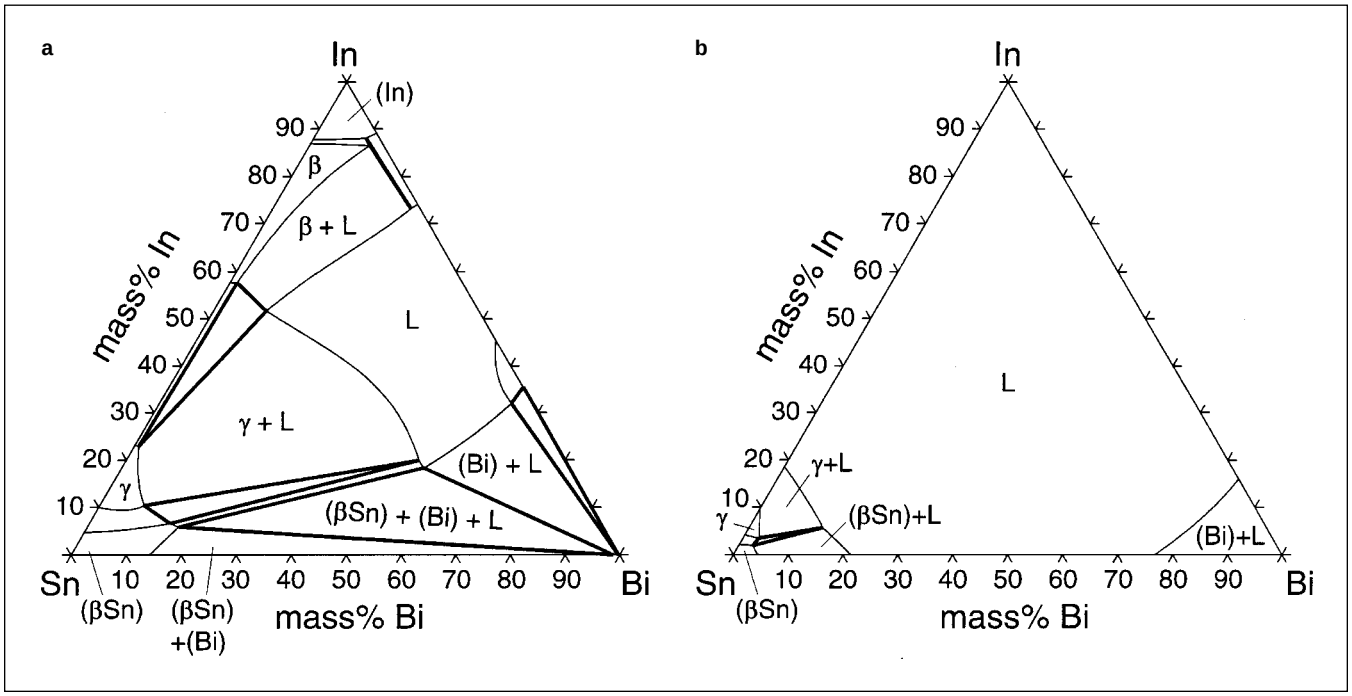

Fig. 3. Isothermal section diagrams of the Sn-In-Bi system at (a) 100°C and (b) 200°C.

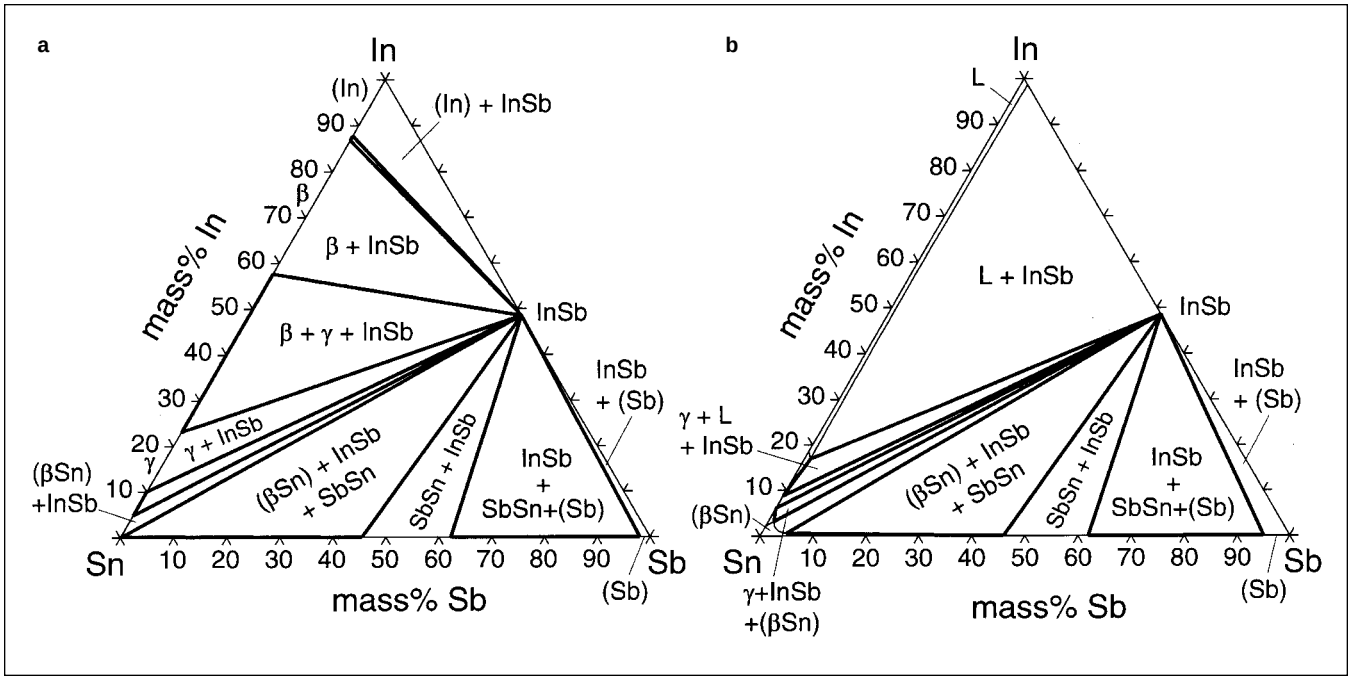

Fig. 4. Isothermal section diagrams of the Sn-In-Sb system at (a) 100°C and (b) 200°C.

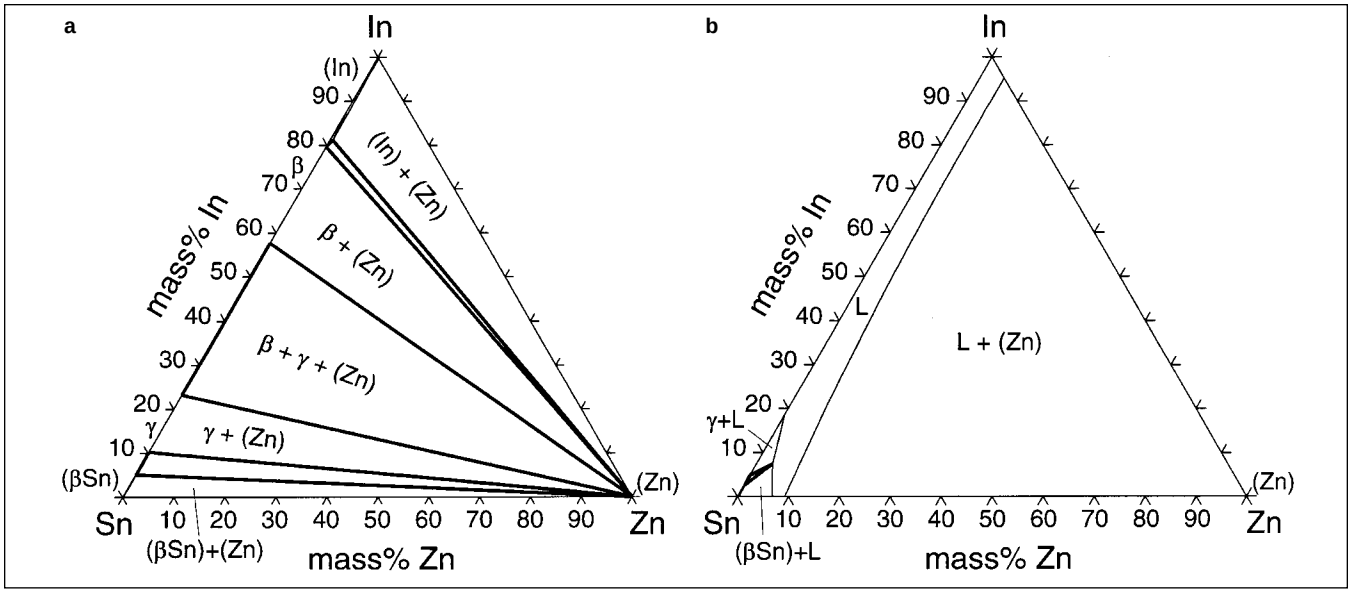

Fig. 5. Isothermal section diagrams of the Sn-In-Zn system at (a) 100°C and (b) 200°C.

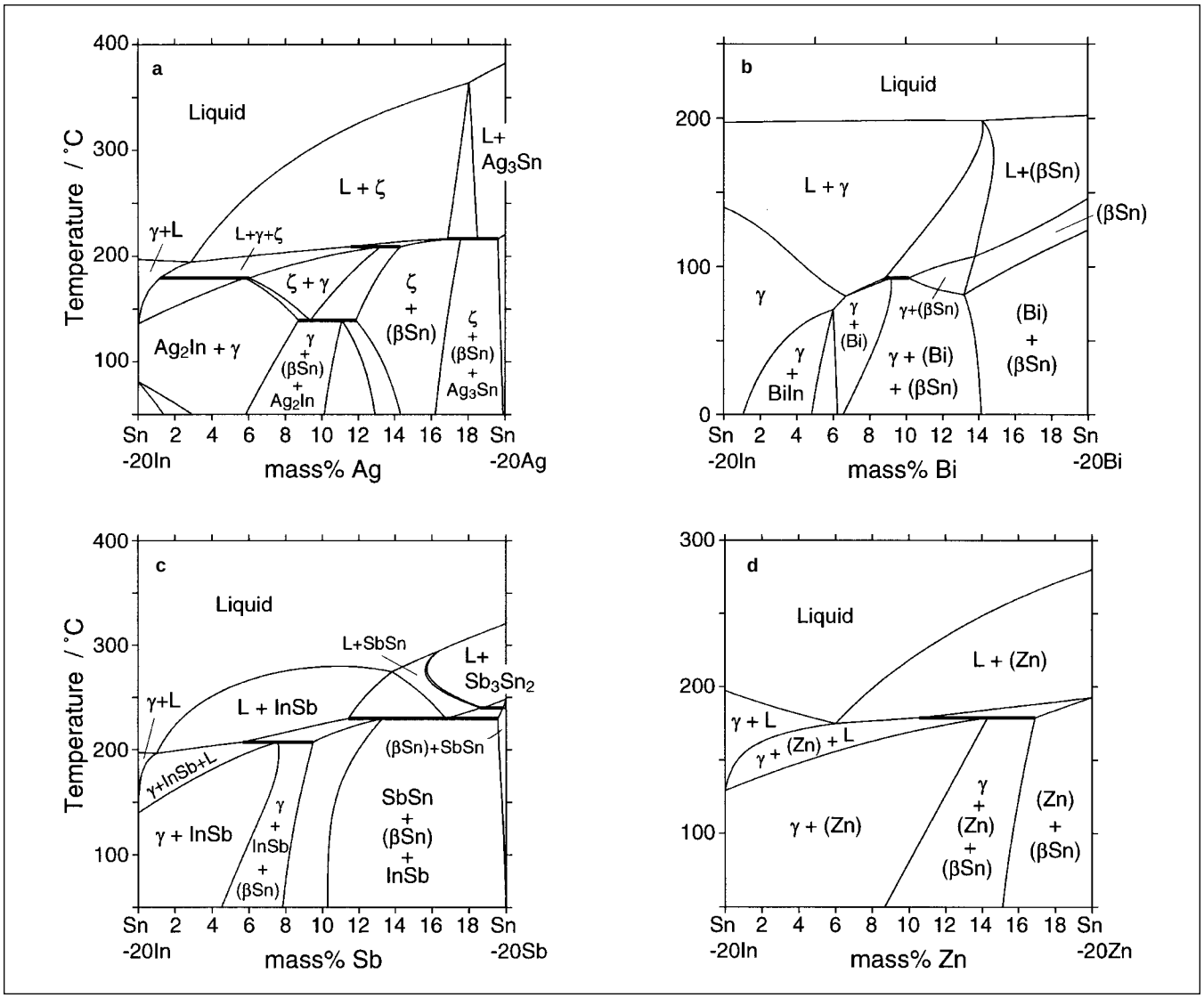

Fig. 6. Vertical section diagrams of the Sn-20mass%In-X ternary system: X= (a) Ag, (b) Bi, (c) Sb, and (d) Zn.

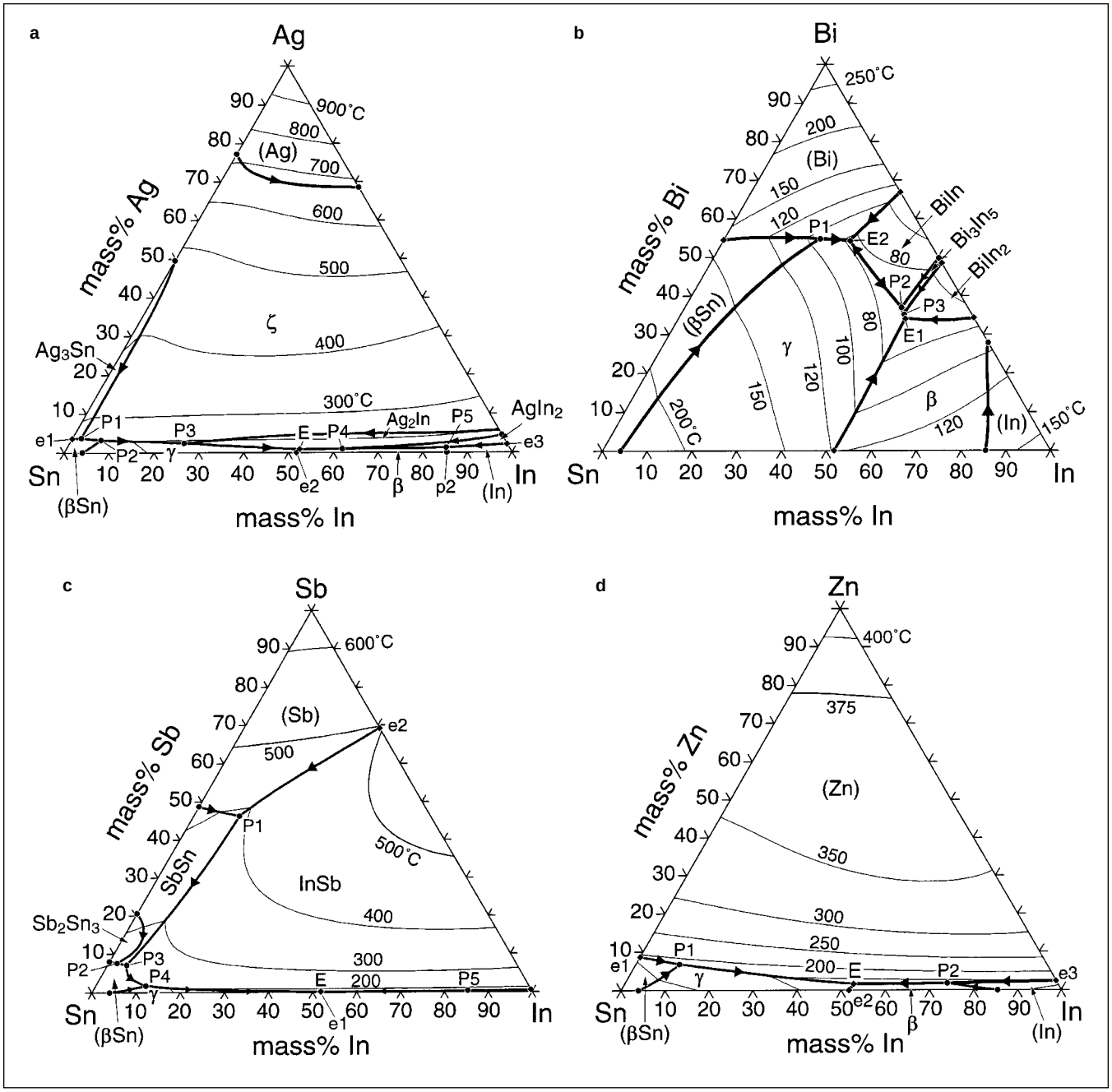

Fig. 7. Liquidus projections of the Sn-In-X ternary system: X= (a) Ag, (b) Bi, (c) Sb, and (d) Zn.

It is worthy of note that the developed Sn-20mass%In-2.8mass%Ag Pb-free solder alloy[20] has the small temperature range of two-phase and three-phase fields containing a liquid phase as shown in Fig. 6a. The Sn-20mass%In-6mass%Zn alloy also has a small range of freezing temperatures desirable for the microstructure of solders, while the temperature range of the two-phase or three-phase fields accompanying the liquid phase is large in the Sn-20mass%In-Bi alloys.

Liquidus and Solidus

The calculated liquidus projections of the four Sn-In-base ternary systems are shown in Fig. 7. It can be seen that the melting temperature of the Sn-In-Bi system is very low, which is suitable for use in a system that requires low melting processing. Figure 8 shows the effect of Ag, Bi, Sb, and Zn on the liquidus and solidus of the Sn-20mass%In alloy. The liquidus temperature increases with increasing Sb and Zn concentration except for the case of low alloying content. As shown in Fig. 1, the eutectic reaction of the Sn-In binary system occurs at 51.7mass%In and 120°C. Figure 9 shows the effect of Ag, Bi, Sb, and Zn on the liquidus temperature of the Sn-51.7mass%In eutectic alloy.

Invariant Reactions

It can be seen from the liquidus projection shown in Fig. 7 that various kinds of invariant reaction of

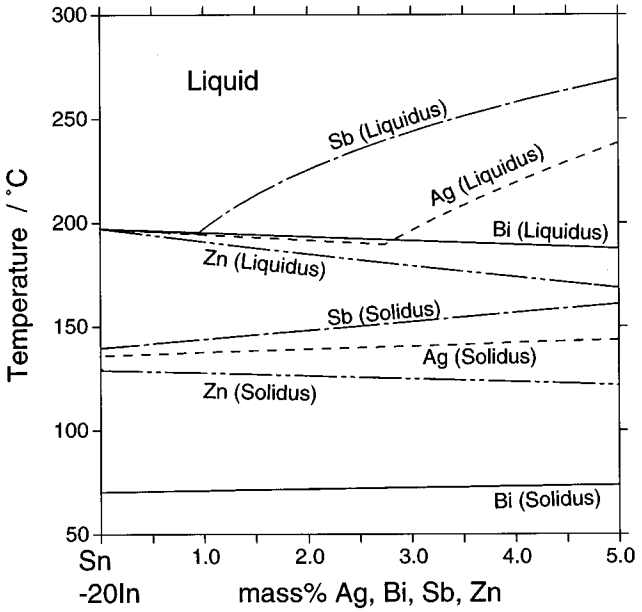

Fig. 8. Effects of Ag, Bi, Sb, and Zn on the liquidus and solidus of Sn-20mass%In alloy.

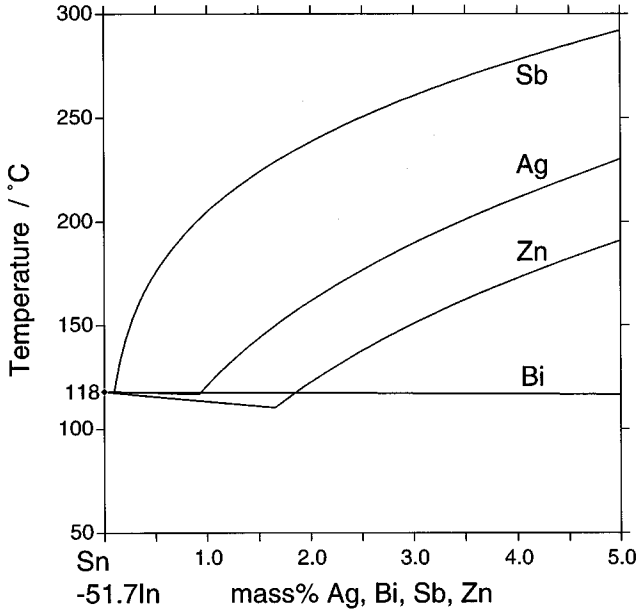

Fig. 9. Effects of Ag, Bi, Sb, and Zn on the liquidus temperature of Sn-51.7mass%In eutectic alloy.

Table II. Invariant Reactions of Sn-In-X (X = Ag, Bi, Sb, and Zn) Systems

System	Type	Reaction	Temperature (°C)	Composition of the liquid phase (mass%)	
				In	X
Sn-In-Ag	P1	$L + Ag_3Sn \Leftrightarrow (\beta Sn) + \zeta$	227	1.9	3.9
	P2	$L + (\beta Sn) \Leftrightarrow \gamma + \zeta$	209	6.8	3.3
	P3	$L + \zeta \Leftrightarrow \gamma + Ag_2In$	180	25.5	2.5
	P4	$L + Ag_2In \Leftrightarrow \beta + AgIn_2$	119	61.1	1.0
	P5	$L + (In) \Leftrightarrow \beta + AgIn_2$	135	84.6	1.4
	E	$L \Leftrightarrow \beta + \gamma + Ag_2In$	114	52.2	0.9
Sn-In-Bi	P1	$L + (\beta Sn) \Leftrightarrow (Bi) + \gamma$	93	21.4	23.9
	P2	$L + BiIn \Leftrightarrow \gamma + Bi_3In_5$	61	48.3	14.7
	P3	$L + Bi_3In_5 \Leftrightarrow \gamma + BiIn_2$	60	49.8	15.0
	E1	$L \Leftrightarrow \gamma + \beta + BiIn_2$	59	50.6	15.3
	E2	$L \Leftrightarrow (Bi) + \gamma + BiIn$	76	28.2	17.5
Sn-In-Sb	P1	$L + (Sb) \Leftrightarrow InSb + SbSn$	388	10.4	46.3
	P2	$L + Sb_2Sn_3 \Leftrightarrow (\beta Sn) + SbSn$	240	1.9	7.7
	P3	$L + SbSn \Leftrightarrow (\beta Sn) + InSb$	230	4.3	7.2
	P4	$L + (\beta Sn) \Leftrightarrow \gamma + InSb$	207	11.4	1.8
	P5	$L + (In) \Leftrightarrow InSb + \beta$	141	85.2	0.3
	E	$L \Leftrightarrow InSb + \beta + \gamma$	118	51.8	0.1
Sn-In-Zn	P1	$L + (\beta Sn) \Leftrightarrow (Zn) + \gamma$	179	9.9	6.6
	P2	$L + (In) \Leftrightarrow (Zn) + \beta$	120	73.2	1.7
	E	$L \Leftrightarrow (Zn) + \gamma + \beta$	107	52.2	1.6

peritectic and eutectic type appear in the Sn-In-X ternary systems. Table II summarizes the reaction type, temperature and composition of the liquid phase in these systems. It is interesting to note that the invariant temperatures of P3 (180°C) of Sn-In-Ag and of P1 (179°C) of Sn-In-Zn systems are very close to the Pb-Sn eutectic temperature (183°C).

APPLICATIONS OF DATABASE

The thermodynamic database allows prediction of various aspects involved in the development of Pb-free solders. Some applications of the database are shown here. Figure 10a shows the calculated vertical section of Sn-In-Zn alloys with constant 9mass%Zn including the experimental data,[21–23] where the Sn-9mass%Zn binary alloy is very close to the binary eutectic composition. Figure 10b shows the effect of In on the Sn-Zn eutectic alloy in the e1-P1 cross section of Fig. 7d. It is obvious that the binary Sn-Zn eutectic reaction is suitably depressed with increasing In content until the ternary peritectic reaction P1 is reached. A very similar phase reaction can be found in

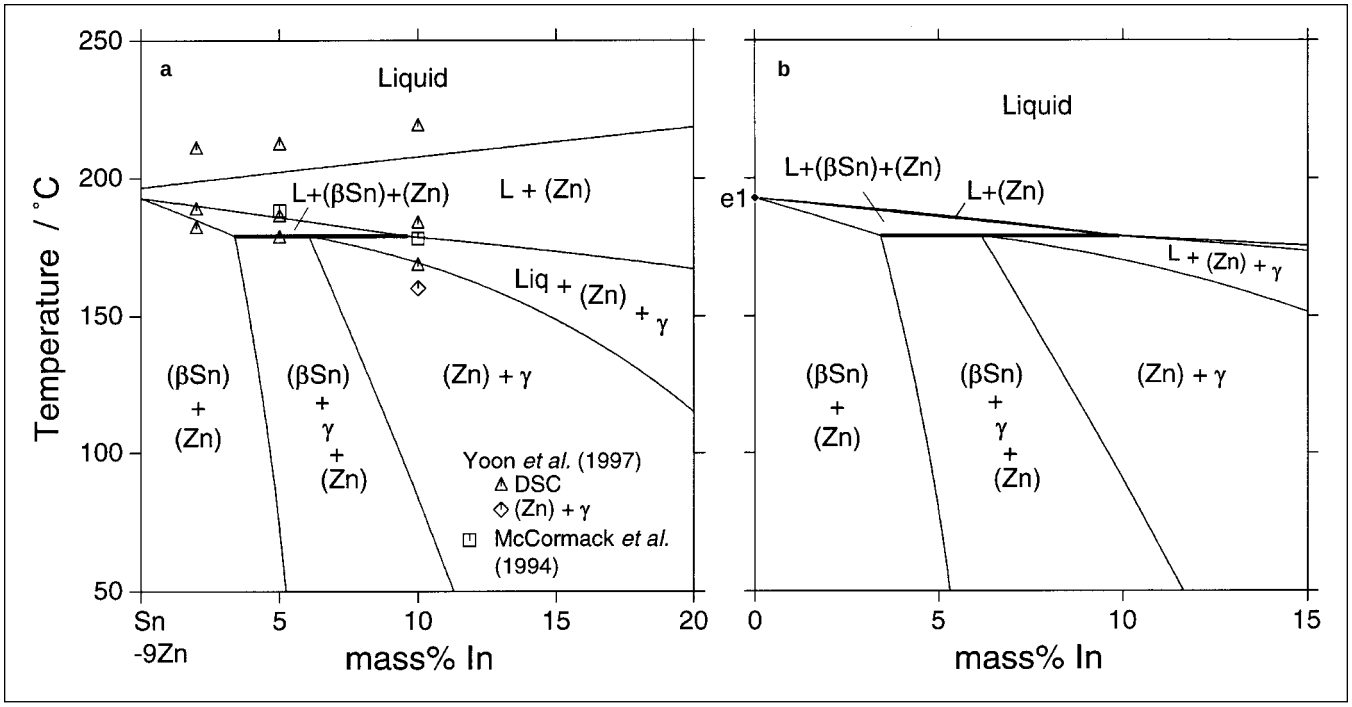

Fig. 10. Vertical section diagram of the Sn-In-Zn ternary system: (a) 9 mass% Zn and (b) e1-P1 cross section of Fig. 7d.

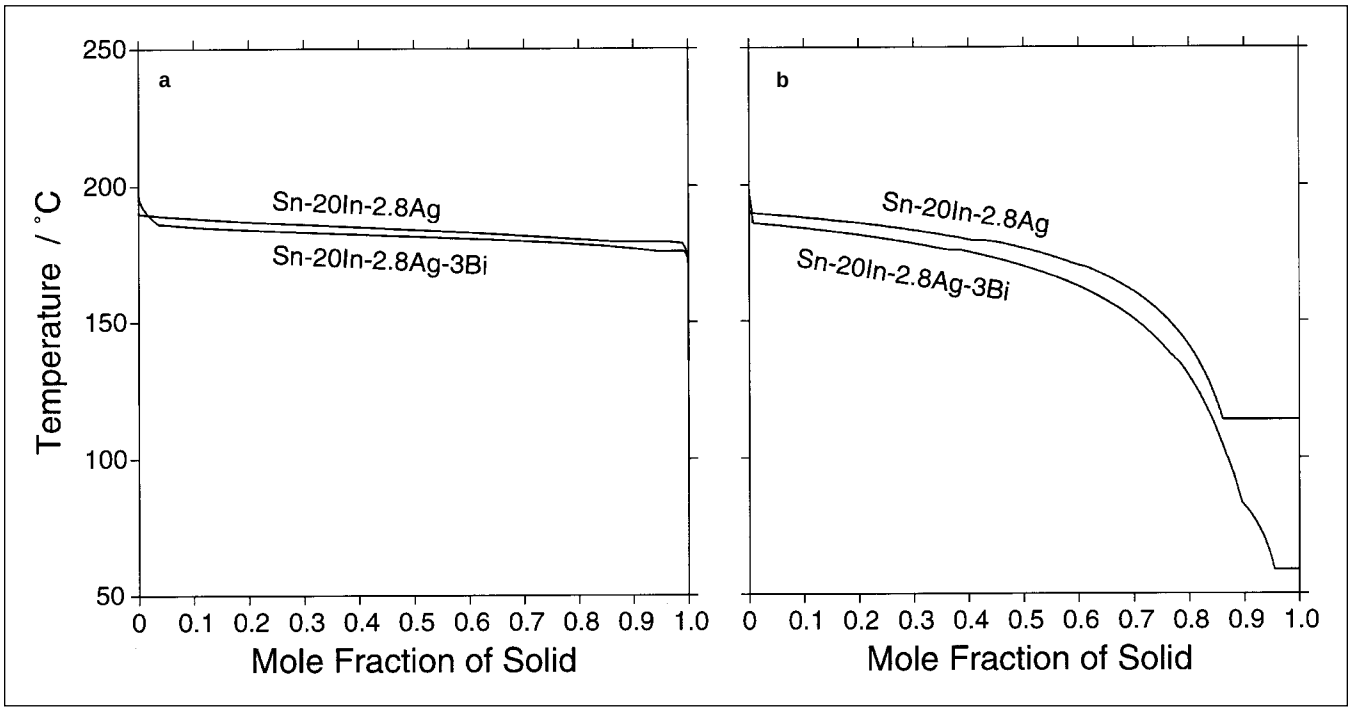

Fig. 11. Phase fraction of solid vs. temperature of Sn-20mass%In-2.8mass%Ag and Sn-20mass%In-2.8mass%Ag-3mass%Bi: (a) equilibrium solidification and (b) non-equilibrium solidification by the Scheil model.

the vertical section of Fig. 10a. It should be emphasized, however, that the respective effects of In addition on the liquidus temperature and the freezing range are remarkably different; the incorporation of In increases the liquidus temperature and the temperature range of the two or three-phase field accompanying the liquid phase at 9mass% Zn, while it decreases both features in the cross section of e1-P1. These facts suggest that the alloys within the range of 2-5 mass%In located at the e1-P1 line, characterized by the similarity of their melting behavior to that of the Sn-Pb eutectic alloy, are more suitable for Pb-free solders than the Sn-9mass%Zn-(2–5)mass%In alloys. These calculations provide important information for use in the design of new solder alloys.

Another application of the thermodynamic data-

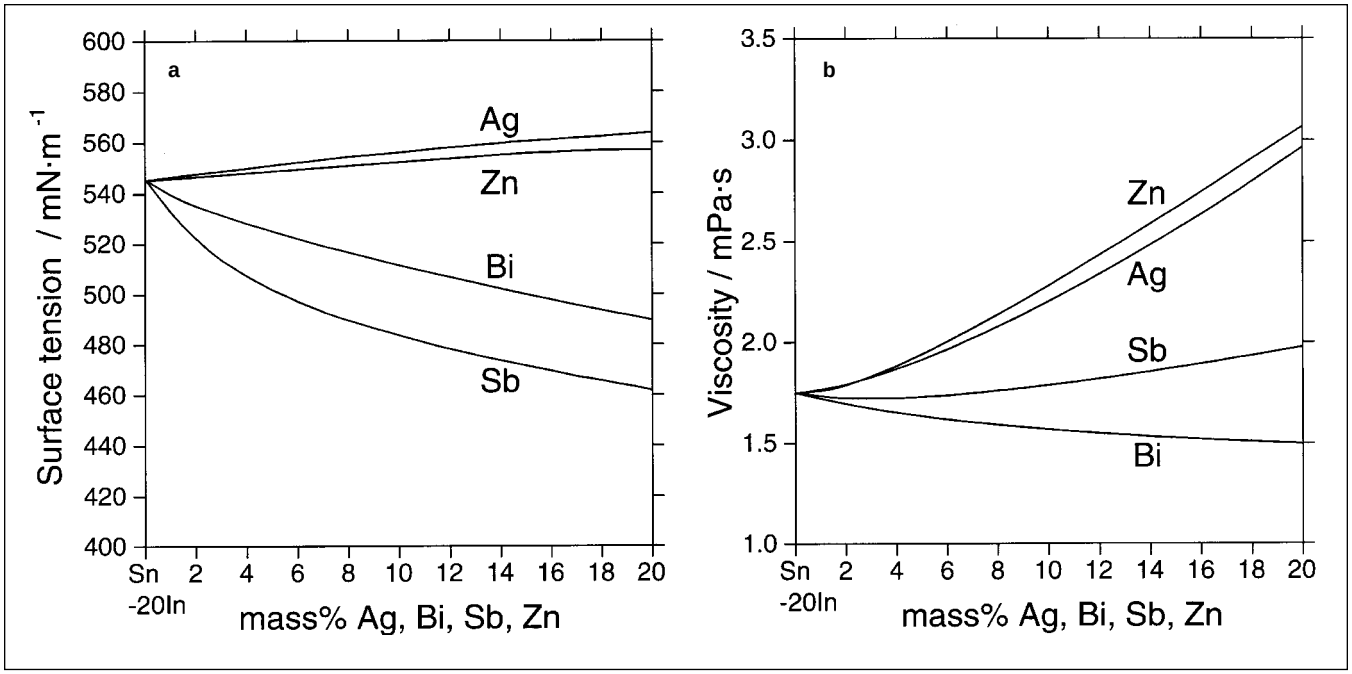

Fig. 12. Effects of Ag, Bi, Sb, and Zn on the (a) surface tension and (b) viscosity of Sn-20mass%In alloy at 250°C.

base is the simulation of the solidification process. Although the Scheil model assumes that local equilibrium exists at the liquid/solid interface and diffusion is absent in the solid phase, Scheil calculation can still provide a prediction close to reality. Figure 11a and b show the calculated phase fraction[22] of solid vs. temperature variation of Sn-20mass%In-2.8mass%Ag[20] and Sn-20mass%In-2.8mass%Ag -3mass%Bi[22] alloys under equilibrium and non-equilibrium solidification conditions, respectively. In comparison with the equilibrium solidification based on the lever rule, the formation of the liquid phase due to segregation in the Scheil calculation increases the freezing range. In particular, the addition of Bi strongly causes liquid formation at low temperature. The presence of the liquid phase at these temperatures due to non-equilibrium solidification is considered to be one of the reasons for the lifting-off phenomenon between the solder and the Cu substrate.[24]

The surface tension and viscosity of the liquid phase can also be calculated using thermodynamic models,[25–27] where the estimation is based on the Gibbs energy of the liquid phase. Figure 12a and b show the effect of Ag, Bi, Sb, and Zn on the surface tension and viscosity of the Sn-20mass%In alloy at 250°C, respectively. It can be seen that Ag and Zn increase both the surface tension and viscosity. This kind of information would be useful when considering the melting behavior, castability and manufacturability of solders.

CONCLUDING REMARKS

The phase equilibria of the Sn-In-X (X: Ag, Bi, Sb, and Zn) systems were studied. Thermodynamic assessments of these systems were also carried out and the resulting data were incorporated in the thermodynamic database which was recently developed by our group.[1,2] The phase diagrams of Sn-In base alloys and their application to the design and development of Pb-free solders using the database were presented. The validity and applicability of this database can be expected to be a powerful tool for solder technology.

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