Thermodynamic Database for Phase Diagrams in Micro-Soldering Alloys

I. OHNUMA, X.J. LIU, H. OHTANI, and K. ISHIDA

Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-yama 02, Sendai 980-8579, Japan

A thermodynamic database for the calculation of phase diagrams in micro-soldering alloy systems, which include the elements Pb, Bi, Sn, Sb, Cu, Ag, and Zn has been developed using the CALPHAD method. The various thermodynamic parameters for describing the Gibbs energies of the different constituent phases have been evaluated by optimizing experimental data on phase boundary compositions and thermochemical properties such as activity, heat of mixing and enthalpy of formation. The resulting database provides the means whereby the liquidus and solidus surfaces, isothermal and vertical section diagrams, phase percentages and the mole fraction of the phase constitutions etc., in multi-component soldering alloys can be readily calculated. Related information such as the surface tension and viscosity of the liquid phase can also be predicted, thus rendering the database as a valuable tool for developing leadbearing and lead-free solders.

Key words: Phase diagrams, database, thermodynamics, Pb-bearing solders, Pb-free solders

INTRODUCTION

Recent progress in the area of surface mounting technology directed towards improvements in the field of interconnection and packaging of modern electronic components and devices has created a need for the development of various microsoldering materials. Current manufacturing technologies are centered around the Pb63mass%Sn eutectic alloy with 183°C as eutectic melting temperature. Apart from the demands for development of alloys with melting temperatures different from the above, additional requirements arising from the environmental and health issues concerning the toxicity of Pb, have necessitated the development of new Pb-free solders. Design and development of such Pb-free solders can be significantly speeded up by the availability of a reliable thermodynamic database for the prediction of phase equilibria, calculation of liquidus, solidus and equilibrium compositions, volume fractions of constituent phases etc. in the multi-component alloys concerned.

The present paper describes the recent progress achieved in the creation and validation of a database for calculation of phase diagrams in the micro-soldering alloy systems, whose main component elements are Pb, Bi, Sn, Sb, Cu, Ag and Zn. The database has been constructed by the *CALPHAD* (CALculation of PHAse Diagrams) method.[1–5]

CALPHAD METHOD

The basics of the well-known CALPHAD method have been described in previous papers[1–4] and books.[5] The outline scheme of the CALPHAD method is shown in Fig. 1. The Gibbs energies of the liquid and solid solution phases are described by the regular solution model, where the Gibbs energy of a phase in the A-B-C ternary system, for instance, is expressed as

$$G = {}^\circ G_A x_A + {}^\circ G_B x_B + {}^\circ G_C x_C$$
$$+ RT(x_A \ln x_A + x_B \ln x_B + x_C \ln x_C)$$
$$+ L_{AB} x_A x_B + L_{BC} x_B x_C + L_{AC} x_A x_C$$
$$+ L_{ABC} x_A x_B x_C \quad (1)$$

where ${}^\circ G_i$ is the Gibbs energy of the pure component i in the respective reference state, x_i the mole fraction of component i and L_{ij} a temperature and composition dependent interaction energy. The Gibbs energies of pure component i in its different phase states; i.e.,
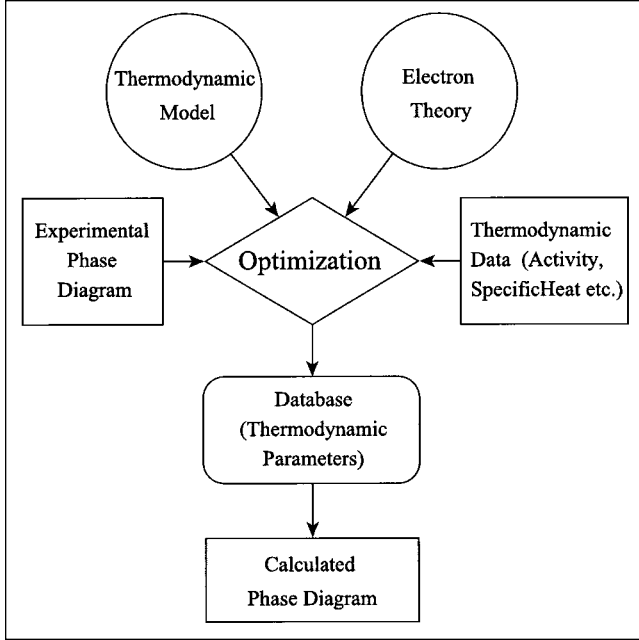
Fig. 1. Scheme of CALPHAD method.

Table I. Thermodynamic Assessments of Ternary Systems

System	Experimental Information	System	Experimental Information
Ag-Bi-Cu	none	Bi-Cu-Zn	many
Ag-Bi-Pb	few	Bi-Pb-Sb	many
Ag-Bi-Sb	none	Bi-Pb-Sn	many
Ag-Bi-Sn	many	Bi-Pb-Zn	many
Ag-Bi-Zn	few	Bi-Sb-Sn	many
Ag-Cu-Pb	many	Bi-Sb-Zn	few
Ag-Cu-Sb	few	Bi-Sn-Zn	many
Ag-Cu-Sn	many	Cu-Pb-Sb	few
Ag-Cu-Zn	many	Cu-Pb-Sn	none
Ag-Pb-Sb	many	Cu-Pb-Zn	many
Ag-{b-Sn	many	Cu-Sb-Sn	many
Ag-Pb-Zn	many	Cu-Sb-Zn	few
Ag-Sb-Sn	few	Cu-Sn-Zn	many
Ag-Sb-Zn	none	Pb-Sb-Sn	many
Ag-Sn-Zn	many	Pb-Sb-Zn	many
Bi-Cu-Pb	few	Pb-Sn-Zn	few
Bi-Cu-Sb	few	Sb-Sn-Zn	few
Bi-Cu-Sn	none	Bi-In-Sn	many
		In-Sb-Sn	many

lattice stability parameters for i, are taken from the *SUITE* (Scientific Group Thermodata Europe)[6] database. The Gibbs energies of intermetallic phases with some solubility range such as the β (SnSb) and the γ (Ag$_5$Zn$_8$) phases are described by the sublattice model.[7] According to this model, the β(SnSb) phase, for example, is divided into two sublattices, I and II, where the sublattice I is occupied predominantly by Sb atoms and the sublattice II predominantly by Sn atoms; i.e., (Sb,Sn)^I(Sn,Sb)^{II}. The Gibbs energy of the β phase is expressed by

$$G = {}^{\circ}G^{\beta}_{Sb:Sb}y^I_{Sb}y^{II}_{Sb} + {}^{\circ}G^{\beta}_{Sn:Sn}y^I_{Sn}y^{II}_{Sn} + {}^{\circ}G^{\beta}_{Sb:Sn}y^I_{Sb}y^{II}_n$$
$$+ {}^{\circ}G^{\beta}_{Sn:Sb}y^I_{Sn}y^{II}_{Sb} + RT(y^I_{Sb}\ln y^I_{Sb} + y^I_{Sn}\ln y^I_{Sn} \quad (2)$$
$$+ y^{II}_{Sb}\ln y^{II}_{Sb} + y^{II}_{Sn}\ln y^{II}_{Sn}) + G^{ex}$$

where $^{\circ}G^{\beta}_{i:j}$ is the Gibbs energy of the hypothetical β phase in which all the sites in sublattice I are occupied by the element i and all the sites of sublattice II are occupied by the element j. The site fraction of elements in each sublattice is denoted by y_i. G^{ex} is the excess energy term, described by an equation similar to Eq. 1, consisting of appropriate interaction energy parameter terms. The quantity G^{ex} in some phases, however, where the homogeneity range is rather limited can be taken to be equal to zero.

The phase equilibria at high pressures can also be calculated in some alloy systems. The Gibbs energy change of element i at pressure P is given by

$$\Delta G^{\phi_1 \rightarrow \phi_2}_i(x,T,P) = \Delta G^{\phi_1 \rightarrow \phi_2}_i(x,T) + (P-P_0)\Delta V^{\phi_1 \rightarrow \phi_2}_i \quad (3)$$

where $\Delta G^{\phi_1 \rightarrow \phi_2}_i(x,T)$ is the Gibbs energy difference between ϕ_1 and ϕ_2 phases, $\Delta V^{\phi_1 \rightarrow \phi_2}_i$ the difference in molar volume of the element i between ϕ_1 and ϕ_2 phases, and P_0 the atmospheric pressure.

The required interaction energy parameters for inputting into the Gibbs energy expressions are evaluated by optimizing experimental data on phase boundary compositions and thermochemical properties such as activity, heat of mixing and enthalpy of formation as shown in Fig. 1.

THERMODYNAMIC DATABASE

The present thermodynamic database developed for micro-soldering alloy systems contains the relevant thermodynamic parameters for calculating the phase equilibria in unary, binary and ternary alloy systems consisting of seven elements Pb, Bi, Sn, Sb,
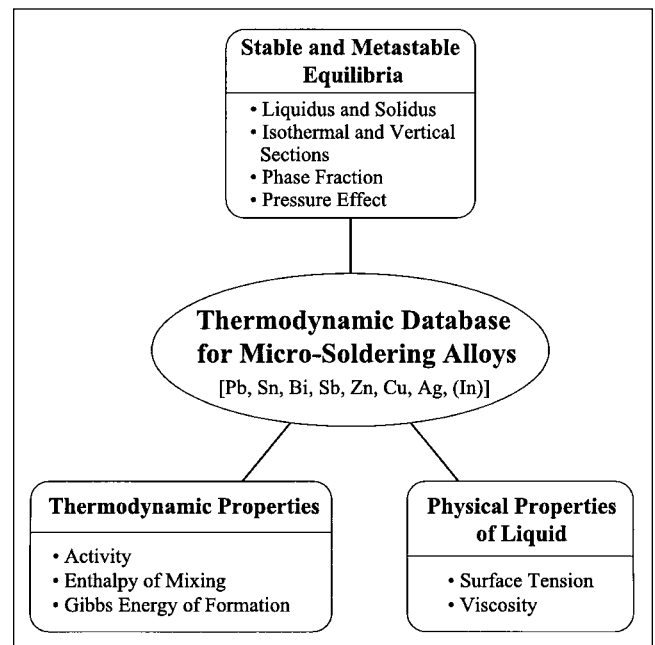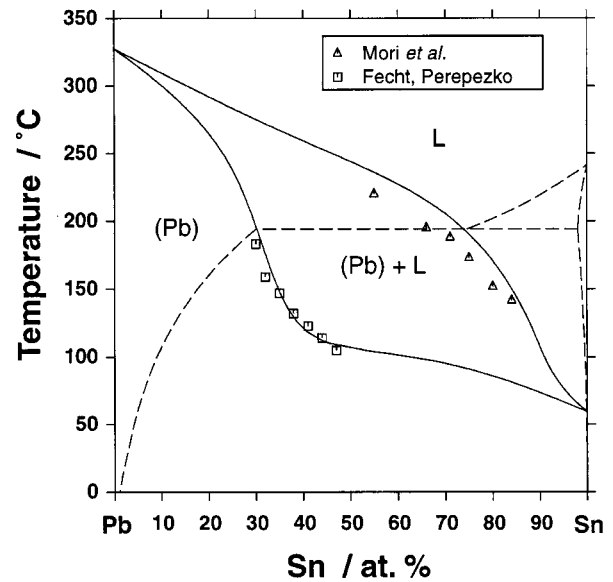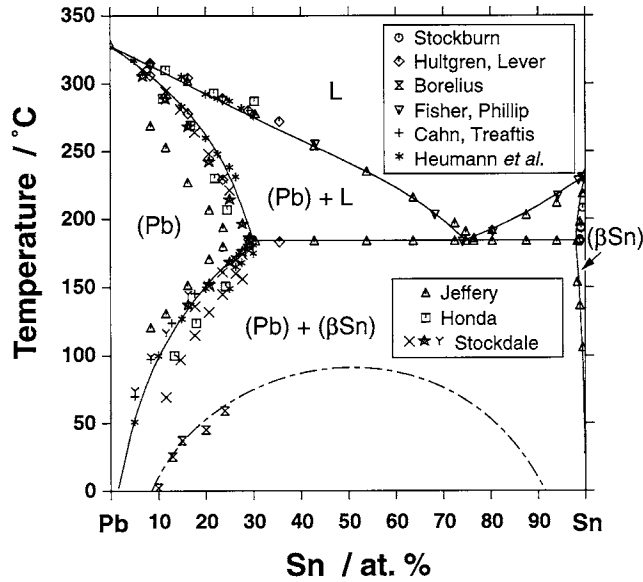

Fig. 2. Contents of thermodynamic database for micro-soldering alloys.

Fig. 3. Calculated (a) stable phase diagram; and (b) metastable liquid/(Pb) phase equilibria in the Pb-Sn binary system.

Cu, Ag and Zn. Thermodynamic assessments of some alloy systems containing In are also included in the database. For some important alloy systems for which there was little or no experimental phase boundary data, experimental work for the determination of phase equilibria such as liquidus, solidus, isothermal and vertical sections, etc. was carried out by DSC (differential scanning calorimetry), x-ray diffraction and EDS (energy dispersion x-ray spectroscopy) measurements. Since many of the previous references on the experimental determinations of phase diagrams in micro-soldering alloy systems were for work before the 1950s, additional experimental work was undertaken in several alloy systems to check the reliability of the experimental phase equilibria reported in these

earlier references. 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 shows the ternary alloy systems that were thermodynamically assessed in the present work. The evaluated thermodynamic parameters have been arranged within the framework of the *Thermo-Calc* software, which was originally developed by Sundman et al.[8]

This thermodynamic database can be used to obtain information relating to the following: stable and metastable phase equilibria, the position of the T_0 line, volume fractions of the phase constituents under specified conditions, values of various thermodynamic quantities such as activity, mixing enthalpy, Gibbs
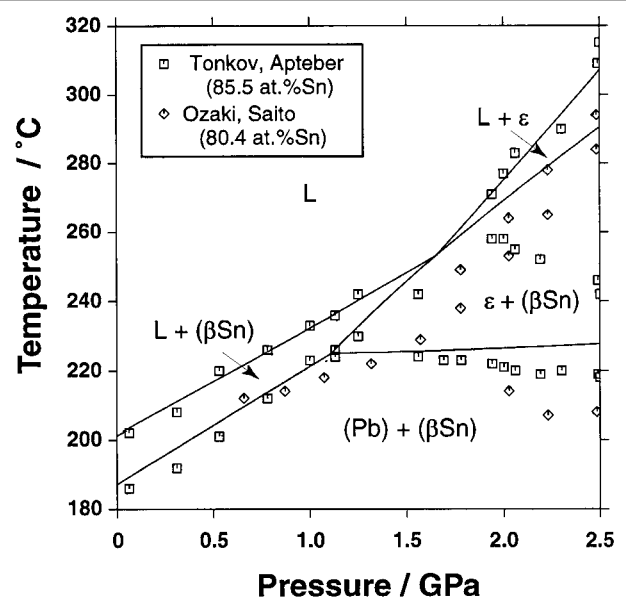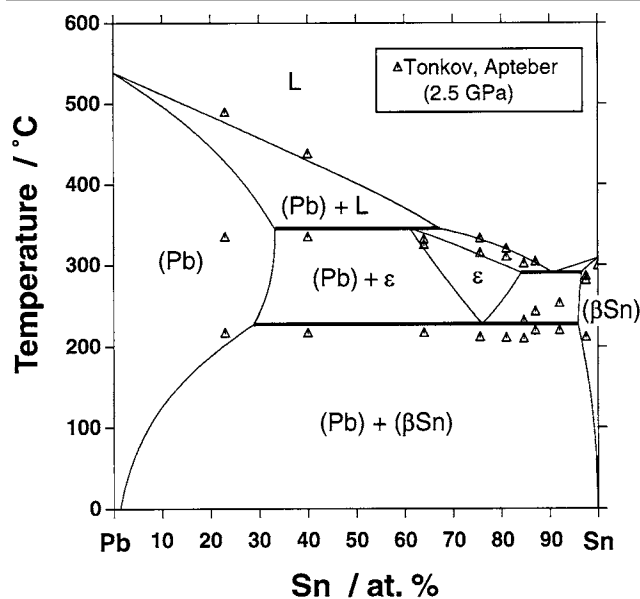
Fig. 4. (a) Pb-Sn binary phase diagram at 2.5 GPa; and (b) effect of pressure on phase boundaries at 85.5 at.% Sn.
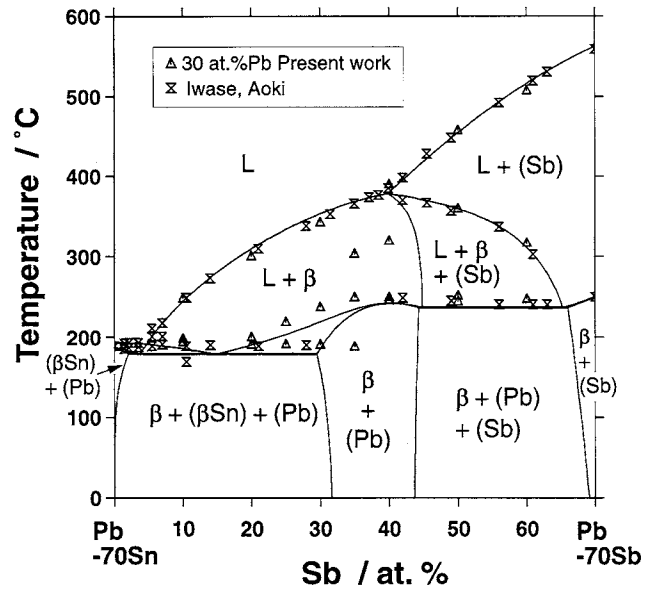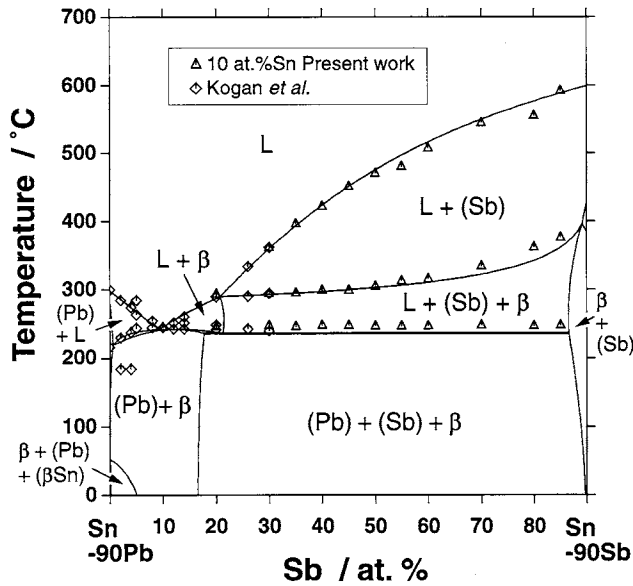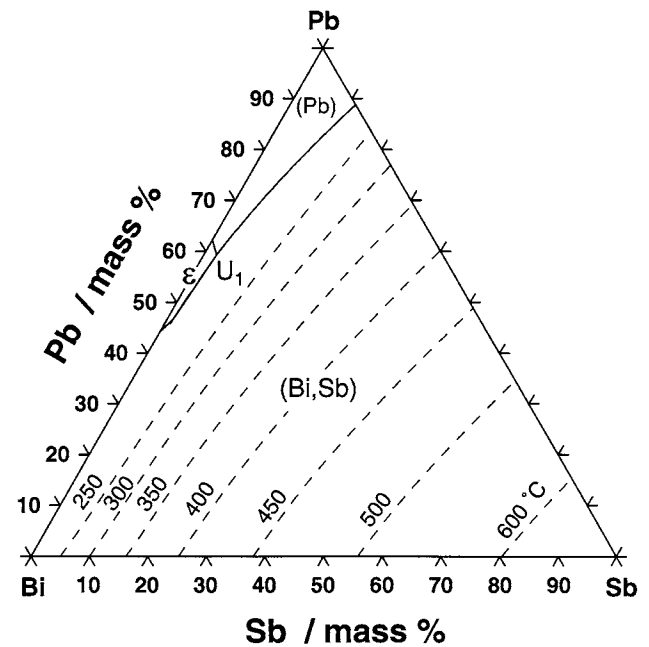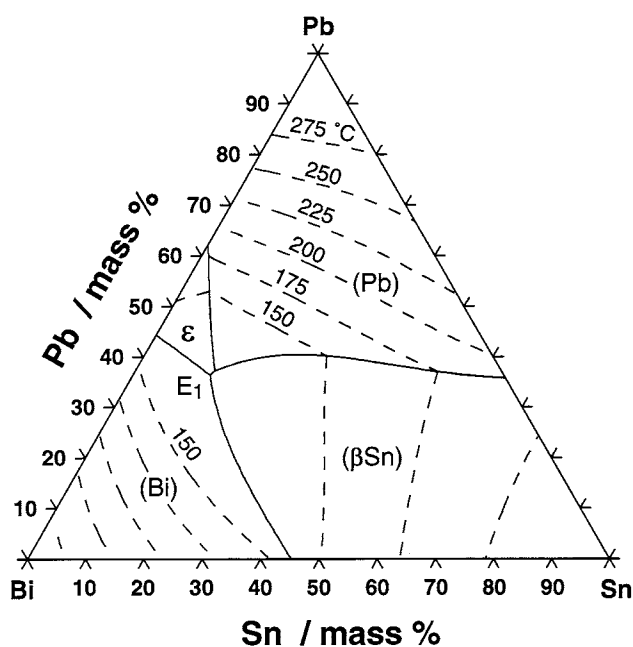
Fig. 5. Vertical section diagrams of the Pb-Sn-Sb system at (a) 10 at.% Sn; and (b) 30 at.% Pb.

energy of formation, driving forces for phase transformation etc., as illustrated in Fig. 2. In addition, physical properties such as surface tension and viscosity in the liquid state, which are very relevant to soldering, can also be calculated from the database. Tanaka and Hara[9] have examined the prediction of surface tension and viscosity in liquid alloys by a number of authors. Tanaka and Iida[10] have developed a successful formalism based on the Butler's theory[11] for calculating the surface tension, while Seetharaman and Sichen[12] have shown that viscosity can be estimated using their recent model. Both models are based on the correct estimation of the Gibbs energy of the liquid phase.

EXAMPLES OF CALCULATION

Pb-Bearing Solders

The Pb-Sn base alloys are extensively used in soldering, because of their low cost, good mechanical properties, wettability, deformability, etc. The stable and metastable phase equilibria in a Pb-Sn binary alloy are shown in Fig. 3.[13] The formation of the metastable two-phase separation in the fcc phase can be forecast by observing the shape of this phase boundary. Actually, a miscibility gap is predicted to exist as shown by the chain line in Fig. 3. Figure 4 shows the phase equilibria at high pressures, where the appearance of a stable area for the high-pressure ε phase is

Fig. 6. Calculated liquidus surface in the (a) Pb-Bi-Sn; and (b) Pb-Bi-Sb systems.
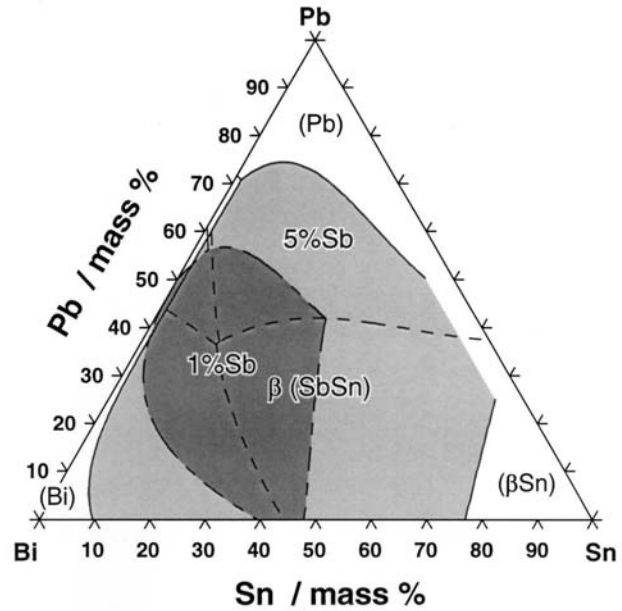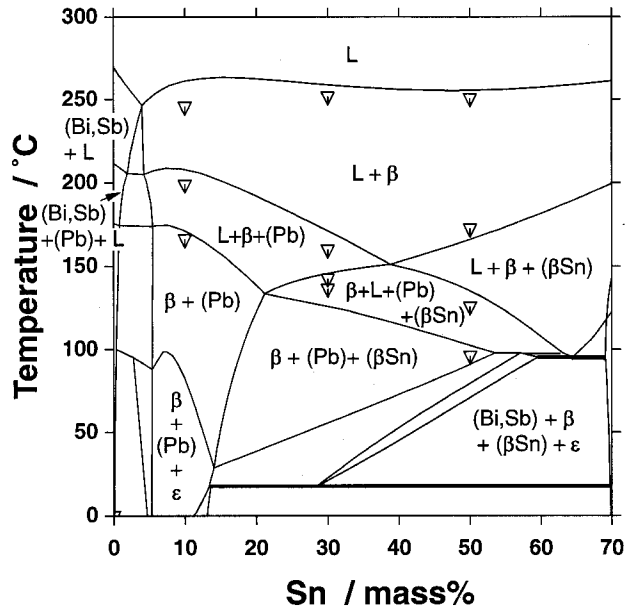
Fig. 7. (a) Calculated vertical section diagram of the Pb-Sn-20mass%Bi-10mass%Sb alloy; and (b) effect of Sb addition on the Pb-Bi-Sn liquidus projection.
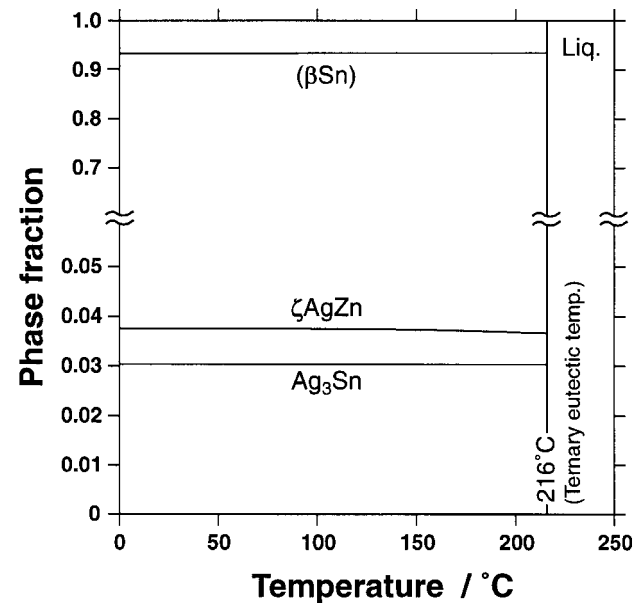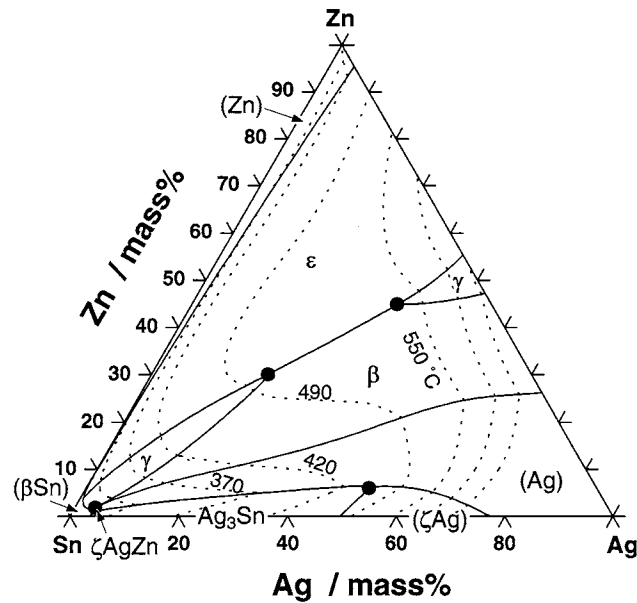

Fig. 8. (a) Liquidus surface; and (b) the phase fraction vs. temperature plot in the Sn-Ag-Zn system.

shown in the composition range of 70 ~ 80 at.% Sn.

Antimony is an important additive for Pb-Sn solders which prevents embrittlement caused by the low temperature transformation of Sn. Figure 5 shows the calculated vertical section diagrams for the Pb-Sn-Sb system, superimposed with experimental data to confirm the validity of the calculation.[13] The agreement between the calculated and observed transitions is quite satisfactory. The other important ternary Pb-base soldering alloys belong to the Pb-Bi-Sn and Pb-Bi-Sb systems, whose liquidus surfaces are shown in Fig. 6. The eutectic point of the Pb-Bi-Sn system at 92°C is denoted by E_1 in Fig. 6a. This alloy system is classified as a soft solder in practical applications.

The thermodynamic assessments of the Pb-Sn-Sb, Pb-Bi-Sn, Pb-Bi-Sb, and Sn-Bi-Sb ternary systems enable the calculation of phase equilibria in the Pb-Sn-Bi-Sb quaternary system. Since there is very little phase diagram information for this system, the phase boundaries were experimentally determined by DSC measurements. Figure 7a shows the comparison between the calculated and the observed phase equilibria in a vertical section of Pb-Sn-20mass%Bi-10mass%Sb alloy. The calculations are based only on the thermodynamic parameters of the four component ternary systems without inclusion of an additional quaternary interaction parameter. The fact that a very good agreement between experiments and
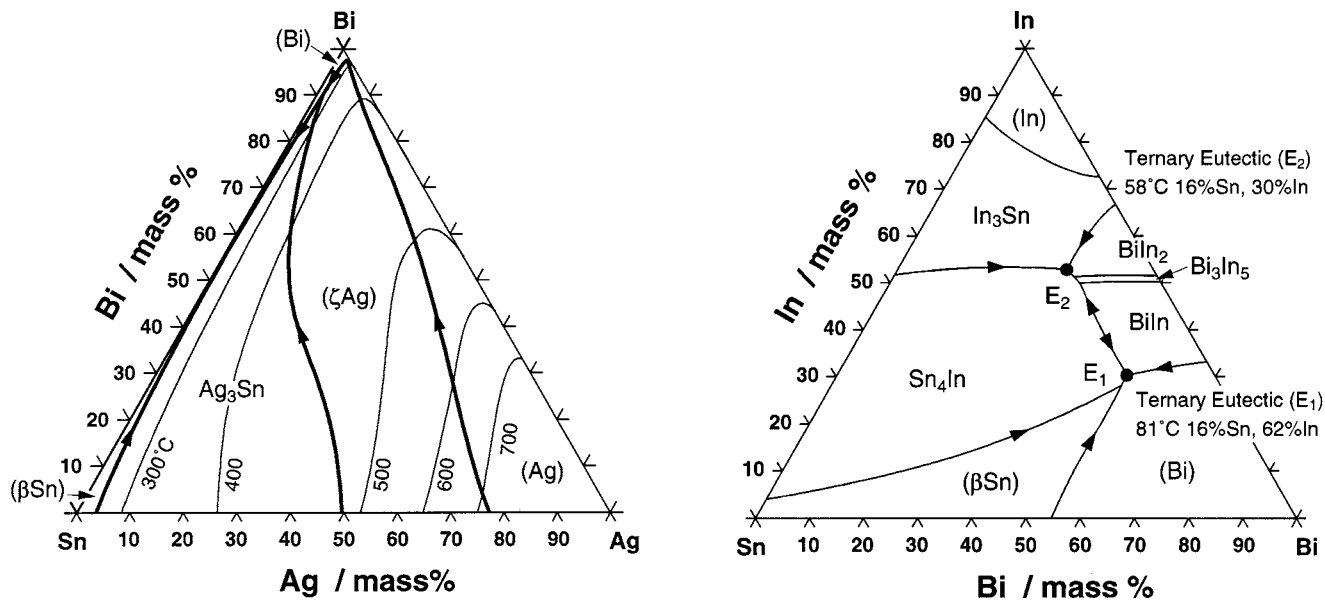
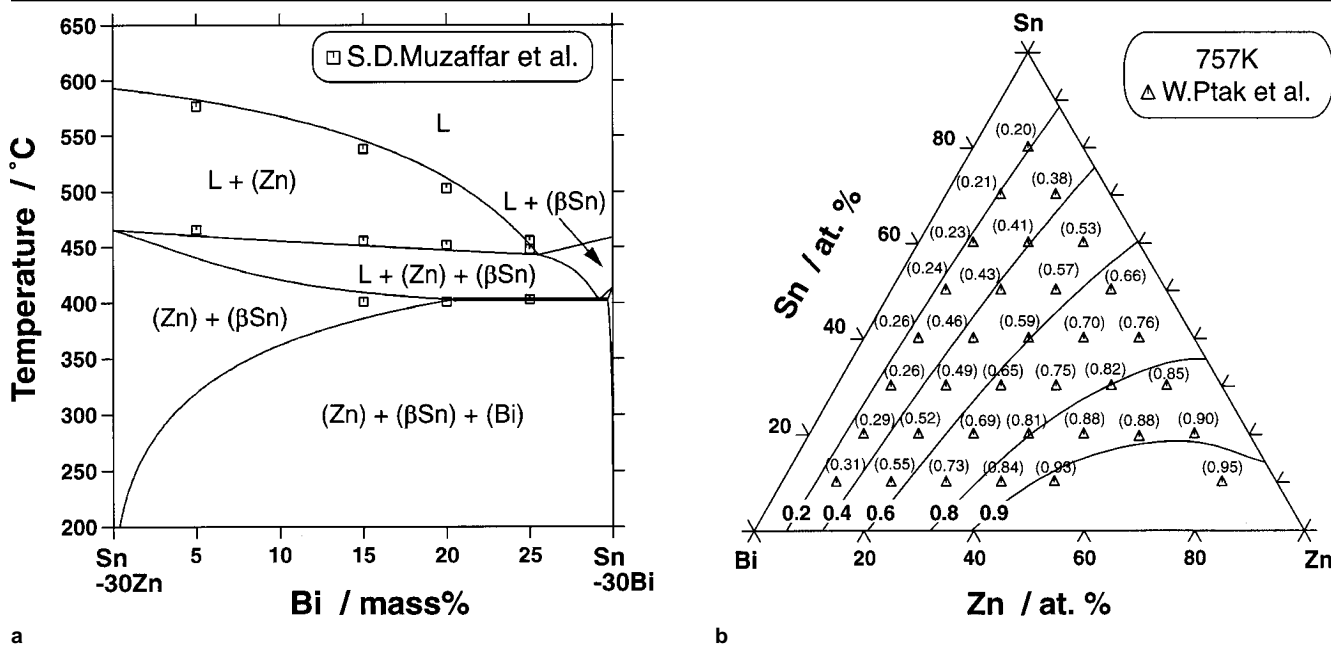Fig. 9. (a) Liquidus surface in the Sn-Bi-Ag system; and (b) liquidus projection in the Sn-Bi-In system.

Fig. 10. (a) Vertical section diagram of the Sn-Bi-Zn system at 70 mass% Sn; and (b) the activitiy of Zn in the liquid phase.

calculation exists, demonstrates that the CALPHAD method is an extremely useful tool in the construction of a complex multicomponent phase diagram, when no experimental information is available in higher order systems. Figure 7b shows the change in the liquidus projection when a small amount of Sb is added to the Pb-Bi-Sn system. The primary β phase field appears in the neighborhood of the Pb-Bi-Sn ternary eutectic point, and the eutectic melting temperature of the alloy rises steeply. The addition of Sb promotes the formation of the intermetallic β phase compound along with Sn. Precipitation of such a high-temperature phase in the solder results in loss of fluidity and the embrittlement of the solder, which explains the empirical observation.

Pb-Free Solders

Interest in Pb-free solders has gathered momentum in recent times and many Pb-free solder alloys have been proposed.[14] But none of the proposed alloys, mostly binary and ternary ones, have been able to satisfy all the required material properties such as melting temperature, mechanical properties, cost, manufacturability, etc. Significant efforts have been made to design Sn-base solders because they have ranges of melting temperatures similar to those of Pb-Sn solders. In view of this, the Sn-Bi-X, Sn-Ag-X, Sn-Zn-X, Sn-Sb-X and Sn-In-X systems might be considered as bases for the new system of Pb-free solder alloys. Several examples of the phase diagrams and
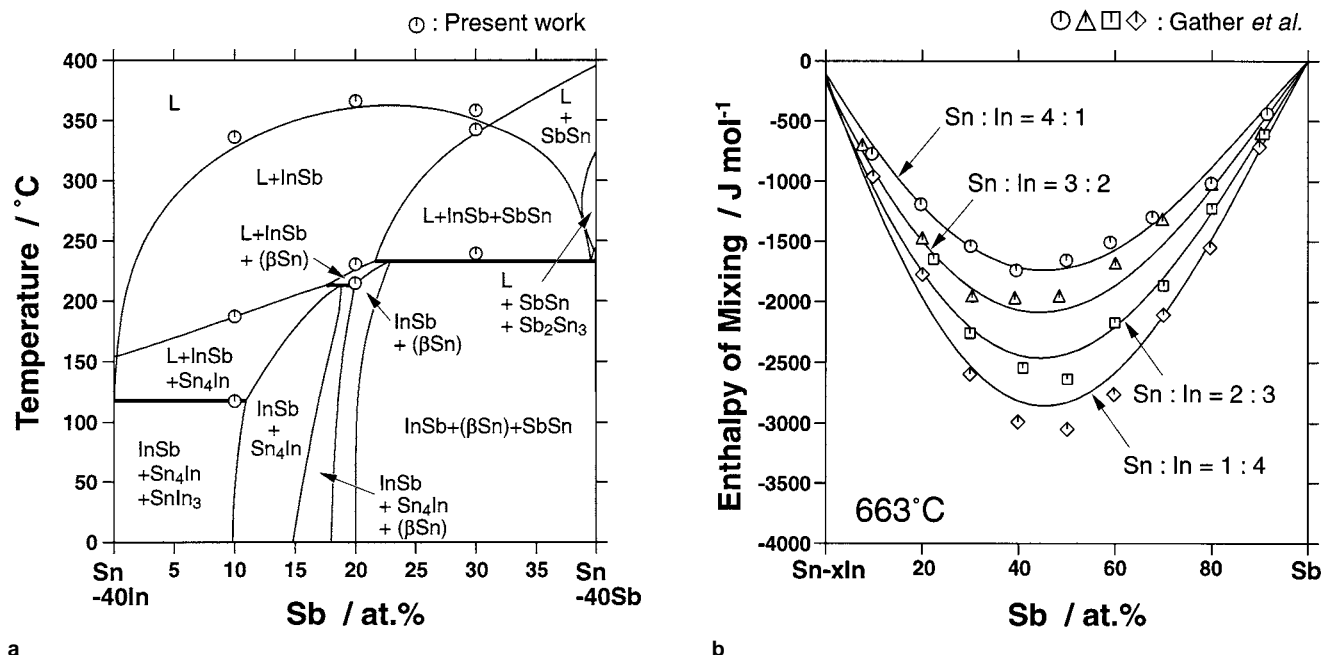
Fig. 11 (a) Vertical section diagram of the Sn-In-Sb system at 60 at.% Sn; and (b) the enthalpy of mixing in the liquid phase at 663°C.
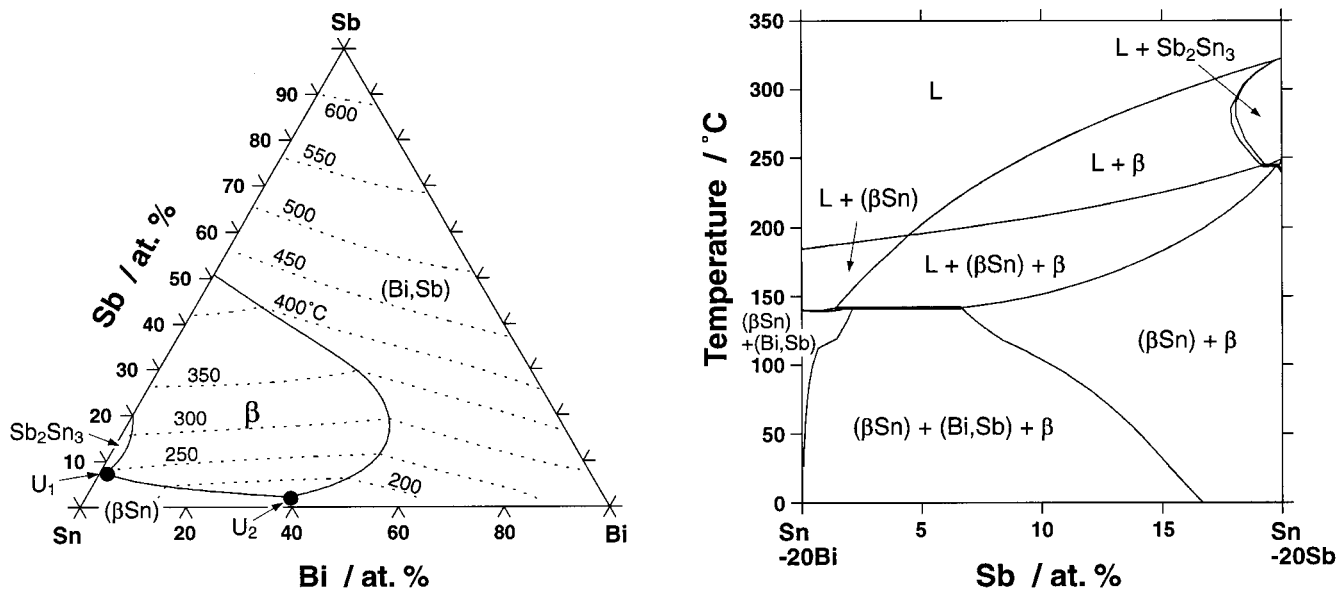

Fig. 12. (a) Liquidus surface; and (b) vertical section diagram of the Sn-Bi-Sb system at 80 at.% Sn.

thermodynamic properties of these Sn-base systems calculated from the database are shown.

Figure 8a shows the liquidus surface of the Sn-Ag-Zn system, where the ternary eutectic point is located at 216°C, at a composition Sn-4mass%Ag-1mass%Zn.[15] Figure 8b shows the variation of the phase fraction with temperature in this eutectic alloy. Figure 9a shows the liquidus surface in the Sn-Bi-Ag system. Figure 9b shows the liquidus projection in the Sn-Bi-In system. The Sn-Bi-In alloy, which has two ternary eutectic points, E_1 and E_2 at 58°C and 81°C, respectively, as shown in Fig. 9b,[16] is suitable for use in a system that requires low melting processing. Figure 10a shows the calculated vertical section diagram[17]

for the 70mass%Sn-Bi-Zn alloy system along with the experimental data[18] for comparison. The thermodynamic activities of components in the liquid phase in this system are shown in Fig. 10b, where the numerical values are the recommended activity data of Zn based on EMF meausrements.[19] Figure 11a shows the calculated vertical section diagram for the 60at.%Sn-In-Sb system. DSC measurements were conducted on alloys of this system to confirm the reliability of the database.[20] Figure 11b shows the comparison of experimental and calculated enthalpy of mixing in the liquid phase of the Sn-In-Sb system.[21] Figure 12 shows the calculated liquidus surface and the vertical section phase diagram at 80at.%Sn[22] for the Sn-Bi-Sb
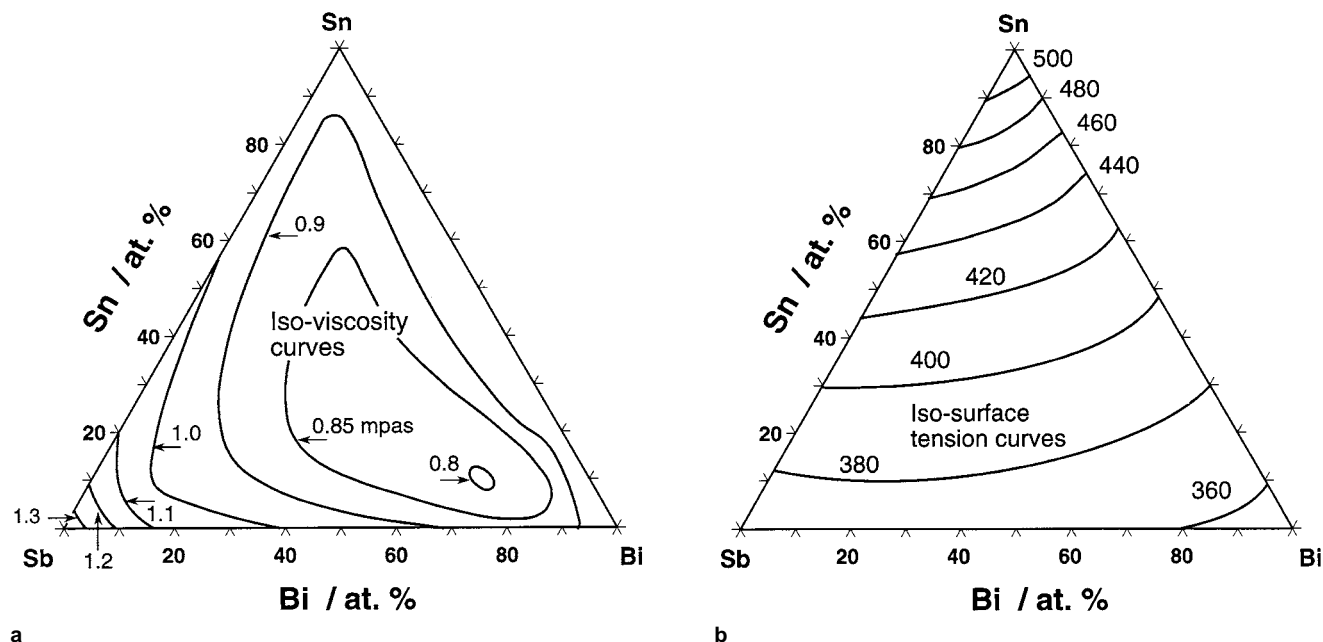
Fig. 13. (a) Viscosity; and (b) surface tension in the Sn-Bi-Sb system at 900 K.

system. The melting temperature of compositions in the region with a small amount of Sb are almost equal to that of the eutectic alloy of the Pb-Sn system currently in use, which means that these alloys could be strong candidates for use as Pb-free solders.

The viscosity and surface tension of Sn-Bi-Sb alloys in the liquid state estimated, using the recently proposed calculation models[9,10,12] and the Gibbs energies of the liquid phase from the thermodynamic database, are shown in Fig. 13. This kind of information would be useful for assessing the melting behavior and the manufacturability of solders from this system.

CONCLUSION

Recent progress in the updating and validation of the database for calculation of phase diagrams in micro-soldering alloy systems, which include the elements Pb, Bi, Sn, Sb, Cu, Ag and Zn is presented. In addition to using earlier experimental information, data generated from experimental determinations of phase equilibria in several binary, ternary and quaternary systems by DSC, EDS and x-ray techniques have also been included in creating the database. This database has been constructed by the CALPHAD method and contains information, not only for calculation of phase diagrams but also for extracting thermodynamic information such as activity, heat of formation enthalpy of mixing, surface energy etc. Several phase diagrams of the Pb-bearing and Pb-free solders have been presented. This database can be used as powerful tool for developing new Pb-free solders.

ACKNOWLEDGEMENT

REFERENCES

1. T. Nishizawa, *Mater. Trans. JIM* 33, 713 (1992).
2. U.R. Kattner, *JOM* 49, 14 (1997).
3. H. Ohtani and K. Ishida, *Thermochimica Acta* 214, 69 (1998).
4. K. Ishida and H. Ohtani, *Computational Materials Design*, ed. T. Saito (Heidelburg, Germany: Springer-Verlag, 1999).
5. N. Saunders and A.P. Miodownik, *CALPHAD* (Lausanne, Switzerland: Pergamon, 1998).
6. A.T. Dinsdale, *CALPHAD* 15, 317 (1991).
7. M. Hillert and L.I. Staffansson, *Acta Chem. Scand.* 24, 3618 (1970).
8. B. Sundman, B. Jansson, and T.O. Anderson, *CALPHAD* 9, 153 (1985).
9. T. Tanaka and S. Hara, *Materia Japan* 36, 47 (1997) (in Japanese).
10. T. Tanaka and I. Iida, *Steel Research* 65, 21 (1994).
11. J.A.V. Butler, *Proc. R. Soc. Lond.* A135, 348 (1932).
12. S. Seetharaman and D. Sichen, *Metall. Mater. Trans. B* 25B, 589 (1994).
13. H. Ohtani, K. Okuda, and K. Ishida, *J. Phase Equilibria* 16, 416 (1995).
14. J. Glazer, *Intern. Mater. Rev.* 40, 65 (1995).
15. H. Ohtani, M. Miyashita, and K. Ishida, *J. Jpn. Inst. Met.* 63, 685 (1999).
16. S. Ishihara, H. Ohtani, and K. Ishida, *Abstracts of the Jpn. Inst. Metals* 121, 386 (1997).
17. D.V. Malakhov, X.J. Liu, I Ohnuma, and K. Ishida, to be submitted to *J. Phase Equilibria*.
18. S.D. Muzaffar, *J. Chem. Soc.* 125, 2341 (1923).
19. W. Ptak and Z, Moser, *Bull. Acad. Polon. Sci.* 19, 1 (1971).
20. S. Ishihara, H. Ohtani, T. Saito, and K. Ishida, *J. Jpn. Inst. Met.* 63, 695 (1999).
21. B. Gather, P. Schroter, and B. Blachnik, *Z. Metallkde.* 76, 523 (1985).
22. H. Ohtani and K. Ishida, *J. Electron. Mater.* 23, 747 (1994).