Phase Equilibria and Thermodynamic Properties of Sn-Ag Based Pb-Free Solder Alloys

Ikuo Ohnuma, Masamitsu Miyashita, Xing Jun Liu, Hiroshi Ohtani, and Kiyohito Ishida

***Abstract*—We have recently developed a thermodynamic database for micro-soldering alloys, alloy database for micro-solders (ADAMIS). ADAMIS which consists of the elements Ag, Bi, Cu, In, Pb, Sb, Sn, and Zn has been constructed by the calculation of phase diagrams (CALPHAD) method. The thermodynamic parameters for describing the Gibbs energy of the liquid and solid phases have been evaluated by optimizing the experimental data on phase boundaries and thermo-chemical properties. In this paper, the phase equilibria and the related thermodynamic properties pertaining to the Sn-Ag-X (X = Bi, In, Cu, and Zn) alloys are examined using ADAMIS. Typical examples of the isothermal and vertical section phase diagrams, liquidus surface, etc. for these promising lead-free solders are presented. In addition, ADAMIS is also applied to calculate the nonequilibrium solidification process using the Scheil model.**

***Index Terms*—CALPHAD, micro-solder alloy, phase equilibria, thermodynamic database.**

I. Introduction

LEAD-TIN base solders have long been the most popular materials for electronic packaging because of their low cost and excellent properties required for interconnecting electronic components. However, the toxic nature of lead and the increasing awareness of its adverse effect on environment and health has given rise to the pressing need for development of lead-free solders in recent years. The nontoxic substitute materials should satisfy the following criteria to serve as effective replacements for lead. They should

1) be in plentiful supply;
2) possess melting and solidifying temperatures not too far away from the existing solder alloys;
3) be highly conductive;
4) possess strength and toughness;
5) be wettable;
6) cost the same as the lead-bearing solder.

It has been suggested earlier that the Sn-Bi-X, Sn-In-X, Sn-Zn-X, and Sn-Ag-X systems could satisfy the foregoing criteria as the promising candidates for lead-free solders [1]. Of these, the Sn-Ag-X system is considered to be the most hopeful alloy for substituting the eutectic lead-tin base solders because, as shown in Fig. 1, the eutectic temperature of the Sn-Ag alloy (221 °C) is close to that of the Pb-Sn system (183 °C). Recently,

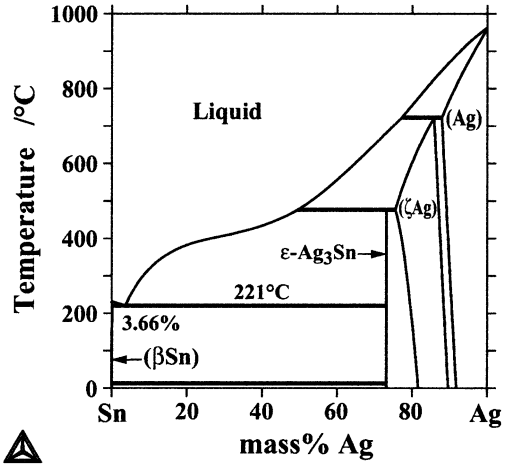

Fig. 1. Calculated phase diagram of the Sn-Ag system.

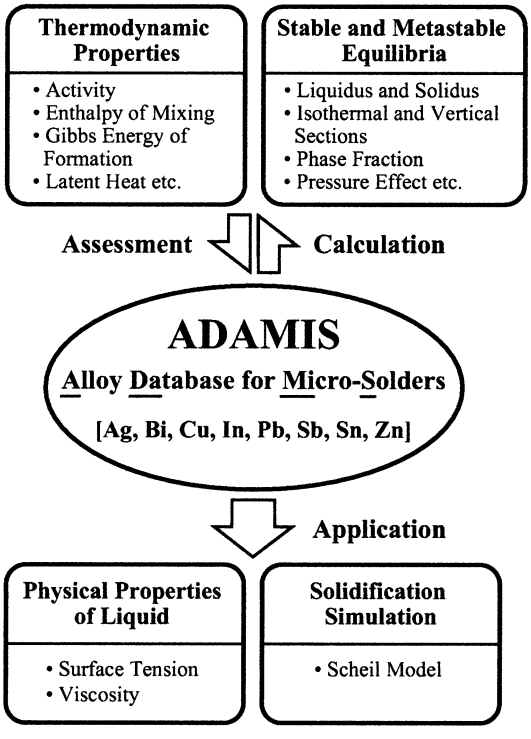

Fig. 2. Scheme of ADAMIS.

the author's group [2], [3] has developed a thermodynamic database alloy database for micro-solders (ADAMIS) for use in designing micro-soldering alloys containing the elements Ag, Bi, Cu, In, Pb, Sb, Sn, and Zn based on the calculation of phase diagrams (CALPHAD) method [4]. Fig. 2 shows the scheme

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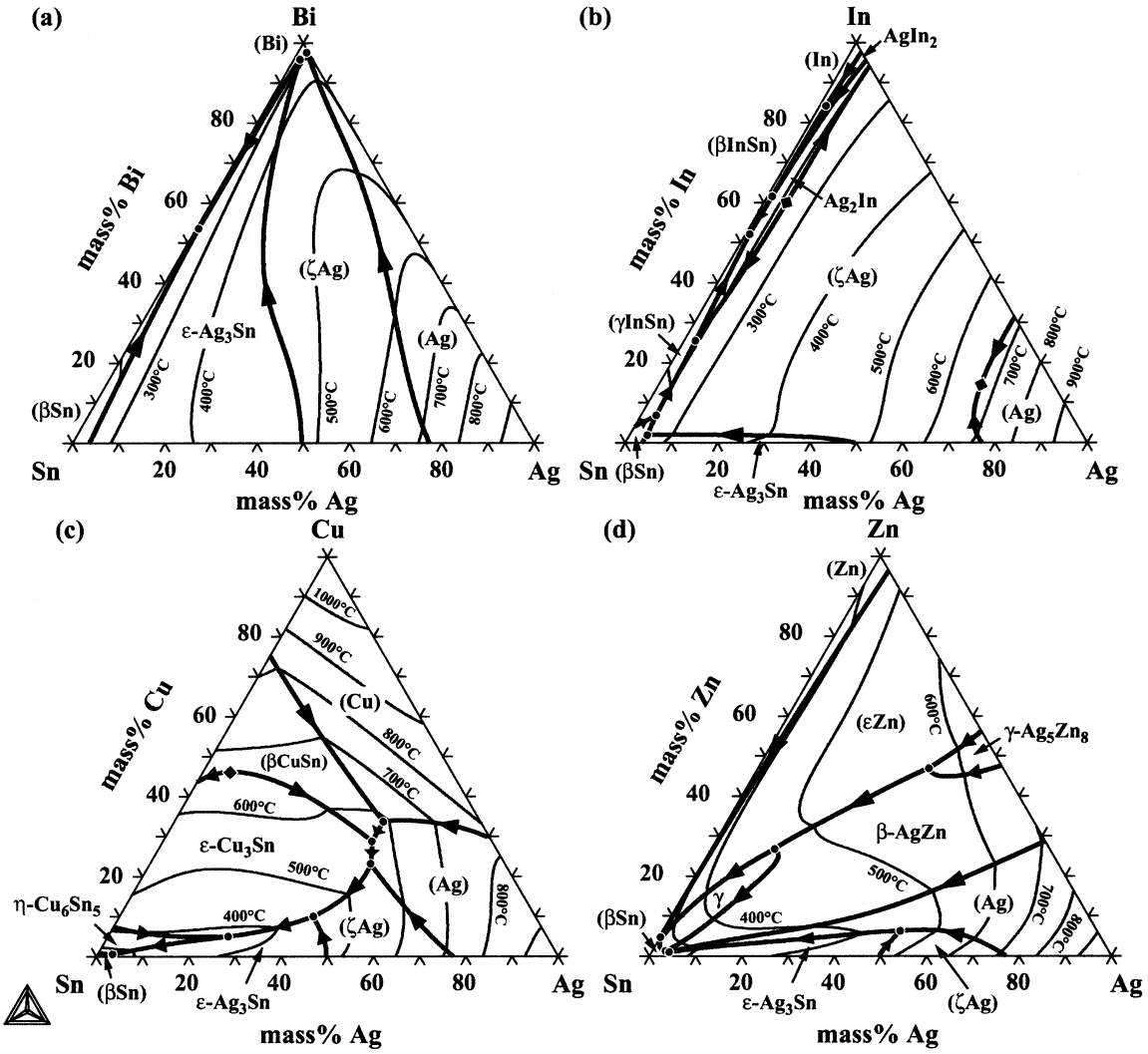

Fig. 3. Liquidus surfaces of Sn-Ag-X (X = (a) Bi, (b) In, (c) Cu, and (d) Zn) ternary systems.

of ADAMIS. In this paper, the phase equilibria and the related properties of the Sn-Ag-X (X = Bi, Cu, In, and Zn) systems calculated using ADAMIS are presented.

II. Thermodynamic Evaluation

The phase equilibria in the Sn-Ag-X ternary alloys were experimentally determined by the differential scanning calorimetry (DSC), energy dispersive x-ray spectroscopy (EDS), x-ray diffraction, and the metallographic techniques.

The thermodynamic parameters for describing the Gibbs energy of the liquid and solid phases of all the binary systems were then evaluated by optimizing the present experimental results as well as the previous data on the phase boundaries and thermochemical properties such as activities, heat of mixing, enthalpy of formation and so on. The lattice stabilities of pure elements were taken from the Scientific Group Thermodata Europe (SGTE) database compiled by Dinsdale [5] and those for some metastable phases were evaluated by our group. The thermodynamic assessments are based on the following binary systems; Ag-Sn [6], [7], Ag-Bi [6], Ag-Cu [8], Ag-In [9], Ag-Zn [7], Sn-Bi [10], Sn-Cu [11], Sn-In [12], and Sn-Zn [7], [13]. The assessments of all the ternary systems were carried out by our group and the details on the Sn-Ag-Bi [14], Sn-Ag-In [9], Sn-Ag-Cu [15], and Sn-Ag-Zn [7] systems were presented elsewhere. The thermodynamic parameters were arranged within the framework of the Thermo-Calc software [16].

III. Results of Calculation

A. Phase Diagrams

Some examples of phase diagram calculations in the Sn-Ag-X ternary alloys are shown. Fig. 3 shows the calculated liquidus surface of the (a) Sn-Ag-Bi, (b) Sn-Ag-In, (c) Sn-Ag-Cu, and (d) Sn-Ag-Zn ternary systems. From these diagrams, the melting temperatures can be obtained for different compositions, facilitating the choice of substitute materials for the Pb-bearing solder alloys. Fig. 4(a)–(d) show the isothermal sections for these ternary systems with the superimposed experimental data. As shown in these diagrams, the agreements between the experimental data and the calculations are quite satisfactory. The effect of alloying elements Bi, In, Cu, and Zn on the phase equilibria of the Sn-3.66mass%Ag eutectic alloy is shown in Fig. 5. This constitutes as the basic information for the alloy design of Sn-Ag base Pb-free solders.

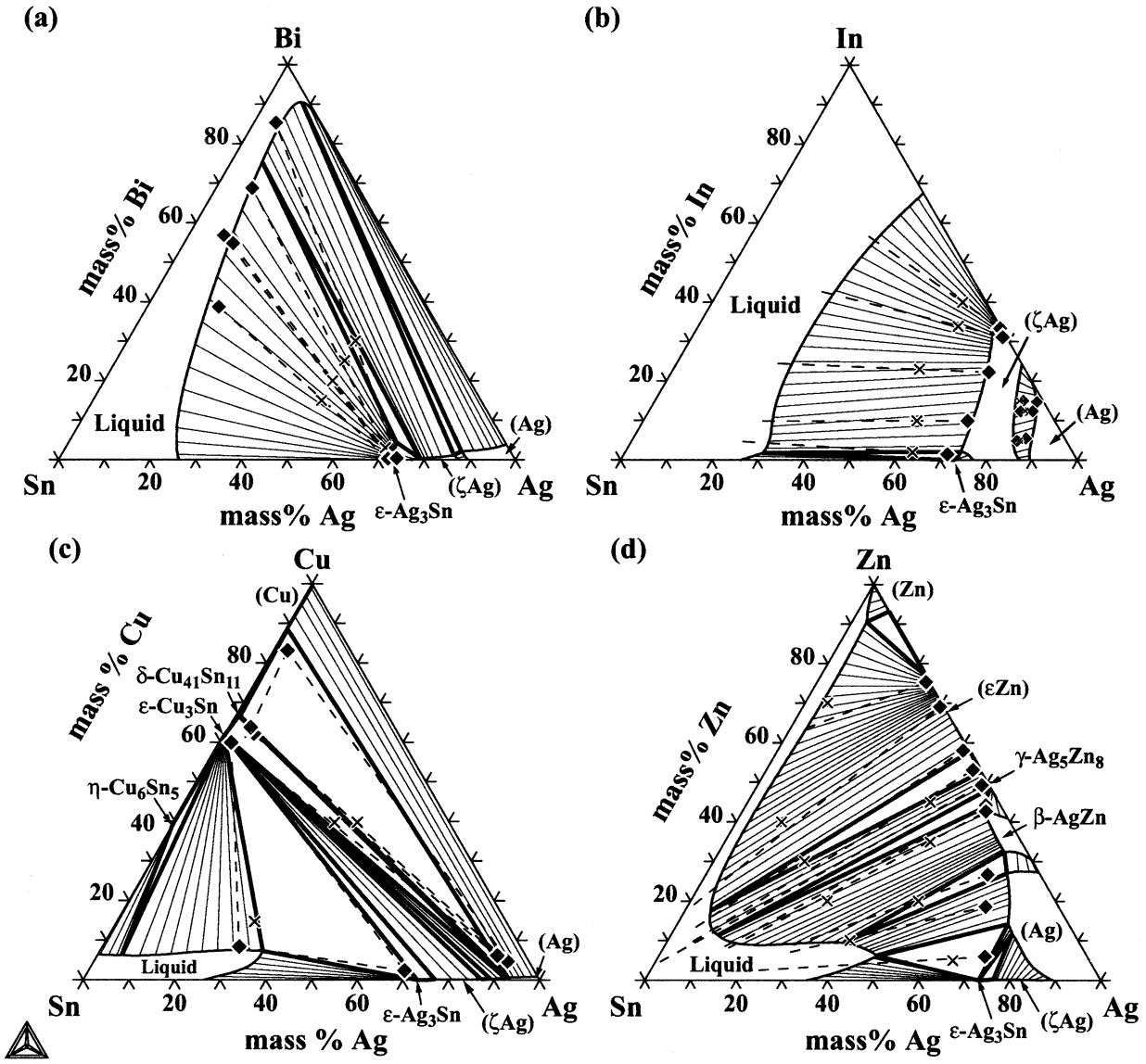

Fig. 4. Iso-thermal section phase diagrams of Sn-Ag-X (X = (a) Bi, (b) In, (c) Cu, and (d) Zn) ternary systems.

B. Solidification Simulation

It has often been observed that nonequilibrium solidification occurs in solder alloy systems during solidification. Therefore, for precision in alloy design, it is necessary to take into account this nonequilibrium effect to satisfactorily simulate the real solidification process in a practical situation. Such a solidification process can be simulated by the Scheil model, assuming local equilibrium at the liquid/solid interface and no diffusion in the solid phase. Fig. 6(a) shows the calculated mass fraction of the solid phases versus the temperature variation of Sn-0.3Ag-0.7Cu alloy under equilibrium (solid curve) and Scheil-model (dashed curve) solidification conditions. In both cases, the solidification starts at 226.9 °C with the primary crystals of (βSn) and is terminated when it reaches the ternary eutectic reaction, Liquid $\Rightarrow$ (βSn) + ε-Ag_3Sn + η-Cu_6Sn_5, at 217.7 °C. The difference between the two cases seems to be quite small. In the so called "Alloy H" of composition Sn-2.0Ag-0.5Cu-7.5Bi (mass%), which is one of the promising candidates for a Pb-free solder [17], solidification would start at 215.5 °C and terminate at 177.9 °C under equilibrium conditions as shown in Fig. 6(b). However, the Scheil simulation exhibits a significant amount of liquid phase would remain even at 139.9 °C. The presence of liquid phase at such a low temperature would be considered a draw-back because this would result in the so-called lift-off defect at the junction between the connecting wire, solder and the Cu substrate [18].

C. Other Properties

The micro-soldering alloy database has a potential to predict other properties such as the surface tension and viscosity of a melt, which can be calculated based on the thermodynamic model [19]–[21]. Fig. 7 shows the calculated surface tension and viscosity of Sn-Ag-Cu liquid alloys at 800 °C. These kinds of information are expected to be useful for assessing the melting behavior and the feasibility of Pb-free solder manufacture.

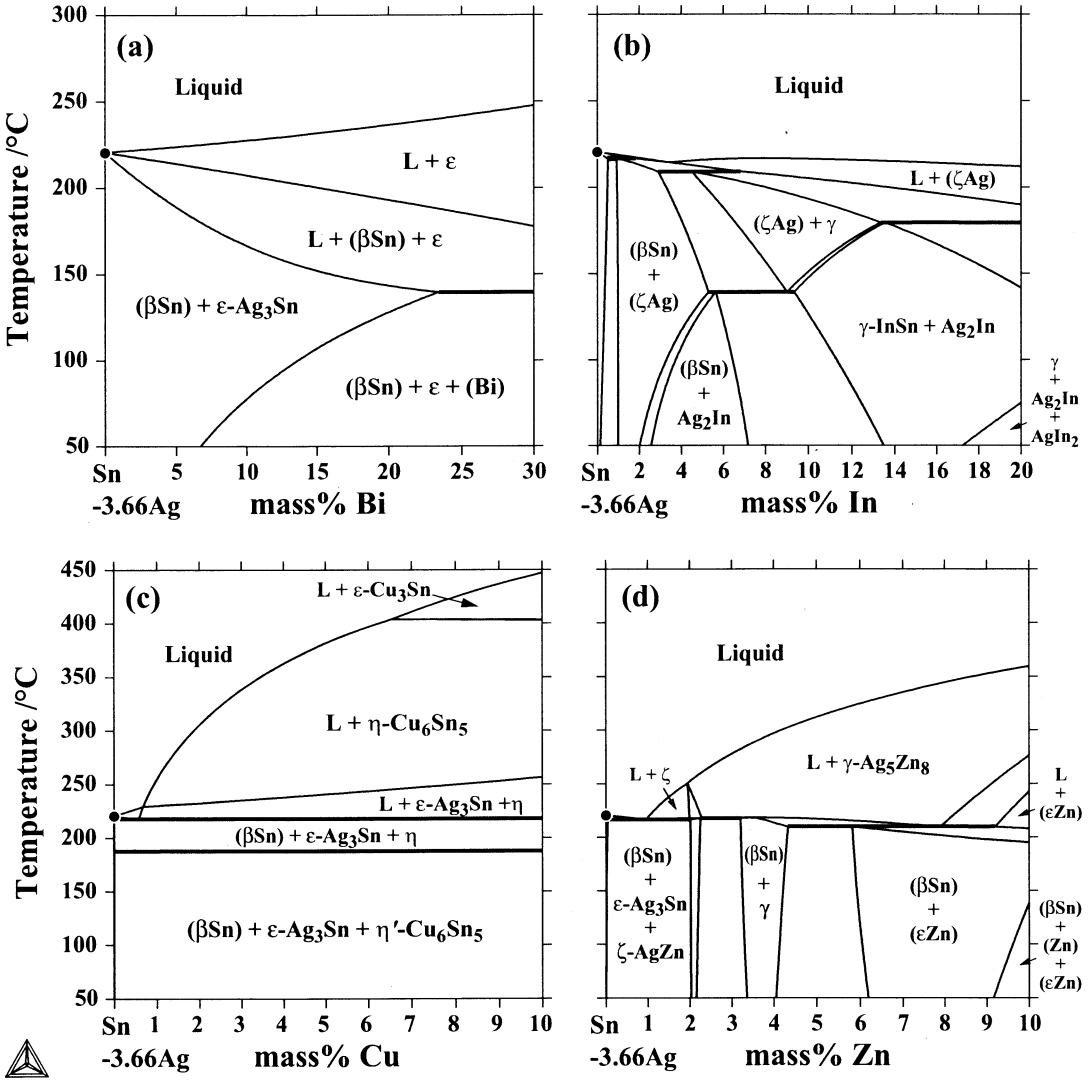

Fig. 5. Vertical section phase diagrams of Sn-Ag-X (X = (a) Bi, (b) In, (c) Cu, and (d) Zn) ternary systems.

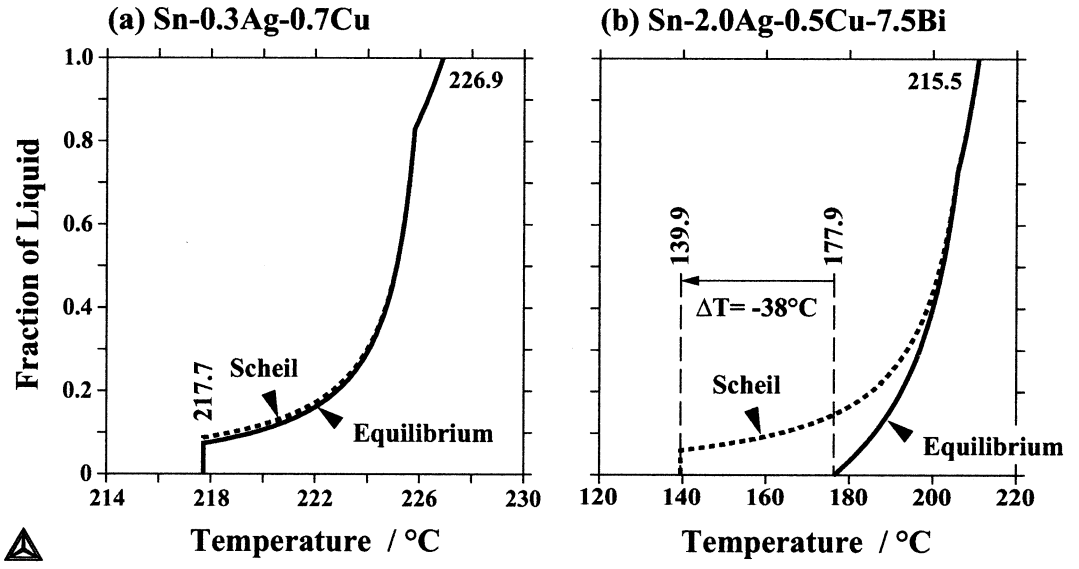

Fig. 6. Equilibrium and nonequilibrium (Scheil model) solidification simulation of (a) Sn-0.3Ag-0.7Cu (mass%) and (b) Sn-2.0Ag-0.5Cu-7.5Bi (alloy H [16]).

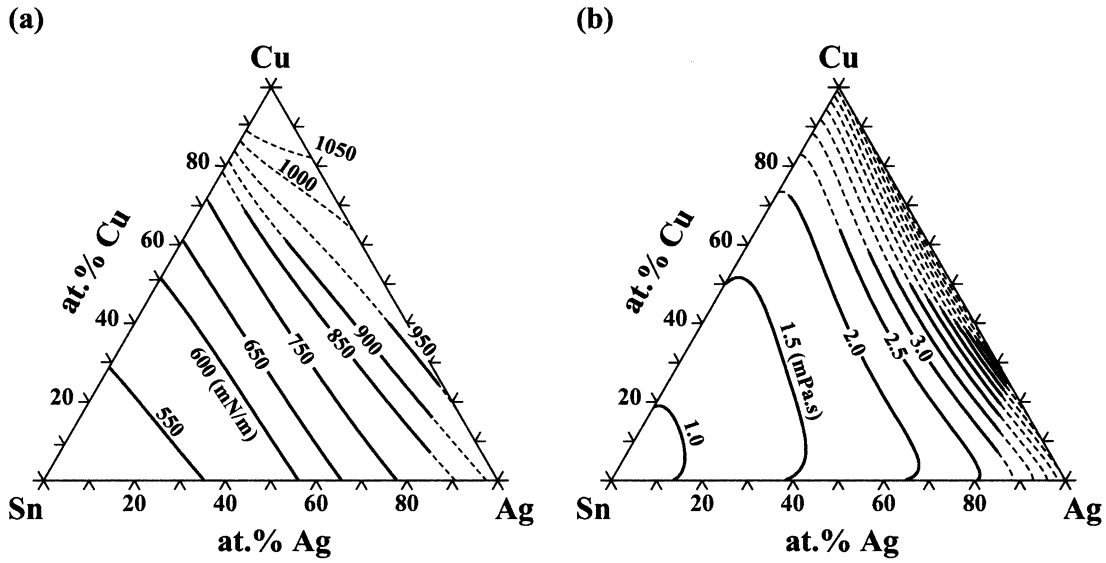

Fig. 7. Calculated (a) surface tension and (b) viscosity of Sn-Ag-Cu liquid alloy at 800 °C.

IV. Summary

Phase equilibria in the Sn-Ag-X (X = Bi, Cu, In, and Zn) ternary systems were investigated and the thermodynamic assessment of these alloy systems were carried out based on the results of the newly determined phase boundaries as well as previous experimental data. It is shown that the present database can be applied for the prediction not only of phase equilibria but also other properties such as nonequilibrium solidification processes, surface tension and viscosity in solder alloys. This database will be quite useful for the alloy design and development of the Pb-free solder alloys.

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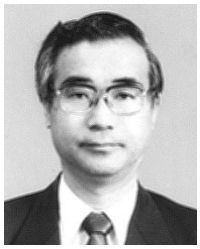

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