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Pb-Free Solders: Part 1. Wettability Testing of Sn-Ag-Cu Alloys with Bi Additions

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Maximum bubble pressure, dilatometric, and meniscographic methods were used in the investigations of the surface tension, density. wetting time, wetting force, contact angle, and interfacial tension of liquid alloys of Sn-Ag-Cu eutectic composition with various additions of Bi. Density and surface tension measurements were conducted in the temperature range 250-900 °C. Surface tensions at 250 °C measured under a protective atmosphere of Ar-H_2 were combined with data from meniscographic studies done under air or with a protective flux. The meniscographic data with a nonwetted teflon substrate provided data on interfacial tension (solder-flux), surface tension in air, and meniscographic data with a Cu substrate allowed determinations of wetting time, wetting force, and calculation of contact angle. The calculated wetting angles from meniscographic studies for binary Sn-Ag eutectic and two ternary Sn-Ag-Cu alloys were verified by separate measurements by the sessile drop method under a protective atmosphere with a Cu substrate. Additions of Bi to both ternary alloys improve the wettability and move the parameters somewhat closer to those of traditional Sn-Pb solders.

Keywords density, meniscographic studies, Pb-free solders, surface tension

1. Introduction

The electronics industry in Europe is facing an impending change; a European Community Memorandum has been issued and it requires the use of Pb-free soldering materials instead of traditional Sn-Pb solders everywhere in the Community after July 1, 2006. The two main substitutes that are currently being considered are the eutectics, Sn-Ag [melting point (m.p.) 221 °C] and Sn-Ag-Cu (m.p. 217-219 °C), with both melting points being higher than that of the Sn-Pb eutectic (m.p. 183 °C), and therefore both will require higher soldering temperatures for industrial applications. This justifies searching for substitute materials with properties closer to those of traditional solders. In 1998, a program was initiated at the Institute of Metallurgy and Materials Science in Krakow in which surface tension, density, and meniscographic measurements were to be made on pure metals, low-melting binary eutectics, and ternary alloys based on Sn-Ag eutectic. Modeling was to be done by the Butler method.[1] Work has progressed and in cooperation with Tohoku University, Sendai, Japan, experimental studies[2-5] of surface tension have been combined with optimized thermodynamic parameters to create the SURDAT database[6,7] for the physical properties of Pb-free solders.

To improve the wettability and to lower the melting temperature of Pb-free solders, cooperation with Tohoku has been extended to include multicomponent alloys based on the Ag-Cu-Sn eutectic composition. Past work has included studies of Bi additions,[8] Sb additions,[9] and combined Bi and Sb additions.[10] In these joint studies, the ADAMIS database was used from Tohoku University. This database contains optimized thermodynamic parameters for modeling of surface tension, phase diagram calculations, and simulation of solidification. Some studies[11] on electrical and mechanical properties have been made at our laboratory as part of our overall solder program.

Among the extensive publications in the literature pertaining to Pb-free solders, two recent publications are particularly important. One is the book of Hwang,[12] which details the property differences between Pb-free solders and traditional Pb-Sn solders wherein the differences in wettability are indicated to be of particular importance. The second publication by Lopez et al.[13] considers the relationship of surface tension and contact angle with wettability. These two reports offer suggestions useful in the analysis of data from the present and previous[14] investigations and will be considered in the discussion section of the present report. The main purpose of the current investigative program is to measure the effects of alloying additions on Pb-free solders. This is to be done by combining surface tension and density data with interfacial tension and contact angle data to find links between these basic data and industrial application of Pb-free solders. The present report is Part I of this phase of the overall investigation and deals with measurements of surface tension by the maximum bubble pressure method, density by dilatometry, and of both surface tension and

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contact angle by meniscographic studies. The alloying addition in this study is Bi. Part II of the investigative program will deal with the modeling of the surface tension of the same Sn-Ag-Cu-Sn-Bi alloy compositions as measured in Part I with modeling results to be compared with experimental results and will be extended to a calculation of the phase diagram and simulation of the solidification. In Parts III and IV, studies similar to the earlier Sn-Ag-Cu-Bi study[8] will be made for quinary Sn-Ag-Cu-Bi-Sb alloys.

2. Experimental Procedure

Surface tension measurements were made by the maximum bubble pressure method, densities were measured dilatometricly, and wetting forces and contact angles were evaluated from meniscographic studies. Test materials were the binary Sn-Ag eutectic and two Sn-Ag-Cu alloys, (Sn-2.76Ag-0.46Cu and Sn-3.13Ag-0.74Cu with numerical values in at.%), whose compositions are near that of the ternary eutectic. These initial studies have now been extended to the quaternary Sn-Ag-Cu-Bi system with four alloy compositions having been studied. A preliminary oral report was presented[9] during Calphad XXXIII. The complete results are discussed in detail in the present paper. A preliminary report on extension to the quinary Sn- Ag-Cu-Bi-Sb system has been presented at the 2005 annual TMS meeting,[10] and a full report is now being prepared for publication. There are several goals for these investigations. One goal of these studies is to expand the limited data in the literature and develop an extensive database for the physical properties of Pb-free solders. Inclusion in this database of meniscographic results should provide a measure of the sensitivity of the wettability of Sn-Ag-Cu alloys to compositional changes and to the presence of foreign species. The ultimate goal is, of course, to develop a Pb-free solder that closely approximates the melting temperature and desirable soldering characteristics of Sn-Pb solders.

After completing the meniscographic studies on the quaternary Sn-Ag-Cu-Bi alloys while using a new method of calibration, examination of the total of the available data indicated that a remeasurement of the three alloys studied by Gasior et al.[14] should be repeated. Results of new measurements at ~250 °C are shown in Fig. 1. The top plot in the figure is the surface tension under a protective gas of an argon-hydrogen mixture over the liquid alloy. The solid circles in the plot represent the three alloys studied by Gasior et al.,[14] and the open circles represent data for alloys of higher Cu concentrations from earlier measurements by Moser et al.[4] It may be noted that the plot correlates with melting temperatures in the ternary phase diagram in the sense that the interfacial tension at first decreases with small Cu additions as the alloys move from the Sn-Ag eutectic toward the lower melting ternary eutectic but rises with increasing Cu content beyond the ternary eutectic composition. The middle plot in Fig. 1 with the open diamond points is the surface tension as measured under atmospheric air. The lower plot with the solid diamond points is the interfacial determination σ_{LF} between solder/flux. For the current study the flux in all cases was

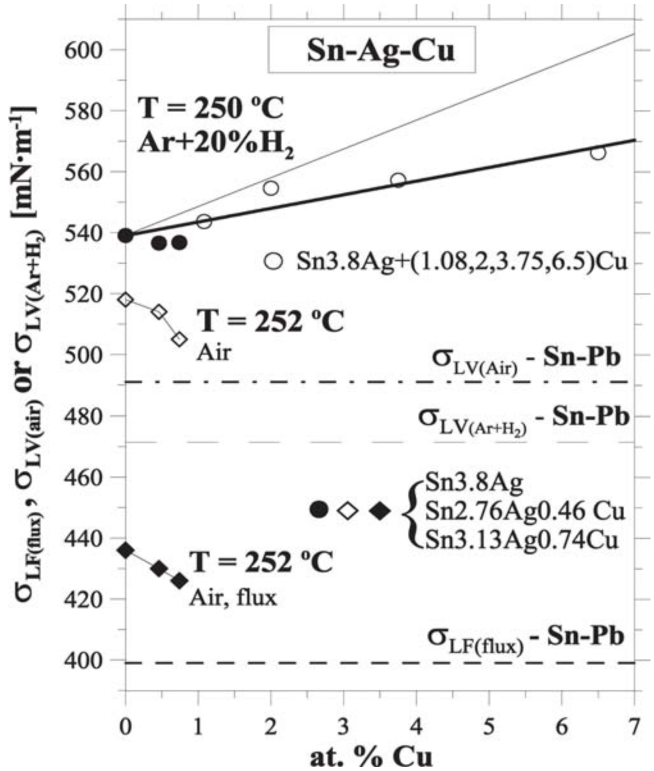


Fig. 1 The plot shows the effect of Cu additions to eutectic Sn-Ag alloy on surface or interfacial tension. Upper and middle plots show results of maximum bubble pressure measurements for surface tension under (upper plot) a protective atmosphere or (middle plot) air from the Miyazaki method.[16] The lower plot represents meniscographic determination of interfacial tension of the solder/flux interface. The open circles in the upper plot are older data,[4] which are included to show that the initial addition of Cu first drop the surface tension from that of the eutectic Sn-Ag solder toward that of the Sn-Ag-Cu ternary eutectic but rise again on the Cu-rich side of the ternary eutectic. Corresponding invariant values for classic Sn-Pb solders are shown by horizontal dashed or dash-dot lines for comparison.

the ROL1(3% solids), which has previously been found to be superior to any other flux that has been tested at our laboratory.[14] This flux is an alcoholic solution of organic solids and rosin activated by halogens. For comparison, values for the equivalent quantities[15] for a Sn-Pb eutectic solder are shown by horizontal lines, and they are in every case lower than the Sn-Ag or Sn-Ag-Cu alloy solders.

Surface tensions for four Sn-Ag-Cu-Bi alloys were measured over the temperature range 250-900 °C by the maximum bubble pressure method under a protective argon-hydrogen atmosphere and the data are plotted in Fig. 2(a) and (b). Two plots are used to avoid a mixed jumble of experimental points. In Fig. 2(a), the triangles are for the 4.02 at.% Bi alloy, and the open and closed triangles represent data from duplicate runs, while the open solid squares represent data for the 6.81 at.% Bi alloy. In Fig. 2(b), the open diamonds represent the 3.86 at.% Bi alloy, and the solid squares represent the 6.62 at.% Bi alloy. In both Fig. 2(a) and (b), data for comparison purposes are shown for

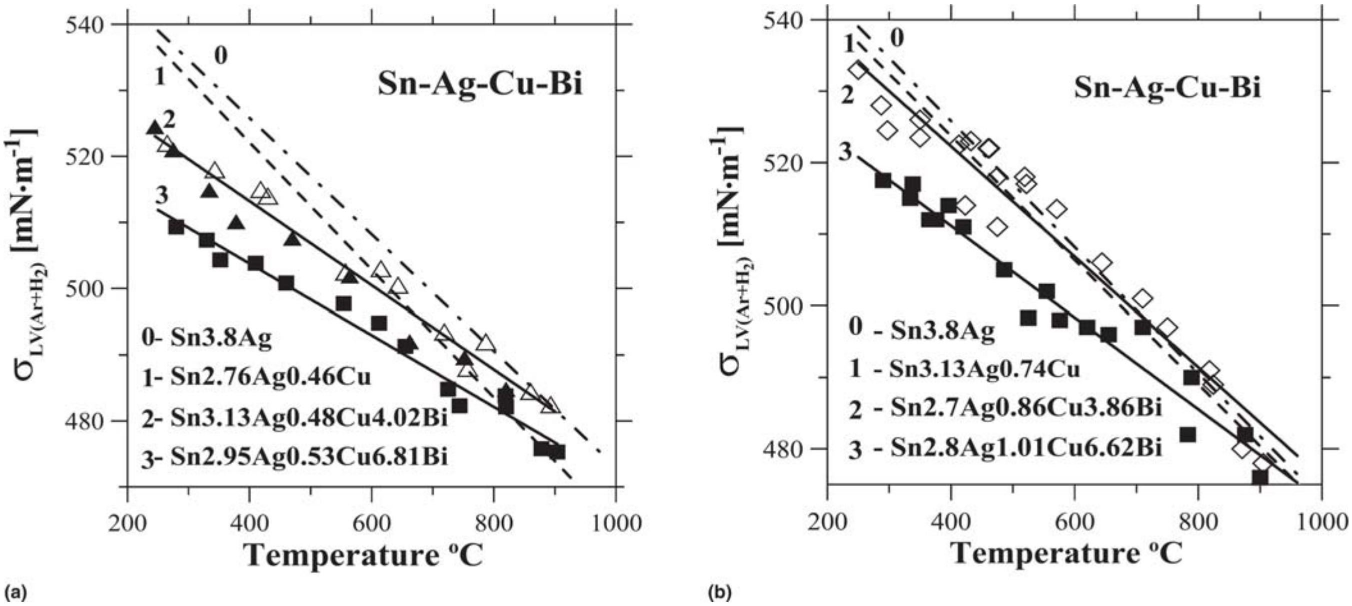


Fig. 2 Temperature dependence of surface tension of four quaternary Sn-Ag-Cu-Bi alloys. The data are divided into two plots to avoid a confusion of data points. In (a) data for 4.02 and 6.81 at.% Bi additions are shown, and in (b) 3.86 and 6.62 at.% Bi additions are shown. The triangles, diamonds, and squares represent individual data points. The solid and open triangles in (a) represent two separate runs to test for reproducibility. The solid lines represent least squares fits to the data points. Data for eutectic Sn-Ag solder is shown in both plots as a dash-dot line, and the dashed line in (a) is for a ternary alloy with 0.46 at.% Cu and in (b) for a 0.74 at.% Cu ternary alloy.

Table 1 Temperature dependencies of the surface tension of four Sn-Ag-Cu-Bi alloys together with comparative values for two near-eutectic Sn-Ag-Cu alloys and eutectic Sn-Ag alloy with uncertainities in slope and intercept (in protective atmosphere Ar+H$_2$)

Alloy, mass%	Alloy, at.%	$\sigma = A + BT$, mNm^{-1}	$\sigma_{250\ °C}$, mNm^{-1}	Err (A), mNm^{-1}	Err (B), mNm^{-1} K^{-1}
Sn3.65Ag(a)	Sn3.8Ag (a)	$= 585.1 - 0.0881T$	539.0 ± 8.2	±8.1	±0.0086
Sn2.56Ag0.26Cu(a)	Sn2.76Ag0.46Cu(a)	$= 587.0 - 0.0964T$	536.6 ± 7.8	±7.4	±0.0086
Sn2.86Ag0.40Cu(a)	Sn3.13Ag0.74Cu(a)	$= 582.1 - 0.0867T$	536.7 ± 6.9	±5.8	±0.0068
Sn2.77Ag0.25Cu6.91Bi	Sn3.13Ag0.48Cu4.02Bi	$= 555.3 - 0.0623T$	522.7 ± 6.2	±5.1	±0.0062
Sn2.56Ag0.27Cu11.45Bi	Sn2.95Ag0.53Cu6.81Bi	$= 540.1 - 0.0541T$	511.9 ± 4.5	±4.8	±0.0053
Sn2.4Ag0.45Cu6.65Bi	Sn2.7Ag0.86Cu3.86Bi	$= 574.6 - 0.0778T$	533.9 ± 8.8	±7.8	±0.0094
Sn2.49Ag0.52Cu11.17Bi	Sn2.86Ag1.01Cu6.62Bi	$= 550.4 - 0.0581T$	520.0 ± 7.9	±7.3	±0.0082

(a) Ref. 14

the eutectic Sn3.8Ag alloy by dash-dot lines and for the ternary Sn3.13Ag0.74Cu and Sn2.76Ag0.46Cu alloys by dashed lines. The solid lines in Fig. 2(a) and (b) represent linear least-squares fits to the experimental points. Numerical representation of these fits are shown with uncertainties in Table 1, and some binary and ternary data are included for comparison. On average, the scatter is ~2-3% but is somewhat less for lower temperature data than for higher temperature data.

Figure 3(a) and (b) are plots of the temperature dependency of the density of the same four Sn-Ag-Cu-Bi alloys, again divided to avoid overlap confusion. Solid squares in Fig. 3(a) represent the 4.02 at.% Bi alloy and in Fig. 3(b) the 3.86 at.% Bi alloy, and the open triangles in Fig. 3(a) represent the 6.81 at.% Bi alloy and in Fig. 3(b) the 6.62 at.% Bi alloy. Again a dash-dot line representing the behavior of the Sn-Ag eutectic alloy and a dashed line representing a ternary Sn-Ag-Cu alloy are shown for comparison. The solid lines represent least-square fits to the experimental data points and numerical values for those fits with their uncertainties are shown in Table 2. Molar volumes are important thermodynamic quantities that can be derived from these densities, and these are plotted in Fig. 4. Again data for binary and ternary molar volumes are shown for comparison.

A meniscograph is a device for measuring the dynamic process of wetting. With a method proposed by Miyazaki et al.,[16] a meniscograph can be used for measuring interfacial tension between solder and flux, surface tension between solder and air on nonwetted teflon samples and on Cu coupons for wetting time, wetting force, and contact angle. More detailed discussions of the procedures can be found in reports of earlier work[4,14] where a graph[14] of the force on a meniscographic balance versus time shows how the wet-

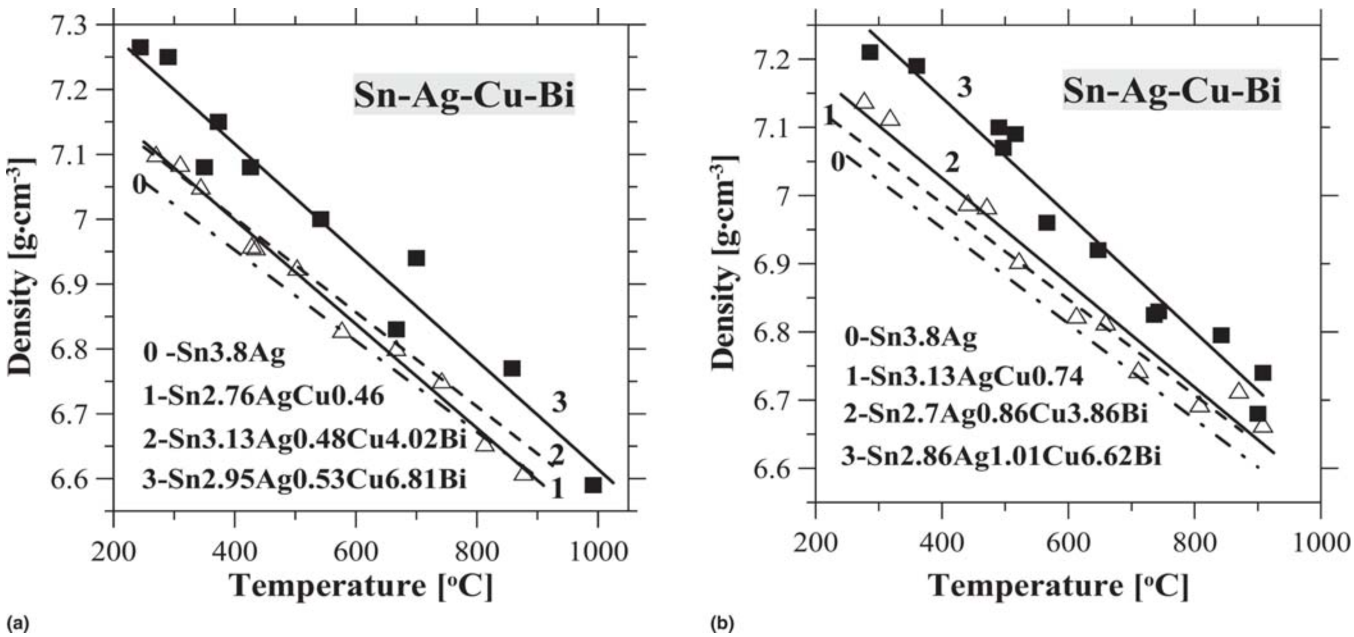


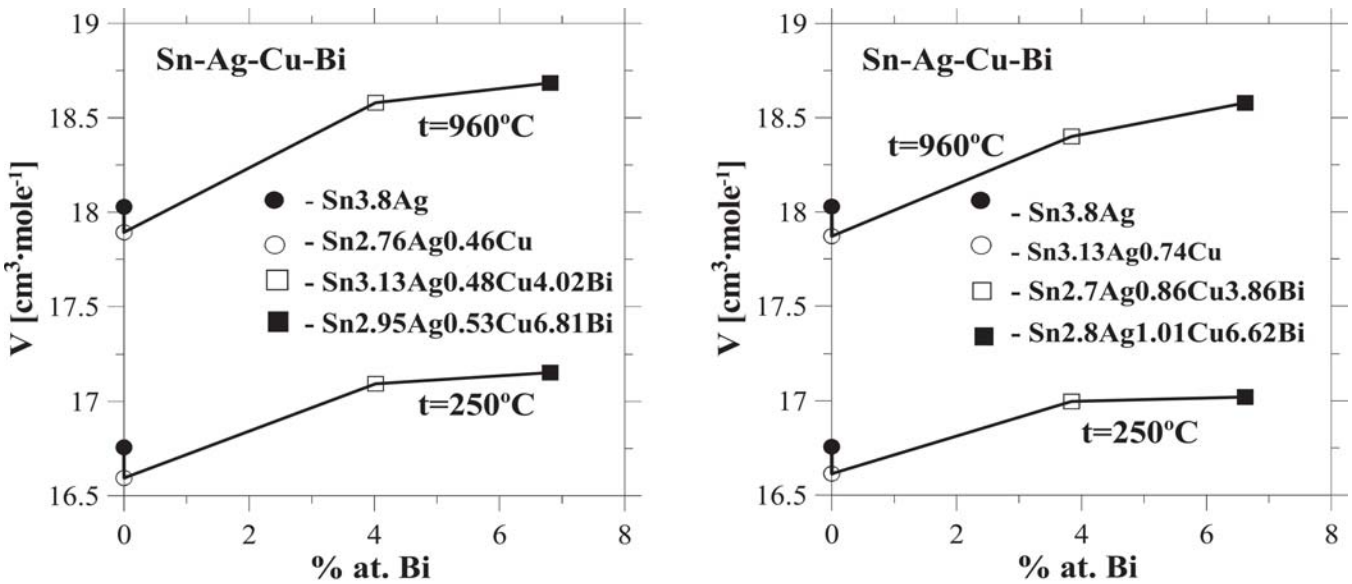
Fig. 3 Temperature dependence of density of four quaternary Sn-Ag-Cu-Bi alloys. The data are divided into two plots to avoid a confusion of data points in (a) data for 4.02 and 6.81 at.% Bi additions are shown, and in (b) 3.86 and 6.62 at. % Bi additions are shown. The triangles, diamonds, and squares represent individual data points. The solid lines represent least squares fits to the data points. Data for eutectic Sn-Ag solder are shown in both plots as a dash-dot line and the dashed line in (a) is for a ternary alloy with 0.46 at.% Cu and in (b) for a 0.74 at.% Cu ternary alloy.

Table 2 Temperature dependencies of the density of four Sn-Ag-Cu-Bi alloys together with comparative values for two near-eutectic Sn-Ag-Cu alloys and eutectic Sn-Ag alloy with uncertainties in slope and intercept (in protective atmosphere Ar+H_2)

Alloy, mass%	Alloy, at.%	$\rho = A + BT$, g cm^{-1}	$\rho_{(250\ °C)}$, g cm^{-1}	Err (A), g cm^{-1}	Err (B), g cm^{-1} K^{-1}
Sn3.65Ag(a)	Sn3.8Ag(a)	$= 7.445 - 0.000739T$	7.059 ± 0.054	±0.042	±0.000051
Sn2.56Ag0.26Cu(a)	Sn2.76Ag0.46Cu(a)	$= 7.458 - 0.000691T$	7.096 ± 0.037	±0.050	±0.000058
Sn2.86Ag0.40Cu(a)	Sn3.13Ag0.74Cu(a)	$= 7.462 - 0.000703T$	7.094 ± 0.027	±0.028	±0.000035
Sn2.77Ag0.25Cu6.91Bi	Sn3.13Ag0.48Cu4.02Bi	$= 7.539 - 0.000802T$	7.119 ± 0.043	±0.049	±0.000059
Sn2.56Ag0.27Cu11.45Bi	Sn2.95Ag0.53Cu6.81Bi	$= 7.678 - 0.000836T$	7.241 ± 0.121	±0.126	±0.000148
Sn2.4Ag0.45Cu6.65Bi	Sn2.7Ag0.86Cu3.86Bi	$= 7.542 - 0.000767T$	7.141 ± 0.078	±0.092	±0.000103
Sn2.49Ag0.52Cu11.17Bi	Sn2.86Ag1.01Cu6.62Bi	$= 7.722 - 0.000859T$	7.272 ± 0.082	±0.096	±0.000105

(a) Ref. 14

ting time and wetting force are determined. The contact angle from meniscographic measurements is a calculated angle whereas the contact angle from a sessile drop measurement is a directly measured angle. A comparison of data for the contact angles from sessile drop and meniscographic values for the binary Sn-Ag eutectic and two ternary Sn-Ag-Cu solders is shown in Table 3 where the meniscographic values are consistently lower by the order of 10-15°. This difference is in a large part attributable to the presence of a flux during meniscographic measurements, which is absent during the sessile drop measurements. Sessile drop measurements were made with a vertical furnace fitted with a macro-convector, which allowed a motion-picture camera to take pictures of a solder drop resting on a Cu substrate under a protective Ar-H_2 atmosphere. The camera was switched on prior to melting of the drop and temperature was raised to the desired temperature of measurement. Both surface tension and contact angle were determined with this apparatus by evaluation of the pictures with a special program designed for that purpose. In Table 4, values for wetting time, wetting force, contact angle, interfacial tension, surface tension with flux under air, and surface tension under a protective atmosphere are given for five quaternary Sn-Ag-Cu-Bi alloys, and other binary and ternary data are included to provide a comparison for evaluation of the effect of Bi addition. In Fig. 5(a) and (b) meniscographic data are used to illustrate the effect of Bi on interfacial tension with the top data representing surface tension under a protective atmosphere, middle data representing the surface tension under air, and the lower data representing the interfacial tension with the presence of a flux.



(a) (b)

Fig. 4 Isotherms of the molar volume of the quaternary Sn-Ag-Cu-Bi alloys compared with binary eutectic Sn-Ag and ternary alloys: (a) Sn2.76Ag0.46Cu with data for 4.02 and 6.81 at.% Bi additions and (b) Sn3.13Ag0.74Cu with data for 3.86 and 6.62 at.% Bi additions.

Table 3 Calculated contact angles from meniscographic studies together with experimental values from sessile drop measurements

		Contact angle	
Type of alloy	**Alloy, at.%**	**Sessile drop method**	**Meniscographic method**
Binary eutectic	Sn3.8Ag	58°	47°
Ternary alloy	(Sn3.8Ag) + 0.46Cu	56°	45°
Ternary alloy	(Sn3.8Ag) + 0.74Cu	61°	46°

3. Discussion

The experimental results indicate that Bi additions to Sn-Ag-Cu alloys decrease the surface tensions of the alloys in both air and in a protective Ar-H_2 atmosphere. The amount of decrease increases with increasing Bi addition. However, in air the surface tension with higher Bi additions is lower than the surface tension of Sn-Pb eutectic alloys, but under an Ar-H_2 atmosphere, the surface tension of the alloys with Bi additions are at all concentrations significantly higher than that of Sn-Pb eutectic alloys. This lowering of surface tension with the addition of an alloying component suggests a qualitative improvement in wettability, but it does not provide a sufficiently generalized metric of wettability. When modeling new solders, a tendency to lower surface tension by alloying additions has in the past often been assumed as sufficient for indication of improved wettability. Therefore, instead of measurements, surface tensions have been calculated by means of Butler's method.[1] The thermodynamic data requisite for such calculations were readily found for binary and ternary systems, but their availability was quite limited for higher-order systems. This difficulty has now been overcome through use of optimized thermodynamic parameters from the ADAMIS database being compiled at Tohoku University in Japan. Surface tension measured under a protective atmosphere determines only one term in the Young-Dupre relation. The use of the sessile drop method can be useful for the determination of contact angles and thence determining the difference ($\sigma_{SV} - \sigma_{SL}$). In this latter relation, σ_{SV} is the substrate-vapor (Cu-gas) tension and σ_{SL} is the substrate-liquid (Cu-solder) interfacial tension, and the sign of the difference will determine whether there will be a tendency for wetting or for beading.

From a practical view with a goal of a practical lead-free solder to function at ~250 °C, the addition to surface tension studies of meniscographic studies are very important because they produce values for wetting force and wetting time and, with inclusion of interfacial tensions, allow calculation of contact angles. Then with the Young-Dupre equation, the more practical relation ($\sigma_{SF} - \sigma_{SL}$) can be evaluated. Here σ_{SF} indicates the substrate-flux interfacial tension with σ_{SF} replacing the foregoing σ_{SV} in the realistic case where a flux is used to facilitate wetting. Thus the technique can be used to select the best flux from among a number of possibilities.

Surface tensions at 250 °C measured under a protective atmosphere of Ar-H_2 were combined with data from meniscographic studies, which were done under air or with a protective flux. Meniscographic data with a nonwetted teflon substrate provide data on interfacial tension (solder-flux), and meniscographic data with a Cu substrate allow determinations of wetting time, wetting force, and surface tension in air, and a calculation of contact angle. Interfacial tensions and contact angles are the two parameters most important as a metric of wettability. The change in these two parameters, which is indicated in Table 4 by values for the sequence from binary, to ternary, to the quaternary Sn-Ag-Cu-Bi alloys, makes clear that the changes in these two parameters correlate with decreasing wetting time and increasing wetting force. Unfortunately the initial results[10] on quinary Sn-Ag-Cu-Bi-Sb alloys do not show a continuation of these trends. Observations make clear that the suggestions concerning the role of wetting time and wetting force in a recent paper by Lopez et al.[13] are correct with respect to the fact that wetting force is not a generalized metric of solderability because it cannot account for the significant effect of the solder/flux interfacial tension on the wetting and spreading phenomenon.[17] On the other hand, wetting time is rather more representative of wetting kinetics than wettability. Because of this, the wetting time and wetting force together with contact angles are often used in practice for comparison of various solders and they do not exhibit a general dependence upon composition as do the interfacial tension in combination with contact angles.

Table 4 Results from meniscographic studies with solder/flux interfacial tension and surface tension in air are evaluated in the manner of Miyazaki et al.[16]
Surface tension values under a protective atmosphere from maximum bubble pressure measurements are also shown

Alloy, mass%	Wetting time τ_z, s	Wetting force after 2 s F_2, mN	Contact angle after 3 s θ_3, °	Interfacial tension solder/flux [1997Miy], mN/m	Surface tension air [1997Miy], mN/m	Surface tension Ar + H_2, mN
Sn3.65Ag(a)	0.38 ± 0.03	5.38 ± 0.18	47 ± 1	436 ± 5	518 ± 6	539.0 ± 8.2
Sn2.56Ag0.26Cu(a)	0.40 ± 0.03	5.52 ± 0.20	46 ± 3	430 ± 6	514 ± 8	536.6 ± 7.8
Sn2.86Ag0.40Cu(a)	0.37 ± 0.02	5.40 ± 0.17	46 ± 2	426 ± 4	505 ± 4	536.7 ± 6.9
Sn2.77Ag0.25Cu6.91Bi	0.21 ± 0.01	6.96 ± 0.02	22 ± 1	399 ± 5	491 ± 8	522.7 ± 6.2
Sn2.56Ag0.27Cu11.45Bi	0.21 ± 0.04	6.72 ± 0.02	25 ± 0	394 ± 4	473 ± 3	511.9 ± 4.5
Sn2.4Ag0.45Cu6.65Bi	0.27 ± 0.02	6.67 ± 0.04	29 ± 1	408 ± 6	488 ± 4	533.9 ± 8.8
Sn2.49Ag0.52Cu11.17Bi	0.18 ± 0.04	6.95 ± 0.12	21 ± 2	397 ± 4	487 ± 6	520.0 ± 7.9
Sn2.76Ag0.27Cu7.44Bi(b)	0.23 ± 0.04	6.97 ± 0.05	23 ± 1	401 ± 4	480 ± 9	520.7 ± 4.2
SnPb	0.32 ± 0.02	7.66 ± 0.04	0.0	491 ± 11	399 ± 5	471.4 ± 6.3

(a) Ref 14, (b) second quaternary alloy with 7.4 mass%. Bi to check reproducibility

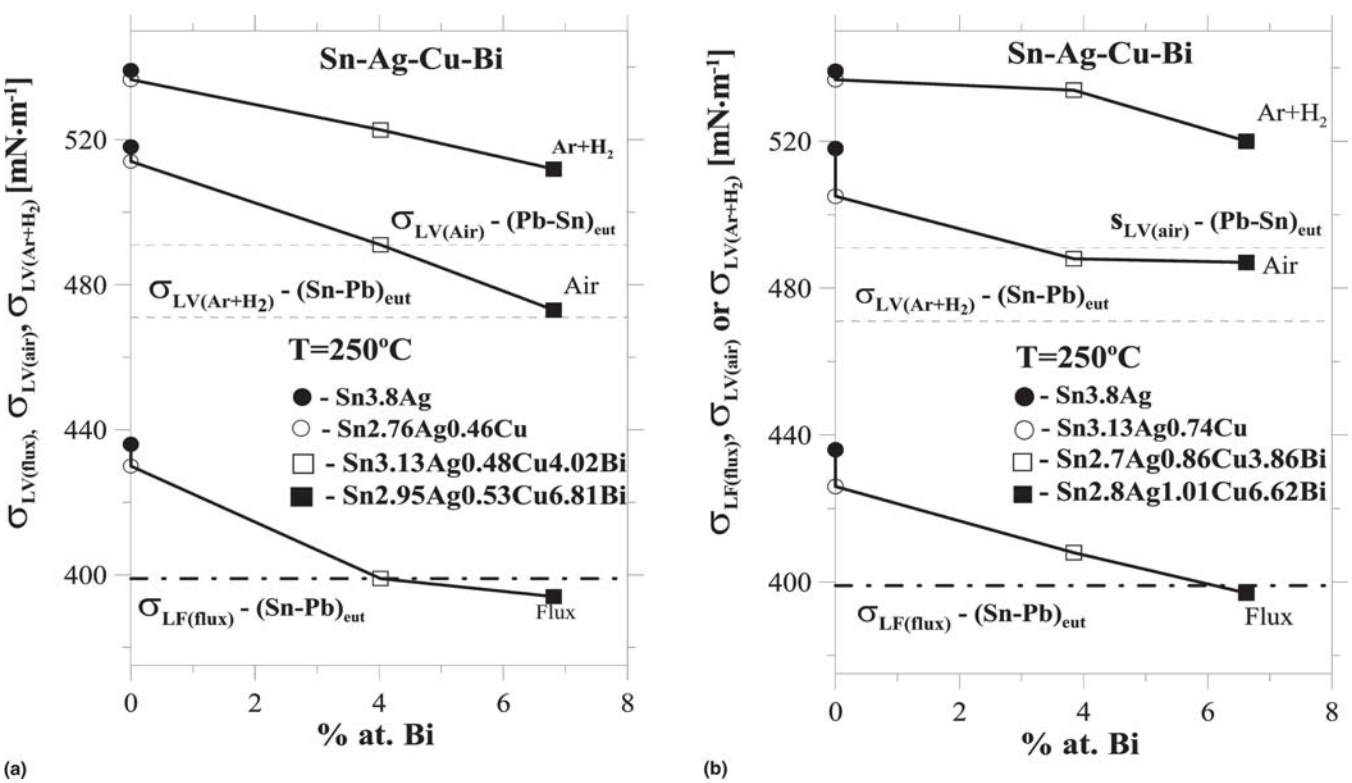


Fig. 5 Comparison of surface tension σ_{LV} from the maximum bubble pressure method (upper plots) under Ar-H_2 protective atmosphere with meniscographic data (middle plot) in air. The lower plots are for interfacial tensions σ_{LF} from meniscographic data for the solder/flux interface. Sn-Pb values are shown for comparison.

Comparisons in Fig. 5 show that surface tensions under a protective atmosphere or in air and of interfacial tension have at ~4 at.% Bi properties comparable to currently used Sn-Pb solders. Therefore, for this alloy, the meniscographic measurements were repeated and are included in Table 4. In Part II of this investigative series, it will be documented why alloys with more that 4 at.% Bi are not recommended for practical applications; this is in agreement with the suggestions of Hwang.[14]

It seems that experimental surface tension and density measurements over an extensive temperature and composition range when compared with Sn-Ag and Sn-Ag-Cu eutectic alloys provide useful information for guiding surface and interfacial tension modification and to provide a basis for modeling, which may reduce the cost of experimental research seeking a solder closer in properties to those of Sn-Pb eutectic solders. Therefore, our extensive data were used to create the SURDAT database[6,7] including surface tension, density, and modeling. Other data that are currently available and relevant are included.

Sn-Pb solders have been in common use since Roman times. When the authors' investigations are viewed as a part of the extensive worldwide search for Pb-free soldering materials to replace Sn-Pb solders for a broad application range, the difficulty of finding materials with properties comparable to Sn-Pb eutectic alloys is obvious.

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