

Wettability Studies of Pb-Free Soldering Materials

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Abstract For Pb-free soldering materials, two main substitutes are currently being considered, consisting of Sn–Ag and Sn–Ag–Cu eutectics, both with melting points higher than that of the Sn–Pb eutectic. Therefore, both will require higher soldering temperatures for industrial applications. Also, both eutectics have a higher surface tension than the Sn–Pb eutectic, requiring wettability studies on adding Bi, Sb, and In to the eutectics to decrease the melting points and surface tension. The experimental results for the surface tension were compared with thermodynamic modeling by Butler’s method and were used to create the SURDAT database, which also includes densities for pure metals, binary, ternary, quaternary, and quinary alloys. To model the surface tension, excess Gibbs energies of the molten components were taken from the ADAMIS database. For the case of the Ag–Sn system, enthalpies of formation of Ag_3Sn from solution calorimetry were used for checking optimized thermodynamic parameters. In the study of Sn–Ag–Cu–Bi–Sb liquid alloys, the range of possible Bi compositions for practical applications has been used to formulate a generalized metric of wettability, which was checked by measurements of the influence of In on the Sn–Ag–Cu system.

Keywords Industrial applications · Interfacial tension · Modeling of Pb-free solders · Surface tension

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1 Introduction

Research in metallurgy and materials science comprises a broad spectrum of experimental thermodynamics, physical properties (surface tension, interfacial tension, wettability), and data correlation including databases. Such a variety of properties may be considered by searching the mutual correlations between thermodynamic properties (emf, calorimetry), physical properties (surface tension, density, viscosity), the structure of liquid alloys, and the character of phase diagrams (experimental or calculated from optimized thermodynamic parameters). Extensive studies on metallic alloys have been carried out for more than 40 years at the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences in Kraków, Poland. Two studies of Li–Sn [1] and Mg–Sn [2] clearly indicate that such correlations exist and are apparent over the range of existence of the Mg_2Sn intermetallic compound in the Mg–Sn system and for Li–Sn where the most stable intermetallic phases are present. In [1] for liquid Li–Sn alloys, selected values of electrical resistivity, Knight shift, integral molar enthalpies, and integral molar excess entropies are provided. In [2], similar behaviors are observed for electrical resistivity, surface tension, viscosity, and integral molar enthalpy for liquid Mg–Sn alloys.

In recent years, research has been concentrated on Pb-free soldering materials important for resolving environmental problems. Through international cooperation with Tohoku University, Japan, within COST 531 Action and with the ELFNET network in Europe, an effort has been initiated since July 2006 to eliminate Pb from solders. This effort has shifted from basic research in the case of wettability studies of Pb-free solders (surface tension, density, Butler's thermodynamic modeling [3]) to meniscographic studies useful for industrial applications and to a search for metrics of wettability to characterize the various alloys. The metrics of wettability, changes in the surface tension (interfacial tension), and contact angle, were based on extensive experimental studies of Sn–Ag–Cu–Bi–Sb alloys and were tested on Sn–Ag–Cu–In and Sn–Zn alloys.

Systematic measurements of the surface tension and density and modeling of the surface tension of candidates to replace Sn–Pb solders were used to create the SURDAT database [4], which have been used to update the NIST lead-free solder database.

2 Surface Tension and Density Data in Protective Atmosphere (Argon + Hydrogen): Examples for Binary Systems

As a substitute for traditional Sn–Pb solders, low melting eutectics with a Sn base combined with such components as Bi, Sb, Ag, In, Cu, and Zn have been considered. In Table 1 are listed the pure components, and binary, ternary, and higher-order systems, for which systematic experimental studies of the surface tension and density have been carried out at the Institute of Metallurgy and Materials. The maximum bubble-pressure method has been used for surface-tension measurements and the dilatometric technique for density. Some details of the experimental methods have been presented in [5]. In general, the temperature dependence of the surface tension and density over an extensive range is linear, and, therefore, the least-squares method has

Table 1 Summary of the investigated systems of Pb-free alloys

Metals	Binary alloys	Multicomponent alloys
Pb	Pb–Sn	(Sn–Ag) _{eut} + In
Sn	Ag–Sn	(Sn–Ag) _{eut} + Bi
In	Ag–In	(Sn–Ag) _{eut} + Cu
Ag	Bi–Sn	(Sn–Ag) _{eut} + Sb
Bi	In–Sn	(Sn–Ag) _{eut} + Cu + Sb
Sb	Ag–Bi	(Sn–Ag) _{eut} + Cu + Bi
Cu	Sb–Sn	(Sn–Ag) _{eut} + Cu + Bi + Sb
Zn	Sn–Zn	
Al	Ag–Sb	
Au	Cu–Sn	
	Cu–Sb	

been used for fitting the experimental results, starting from liquid Sn–Pb alloys. Data for the Sn–Pb eutectic were used for comparison with new Pb-free solders. Surface-tension measurements (in a protective atmosphere) were made over an extensive range of temperature, enabling use of data at 523 K for correlation with interfacial tension and surface tension measured in air in meniscographic studies in cooperation with industrial institutes.

In recent years, two main substitute materials for Sn–Pb traditional solders have been recommended for practical applications based not only on limited wettability data, but also taking into consideration the mechanical and electrical properties [6]. Two recommended alloys are the Sn–Ag (m.p., 494 K) and Sn–Ag–Cu (m.p., 490–492 K) eutectics which have melting points higher than that of Sn–Pb (456 K) and therefore require higher soldering temperature for industrial applications. In addition, Sn–Pb [7] has a lower surface tension than both of these new eutectics, which justifies a search for substitute materials with properties closer to those of traditional solders by the addition of constituents to both eutectics that decrease the surface tension and the melting temperature.

Some examples of the effect of the addition of Bi and Sb to both Sn–Ag and Sn–Ag–Cu eutectics will be presented, starting from the surface tension and density of liquid Sn–Ag alloys. This also included a eutectic composition with $X_{\text{Sn}} = 0.962$ [8], for which the surface tension and density are shown in Fig. 1a, b. The addition of Sn to Ag decreases the surface tension and the distance to the Sn–Pb eutectic.

For the case of the In–Sn system, due to the nearly same values of surface tension and density of In and Sn, practically no change in the temperature dependence of both physical properties is observed as indicated in Fig. 2a, b [9]. The same is true for other studies of ternary and quaternary systems.

In the systematic studies of the systems listed in Table 1, it was confirmed that Butler's method [3] is suitable for thermodynamic modeling of the surface tension; however, the nonlinear temperature dependence of the surface tension in this model is probably connected with the assumed constant parameters, which should be temperature dependent. This was analyzed in a previous paper on Ag–Bi liquid alloys [10]. To model the surface tension, Butler's method requires data of the excess Gibbs energies of the components of the investigated liquid alloys of the bulk phase (from the

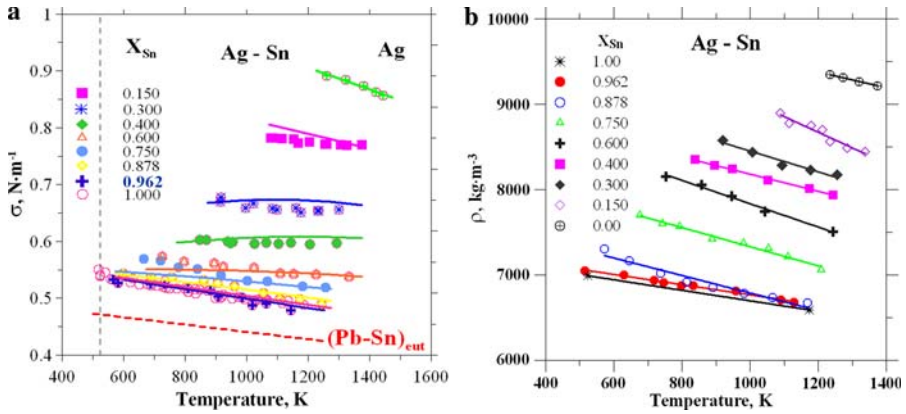


Fig. 1 (a) Temperature dependence of the surface tension of liquid Ag–Sn alloys (experimental points) compared with eutectic Sn–Pb [7] and modeling by Butler’s method (solid lines) and (b) temperature dependence of density for the same alloys from [8]

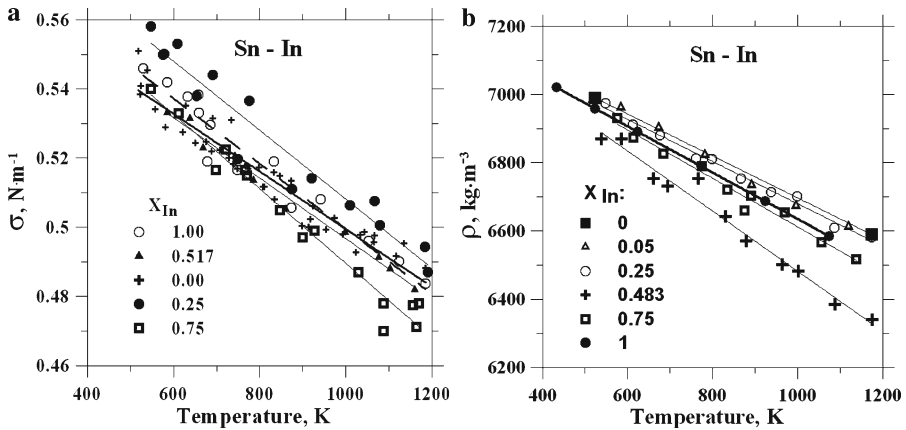


Fig. 2 (a) Temperature dependence of the surface tension of liquid Sn–In alloys from [9] and (b) temperature dependence of the density of liquid Sn–In alloys from [9]

ADAMIS database [11]), and the values of the surface tension of the pure components (from [4]).

3 Determination of Enthalpy of Formation of Ag₃Sn from Solution Calorimetry

The thermodynamic parameters of the Sn–Ag system, collected in the ADAMIS database and used for phase diagram calculations and modeling of the surface tension, were checked by studies of enthalpies of formation of Ag₃Sn from solution calorimetry in liquid tin [12].

In solution calorimetry, the enthalpy of formation ΔH_{Ag_3Sn} is obtained from the difference of thermal effects accompanying the dissolution in the tin bath of Ag₃Sn

Table 2 Values of the enthalpy of formation of Ag_3Sn and the enthalpy of solution of Ag in liquid Sn compared with literature data from [12]

Enthalpy of solution of Ag ($\text{kJ} \cdot \text{g}_{\text{at}}^{-1}$)		Enthalpy of formation of Ag_3Sn			
This study:	15.03 \pm 0.25	This study	[14]		
[13]	15.3 \pm 0.13	Temp (K)	ΔH_f ($\text{kJ} \cdot \text{mol}_{\text{at}}^{-1}$)	St. Dev.	ΔH_f ($\text{kJ} \cdot \text{mol}_{\text{at}}^{-1}$)
[14]	15.02 \pm 0.15	297	2.8	0.7	-4.3 \pm 0.23
[15]	15.9 to 16.3 \pm 0.6	298	3.2	0.7	
		505	3.0	0.2	
		576	3.1	0.2	-4.4 \pm 0.23
		631	2.9	0.3	
		633	3.0	0.3	
		Average	-3.0	0.4	

and pure components Ag and Sn:

$$\Delta H_{\text{Ag}_3\text{Sn}} = 0.75\Delta H_{\text{Ag}}^{\text{ef},0} + 0.25\Delta H_{\text{Sn}}^{\text{ef},0} - \Delta H_{0.75\text{Ag}0.25\text{Sn}}^{\text{ef},0} \quad (1)$$

where $0.75\Delta H_{\text{Ag}}^{\text{ef},0}$, $0.25\Delta H_{\text{Sn}}^{\text{ef},0}$, and $\Delta H_{0.75\text{Ag}0.25\text{Sn}}^{\text{ef},0}$ are the thermal effects accompanying the dissolution of the components and Ag_3Sn in the bath.

The experimental enthalpy of formation of Ag_3Sn of $-3.0 \pm 0.4 \text{ kJ} \cdot \text{mol}^{-1}$ of atoms is close to the calculated value $-2.8 \text{ kJ} \cdot \text{mol}^{-1}$ of atoms from the ADAMIS database and similar to the enthalpy of solution of Ag in liquid Sn compared with literature results [13–15]. Values of the enthalpy of formation of this study summarized in Table 2 show differences when compared with Kleppa [14] results for the same standard: solid Ag and solid Sn.

4 Surface Tension and Density Data in Protective Atmosphere (Argon + Hydrogen) for Higher-Order Systems

As for the Ag–Sn system, systematic experimental studies of the surface tension and density, and modeling of the surface tension for higher-order systems with the addition of Bi, Sb, and In starting with the ternary Sn–Ag–Cu eutectic to elaborate materials having properties close to the traditional Sn–Pb solders. The starting point involved measurements of the surface tension and density of $(\text{Sn–Ag})_{\text{eut}}$ with various amounts of Cu added, focusing particularly on two alloys, Sn2.76Ag0.46 Cu and Sn3.13Ag0.74Cu, as shown in Fig. 3a, b. In Fig. 3a is plotted the temperature dependence of the surface tension from [16], while in Fig. 3b isothermal measurements are compared with calculations from Butler’s model [3]. In Fig. 3c the temperature dependence of the density is plotted. These two starting alloys, Sn2.76Ag0.46 Cu and Sn3.13Ag0.74Cu, close to the Sn–Ag–Cu eutectic were used in further wettability studies to analyze the effects of the additions of Bi, Sb, and In (in bold in Fig. 3a, c).

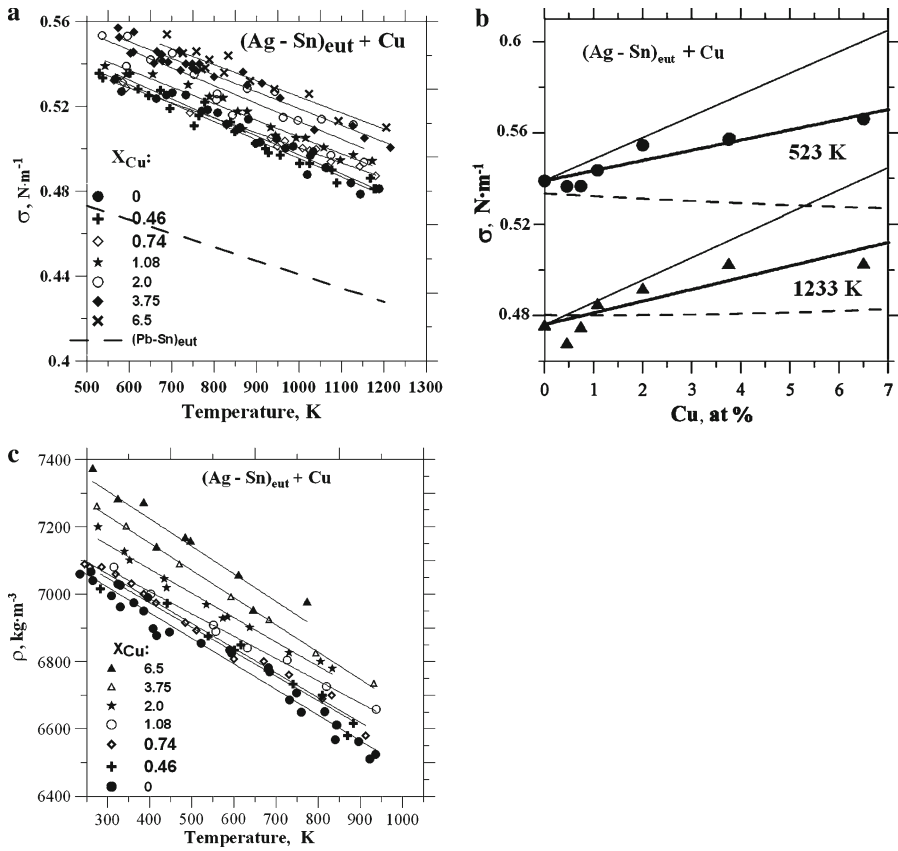


Fig. 3 (a) Temperature dependence of the surface tension for Sn–Ag–Cu alloys [16] illustrates the distance from investigated Pb-free alloys, (b) isotherms of the surface tension calculated at 523 K and 1,233 K of liquid Sn–Ag–Cu alloys; points taken from [16]; dotted lines are the calculated results from Butler’s model, and (c) temperature dependence of density of liquid Sn–Ag–Cu alloys from [16]

Now, from [17] that are present in Fig. 4a, b surface-tension measurements of two alloys, Sn_{2.76}Ag_{0.46}Cu and Sn_{3.13}Ag_{0.74}Cu, with various amounts of Bi added. Next, in Fig. 5a, b calculated isotherms of the surface tension of quaternary alloys are presented starting from the ternary alloys, Sn_{2.76}Ag_{0.46}Cu and Sn_{3.13}Ag_{0.74}Cu (in at%). On the vertical axes, surface-tension data from [8] and [16] are plotted for ternary and binary systems. The calculated surface tension at both temperatures, 523 K and 1,233 K, show a decreasing character with the addition of Bi, similar to experimental data at 1,233 K. The behavior of experimental data at 1,233 K is the result of combining the surface-tension results for quaternary alloys with the binary and ternary results at higher temperatures, as observed in the temperature dependences. The modeling of the surface tension always shows the decreasing tendency of the surface tension with the addition of Bi.

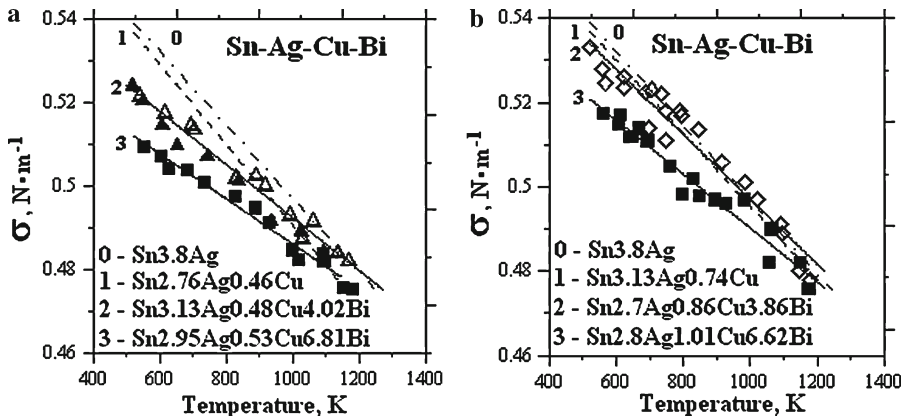


Fig. 4 (a) Temperature dependence of the surface tension of the quaternary Sn–Ag–Cu–Bi alloys (solid line average from [4]) compared with binary Sn–Ag eutectic and ternary Sn_{2.76}Ag_{0.46}Cu alloy and (b) temperature dependence of the surface tension of the quaternary Sn–Ag–Cu–Bi alloys (solid line average from [4]) compared with binary Sn–Ag eutectic and ternary Sn_{3.13}Ag_{0.74}Cu alloy

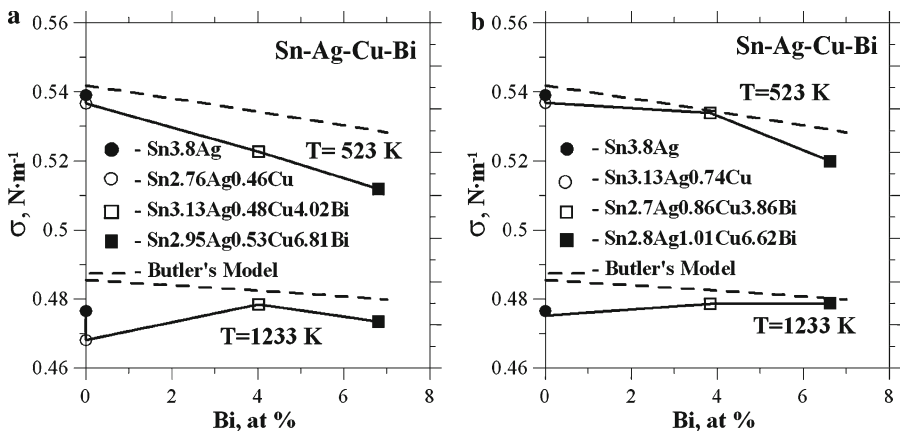


Fig. 5 Isotherms of the surface tension measured in protective atmosphere at 523 K and 1,233 K compared with calculated data using Butler's method: (a) adding Bi to Sn_{2.76}Ag_{0.46}Cu alloy and (b) adding Bi to Sn_{3.13}Ag_{0.74}Cu alloy

Results of the influence of In on the surface tension and density of (Sn_{3.13}Ag_{0.74}Cu) were presented on Mid Term of COST 531 in Genoa 2006 [18], still showing the properties of the In–Sn system (Fig. 6a, b).

5 Meniscographic Studies in Air

The physics of wetting is governed by the Young–Dupré relation [16] combining wettability (σ_{SV} or σ_{SF}) with the tendency to form an intermetallic compound (IMC) denoted by σ_{SL} , the surface tension by σ_{SV} , or the interfacial tension by σ_{SF} , and the

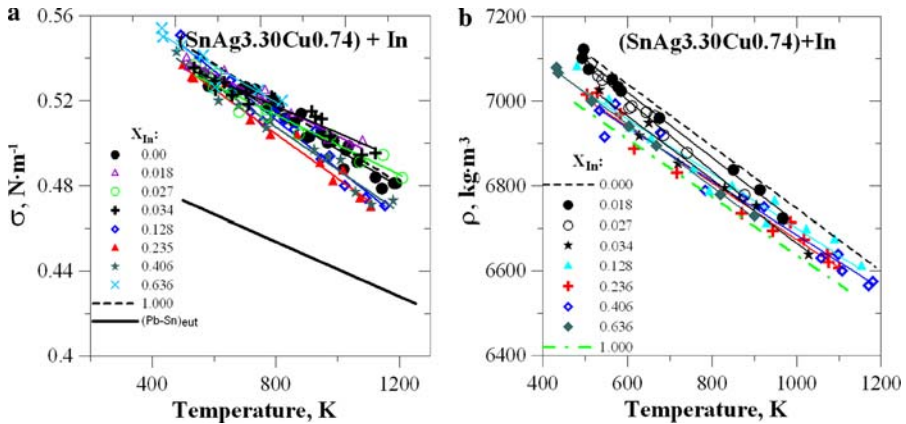


Fig. 6 (a) Temperature dependence of the density of (Sn 3.13Ag 0.74Cu) + In liquid alloys and (b) temperature dependence of the surface tension of (Sn 3.13Ag 0.74Cu) + In liquid alloys

contact angle by ϕ . L indicates liquid solder, S denotes the solid substrate usually Cu, V represents the protective gas, and F denotes the flux. This is illustrated by two examples.

First, for surface-tension measurements performed under a protective gas:

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \phi \tag{2}$$

In Eq. 2, σ_{LV} shows the surface tension measured, for instance, by the maximum bubble-pressure method. Therefore, only one term in the Young–Dupré relation is determined, noting that a decrease in the surface tension represents an improvement of wettability. The sessile drop method can be used for direct determination of contact angles, and hence, determination of the difference $(\sigma_{SV} - \sigma_{SL})$. The sign of the difference will indicate whether there will be a tendency for wetting or for beading.

Second, for meniscographic measurements of interfacial tension using flux:

$$\sigma_{SF} = \sigma_{SL} + \sigma_{LF} \cos \phi \tag{3}$$

The meniscographic method is used for measuring the dynamic process of wetting. As proposed by Miyazaki et al. [19], the meniscographic method can be used for measuring the interfacial tension between solder and flux, the surface tension between solder and in air on non-wetted Teflon samples and on Cu coupons for the wetting time, wetting force, and contact angle. More detailed discussion of the procedure can be found in an earlier report [16]. The contact angle from meniscographic measurements is a calculated angle, which can be compared with direct contact angle determination by the sessile drop method.

It is not possible to quantify wettability on either the Cu/flux (σ_{SF}) or the Cu/gas (σ_{SV}) interphase based on a correlation with the contact angle, but for practical applications for Sn–Pb and Pb-free solders in meniscographic tests, the wetting force is

monitored as a function of time to evaluate the interfacial tension and contact angles. The shortest wetting time, the highest wetting force, and the lowest contact angle were considered previously as indications of good wettability.

From an application point of view with the goal of the availability of a practical Pb-free solder to function at about 523 K, the addition of meniscographic studies to the surface-tension studies is very important because they allow selection of a real metric for wettability. Then, with the Young–Dupré equation, a more practical relation ($\sigma_{\text{SF}} - \sigma_{\text{SL}}$) can be evaluated. Here σ_{SF} indicates the substrate–flux interfacial tension with σ_{SF} replacing the previous σ_{SV} in a 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.

The values of the contact angle indicate the degree of wettability: $0^\circ < \varphi < 30^\circ$ —very good wetting, $30^\circ < \varphi < 40^\circ$ —good wetting, $40^\circ < \varphi < 55^\circ$ —acceptable wetting, $55^\circ < \varphi < 70^\circ$ —poor wetting, and $\varphi > 70^\circ$ —very poor wetting.

6 Results and Discussion

To proceed from surface tension and density results in a protective atmosphere toward practical applications, a temperature of 523 K was selected and for the same (Sn–Ag)_{eut} alloy, Cu additions were tested: Sn2.76Ag0.46Cu, Sn3.13Ag0.74Cu as shown previously in Fig. 3a, and now plotted in the upper part of Fig. 7 with meniscographic results for the interfacial tension and surface tension in air. The top plot in Fig. 7 shows the surface tension under a protective gas. The solid circles in the plot represent alloys studied by Gaşior et al. [16]. It can be noted that the plot correlates with the 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 alloys but increases with increasing Cu content beyond the ternary eutectic compositions. The lower plot with the solid diamond points is the interfacial determination σ_{LF} between solder/flux. For comparison, values for the equivalent properties for a Sn–Pb eutectic solder are shown by horizontal lines [7], and they are in every case lower than for the Sn–Ag or Sn–Ag–Cu solders. Generally speaking, data for the surface tension σ_{LV} , obtained by the maximum bubble-pressure method in an Ar + H₂ atmosphere are slightly higher than the data from the meniscographic technique for the interfacial tension σ_{LF} since fluxes decrease wettability. Also, the surface tension from the meniscographic method measured in air is lower than that from the maximum pressure method (Ar + H₂) due to various tendencies toward oxidation of the traditional Sn–Pb solders in comparison to Pb-free materials, discussed in [16].

The contact angle from meniscographic measurements is a calculated angle, which can be compared with a direct contact angle determination from the sessile drop method. A comparison of data for the contact angles from the sessile drop method and meniscographic values for the binary and two ternary alloys, Sn2.76Ag0.46Cu and Sn3.13Ag0.74Cu, is shown in Table 3 where the meniscographic values are consistently lower. This difference can be attributed to the presence of a flux during meniscographic measurements.

Fig. 7 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 [19]. Lower plot represents meniscographic determination of interfacial tension of the solder/flux interface. Open circles in the upper plot are older data [20], which are included to show that the initial addition of Cu first drops the surface tension from that of the eutectic Sn–Ag solder toward that of the Sn–Ag–Cu ternary eutectic but rises again on the Cu-rich side of the ternary eutectic. Corresponding invariant values for classic Sn–Pb solders are shown by horizontal dashed or dashed-dotted lines for comparison

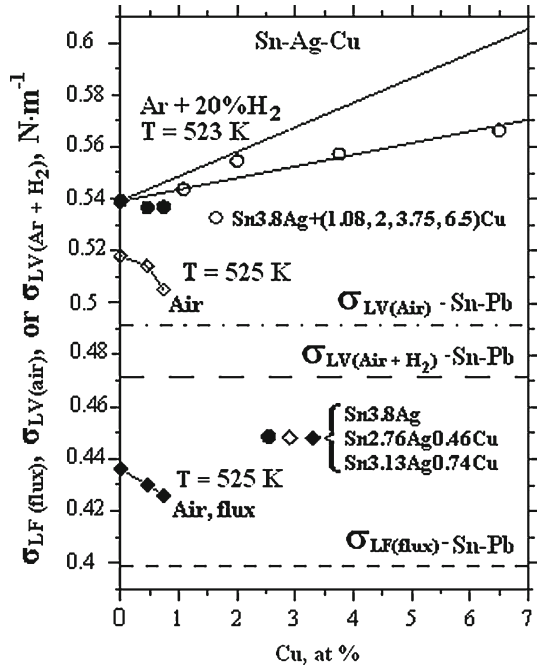


Table 3 Calculated contact angles from meniscographic studies and from the sessile drop method from [17]

Type of alloy	Alloy (at%)	Contact angle	
		Sessile drop method	Meniscograph method
Binary eutectic	SnAg3.8	58°	47°
Ternary alloy	(SnAg3.8) + 0.46Cu	56°	45°
Ternary alloy	(SnAg3.8) + 0.74Cu	61°	46°

Various amounts of Bi and Sb were added to these two ternaries for studies of the surface tension in a protective atmosphere and in meniscographic measurements of interfacial tension using fluxes (obtained in cooperation with industrial institutes). For a comparison of the results, a temperature of 523 K was selected since it represents the lower range of surface-tension measurements in a protective atmosphere, it represents a temperature used in meniscographic measurements, and it is a temperature applicable in industrial soldering using Pb-free materials.

A similar comparison to that in Fig. 7 has been tested for the case of Bi additions to both ternary alloys, Sn₇₆Ag_{0.46}Cu and Sn_{3.13}Ag_{0.74}, and is shown in Fig. 8a, b [17]. In Fig. 8a, b the meniscographic data are used to illustrate the effect of Bi on the interfacial tension with the top data representing the surface tension under a protective atmosphere, the middle data representing the surface tension under air, and the lower data representing the interfacial tension with the presence of a flux.

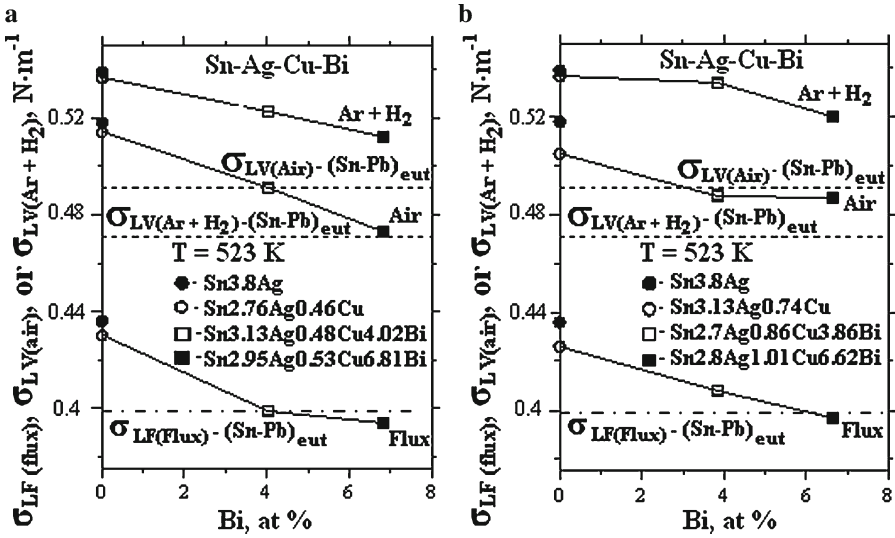


Fig. 8 Comparison of surface tension from the maximum bubble-pressure method (upper part in argon with hydrogen) with meniscographic technique (middle plot in air) and with interfacial tensions of the quaternary Sn–Ag–Cu–Bi alloys. Various dotted lines for $(\text{Sn-Pb})_{\text{eut}}$ indicate the distance from the investigated Pb-free alloys. On vertical axis are plotted data for the binary Sn–Ag eutectic and ternary alloys (a) Sn2.76Ag0.46Cu and (b) Sn3.13Ag0.74Cu

Generally speaking, data for the interfacial tension are lower than those for the surface tension because the fluxes decrease the surface energy. The experimental results indicate that Bi additions to Sn–Ag–Cu alloys [17] decrease the surface tensions of the alloys in both air and in the protective Ar–H₂ atmosphere. The magnitude of the decrease increases with the amount of Bi added to the alloy. However, in air the surface tension with higher Bi content is lower than the surface tension of Sn–Pb eutectic alloys, but under an Ar–H₂ atmosphere, the surface tensions of the alloys with added Bi are, at all concentrations, significantly higher than that of Sn–Pb eutectic alloys. This decrease of the surface tension with the addition of an alloying component suggests a qualitative improvement in wettability, but it does not provide a sufficiently generalized metric for wettability.

In [17], based on an analysis of the data for wetting time, wetting force, contact angles, interfacial tension (solder/flux), surface tension in air, and surface tension in Ar–H₂ atmosphere for alloys starting from the binary Sn–Ag eutectic, through Sn76Ag0.46Cu and Sn3.13Ag0.74, with various amounts of Bi added, it was recognized that the interfacial tension and contact angle are the two parameters that are most important as metrics for indicating wettability. Changes in these two parameters correlate with decreasing wetting time and increasing wetting force.

Unfortunately, the initial results [21, 22] on quinary Sn–Ag–Cu–Bi–Sb alloys, when adding various amounts of Sb to the quaternary Sn–Ag–Cu–Bi alloys investigated in this report do not show a continuation of the observed trends. Observations make it clear that the suggestions concerning the role of wetting time and wetting force in a

recent paper by Lopez et al. [23] are correct with respect to the fact that the 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 [24]. On the other hand, the 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 on composition as does the interfacial tension in combination with contact angles or the surface tension in combination with contact angles.

In [25] the ADAMIS database was used for calculation of various phase equilibria of the quaternary Sn–Ag–Cu–Bi alloys investigated in this report and for simulation of the solidification under equilibrium, and along with Scheil's model, have shown that the alloys with higher Bi concentrations are characterized by the lifting-off failure due to the segregation of Bi at the solder/substrate boundary. It was recognized that the beneficial influence of Bi additions (Fig. 8a, b) on wettability and a decrease of melting temperature seem evident, but the search for a suitable concentration is a compromise of various factors, especially in view of the tendency for the lifting-off failure. The same tendency was reported by Hwang [6] when discussing the Sn 3.1Ag 0.5Cu 3.1Bi (in mass%) alloy. From the present study and the work of Hwang [6] and Takao et al. [26] the conclusion can be drawn that the optimal concentration of Bi in the quaternary Sn–Ag–Cu–Bi solders should be in the range of 1–3.1 mass%.

Previously mentioned studies of In additions to Sn and Sn–Ag [9,18] for (Sn3.13Ag0.74Cu) + In were continued in co-operation with the Slovak Academy of Sciences [27]. One of the reasons for these joint studies was to test the developed metric of wettability when investigating the influence of Bi and Sb additions to Sn2.76Ag0.46Cu and Sn3.13Ag0.74. No change of the temperature dependence in alloys when In and Sn are simultaneously present should be reflected by the change of the contact angle. Actually, it was confirmed in studies of Sn–Ag–Cu–In [27] and Sn–Zn–In alloys [28].

7 Conclusions

The use of the surface tension and contact angle or the interfacial tension and contact angle as a metric for wettability was tested in extensive studies of Bi and Sb additions to ternary Sn–Ag–Cu eutectics and extended to the use of the contact angle in alloys when In and Sn are simultaneously present. This was confirmed on Sn–Ag–Cu–In soldering materials and constituent alloys and on In additions to Sn–Zn alloys.

It should be observed that, until now, the properties of new Pb-free alloys including also Sn–Ag and Sn–Ag–Cu eutectics are different from those of the traditional solders used since the Roman times, considering the melting temperature, wettability, mechanical properties, manufacturability, and the cost. Thus, the new tendency is to rely on Sn–Zn eutectic alloys, however, requiring for practical applications a protective atmosphere due to the presence of zinc and its tendency toward oxidation.

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