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ORIGINAL PAPER

The density and surface tension of In–Sn and Cu–In–Sn alloys

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Abstract The density and surface tension of binary In–Sn and ternary Cu–In–Sn alloys have been measured by a sessile-drop method. Decrease of the density and of the surface tension was observed with rising temperature. With increased Sn content in the alloys, the density increased while the surface tension reduced slightly. Addition of Cu could significantly increase the density and surface tension in the Cu–In–Sn system. The surface tension of the Cu–In–Sn alloys was also calculated by means of Butler's equation, and compared with experimental values, showing good agreement.

Keywords Metals · Lead-free solders · Database · Butler's equation

Introduction

In recent years, substantial efforts have been made to design lead-free solders. Potential candidates under investigation are based on Sn-containing alloys. Among these, attention has been paid to In–Sn and Cu–In–Sn alloys to replace Pb–Sn solders in some applications, because In–Sn has a suitable melting temperature and good wetting behaviour. Meanwhile, the mechanical properties can be improved through the addition of Cu [1–3].

Surface tension is a very important parameter for the design of solders. Although many authors [4–6] have already studied the surface tension of In–Sn alloys over a wide range of temperature, some contradictions still exist. The surface tension of pure In is reported as higher than that of tin in [4, 5], but Novakovic [6] reported the opposite. On the other hand, the values for Cu–In–Sn are still unknown. In this work, firstly the density and surface tension of pure In, Sn and In–Sn alloys were measured by a sessile-drop method. Then, the density and surface tension of Cu–In–Sn ternary alloys were determined for three vertical sections using the same experimental method. The influence of the addition of Cu on the density and surface tension of the binary In–Sn system was investigated. Results of earlier studies on pure In, Sn and the In–Sn binary system are presented in the discussion. The surface tension was also calculated based on Butler's equation using thermodynamic data.

Results and discussion

In–Sn binary

A total of seven samples, including five binary In–Sn alloys as well as the pure elements, were investigated in the temperature range from 400 to 800 °C. The data for density and surface tension of each alloy decreased linearly with rising temperature. The results were analysed using the least-squares method, and the obtained linear equations are presented in Table 1.

The temperature dependence of the density and surface tension of pure In and Sn are presented in Figs. 1 and 2, respectively, and compared with other recent works [5–7]. Both the density and surface tension of pure In and Sn have

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Table 1 Density ρ and surface tension σ for pure In, Sn and In–Sn alloys

x_{Sn}	$\frac{\rho = A + B \cdot t(^\circ\mathrm{C})}{\mathrm{g\,cm^{-3}}}$	R^2	$\frac{\sigma = A + B \cdot t(^\circ\mathrm{C})}{\mathrm{mN \cdot m^{-1}}}$	R^2
0	$7.204 - 8.58 \times 10^{-4} t$	0.9974	$575.65 - 0.1005t$	0.9861
0.1	$7.248 - 9.26 \times 10^{-4} t$	0.9961	$573.70 - 0.0992t$	0.9938
0.3	$7.277 - 9.07 \times 10^{-4} t$	0.9973	$573.29 - 0.1020t$	0.9862
0.5	$7.257 - 8.56 \times 10^{-4} t$	0.9983	$560.76 - 0.0866t$	0.9820
0.7	$7.278 - 8.04 \times 10^{-4} t$	0.9987	$555.29 - 0.0830t$	0.9840
0.9	$7.213 - 6.81 \times 10^{-4} t$	0.9950	$558.12 - 0.0878t$	0.9724
1	$7.222 - 7.15 \times 10^{-4} t$	0.9980	$565.58 - 0.0904t$	0.9759

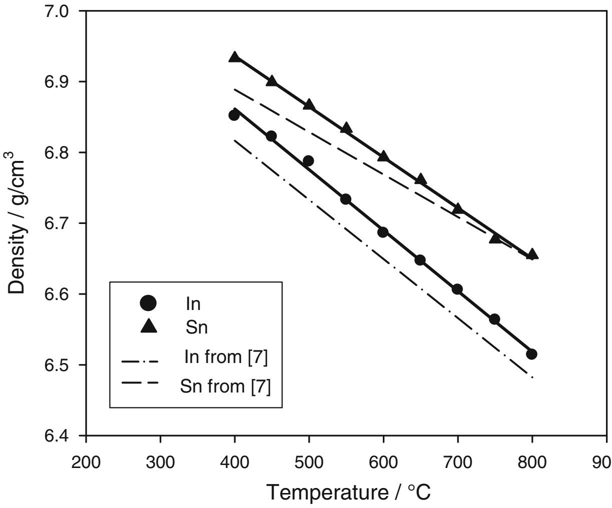


Fig. 1 Temperature dependence of the density of pure In and Sn compared with data from David [7]

similar values. Pure Sn has higher density but shows lower surface tension. The density values in the present work agree very well with the data from David's *Handbook* [7]. Moser [5] reported very similar results of the surface tension, which he measured using two different experimental methods.

Figures 3 and 4 present the experimental data for In–Sn alloys together with pure In and Sn. Due to the fact that the density and surface tension of pure In and Sn are nearly the same, the values of several binary In–Sn alloys are also practically the same. Increase of the density and decrease of the surface tension can be observed from the In-rich to the Sn-rich side, which agrees with the results for pure In and Sn. Figure 5 shows the surface tension as a function of the composition of the In–Sn alloy at 400 °C compared with earlier studies using different experimental methods [4–6]. Most works show a negative deviation from linear behaviour.

Cu–In–Sn ternary

The density and surface tension of Cu–In–Sn ternary alloys (three vertical sections with 10, 20, 30 at% Cu and In-to-Sn ratio from 1:9 to 9:1) were measured in the same way as for the binary In–Sn system. Figures 6 and 7 present the results of all the investigated Cu–In–Sn alloys. The density values of all compositions show linear dependence on temperature, while the surface tension values of some compositions scatter around the linear lines, as shown in Fig. 7. Considering that the deviations were small, the least-squares method was used and led to the linear equations listed in Table 2. All the equations show a negative temperature coefficient. It can be seen that density values rise while surface tension values decrease from the In-rich (In:Sn = 9:1) to the Sn-rich side (In:Sn = 1:9) for most compositions.

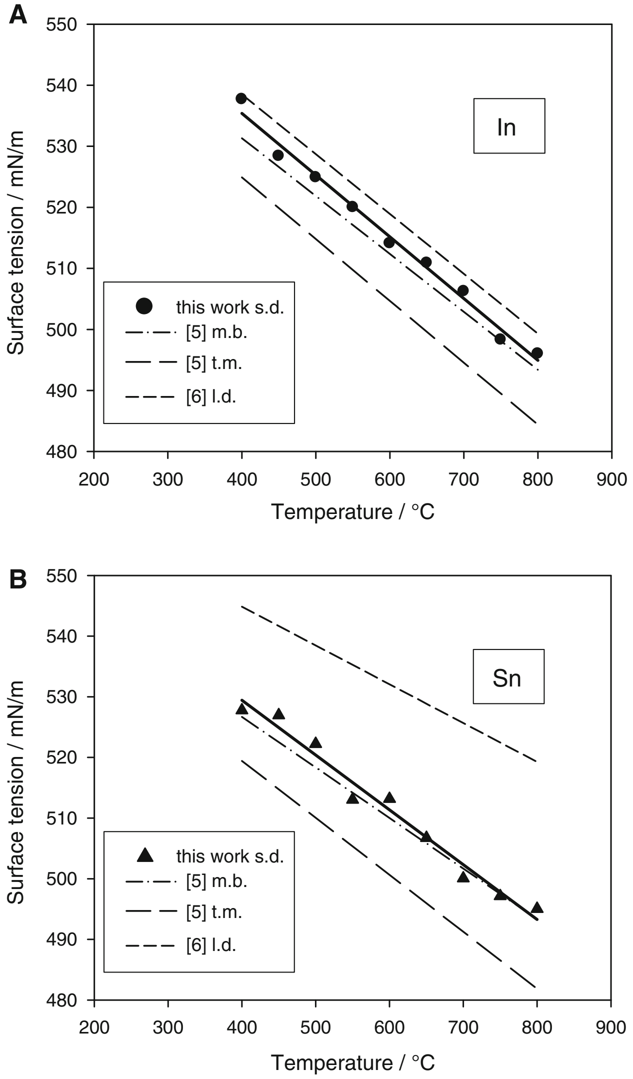


Fig. 2 Temperature dependence of the surface tension of **a** pure In and **b** pure Sn compared with the other works using different experimental methods [5, 6] (*s.d.* sessile-drop method, *m.b.* maximum-bubble-pressure method, *t.m.* tensiometric method, *l.d.* large-drop method)

The density and surface of In/Sn = 1 alloys in three vertical sections at 800 °C are shown in Fig. 8. Addition of Cu markedly increases the density and surface tension of

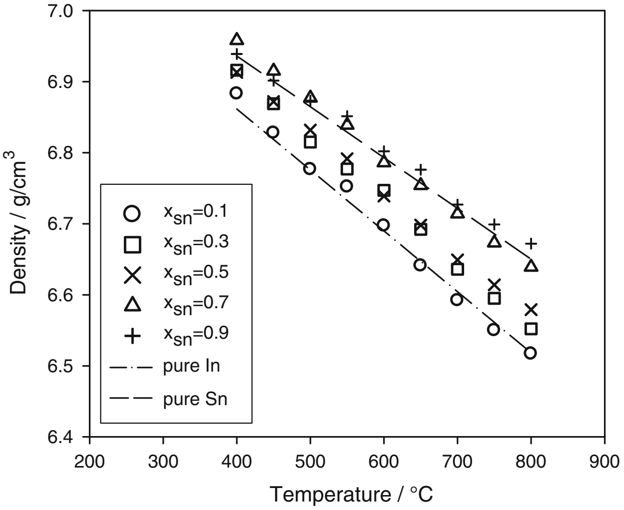


Fig. 3 Experimental density values for In–Sn alloys compared with pure In and Sn values obtained in this work

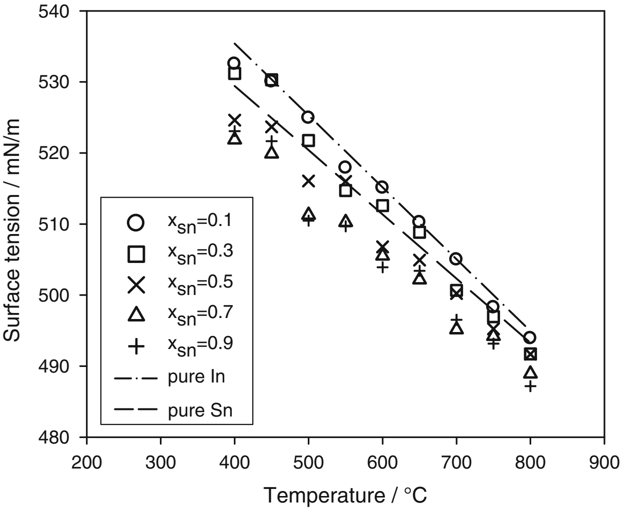


Fig. 4 Experimental surface tension values for In–Sn alloys compared with pure In and Sn values obtained in this work

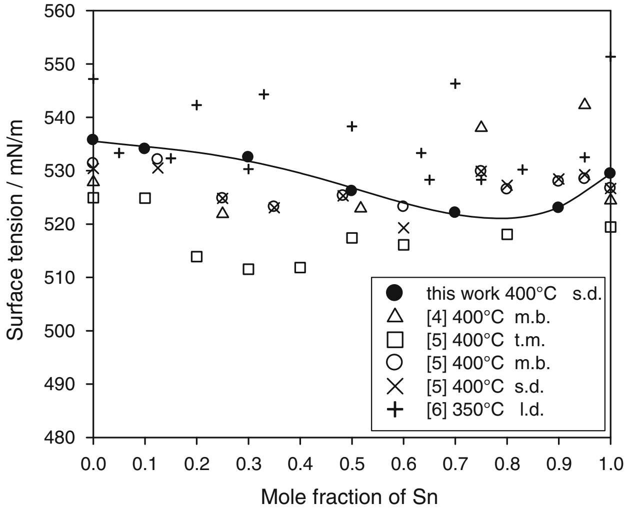


Fig. 5 Surface tension dependence on composition of the In–Sn alloy at 400 °C in this work, together with earlier studies using different experimental methods [4–6]. (*s.d.* sessile-drop method, *m.b.* maximum-bubble-pressure method, *t.m.* tensiometric method, *l.d.* large-drop method)

In/Sn = 1 alloys. It should be noticed that the increase of density and surface tension with addition of copper are both linear in the investigated In–Sn-rich part of the Cu–In–Sn ternary system.

Calculation

According to Butler's equation [8], the surface tension of liquid alloys can be expressed using the density and surface tension of pure metals and thermodynamic data as

$$\sigma = \sigma_i + \frac{RT}{S_i}\ln\frac{x_i^S}{x_i^b} + \frac{1}{S_i}\left({}^{E}G_i^S - {}^{E}G_i^b\right) \qquad (1)$$

where σ_i is the surface tension of pure component i, and x_i^S and x_i^b are the mole fraction in the surface and the bulk phase, respectively. S_i is the molar surface area, which can be calculated from the following equation:

$$S_i = 1.091 N^{\frac{1}{3}} V_i^{\frac{2}{3}}, \qquad (2)$$

where N is the Avogadro number and V_i is the molar volume of component i. ${}^{E}G_i^S$ and ${}^{E}G_i^b$ in Eq. 1 are the partial excess Gibbs free energies of component i in the surface and bulk phase, respectively. ${}^{E}G_i^b$ can be obtained from the literature, and it is assumed that ${}^{E}G_i^S = 0.83 \times {}^{E}G_i^b$ for liquid metals [9]. With the following relation:

$$\sum\nolimits_{i=1}^{n} X_i^S = 1, \qquad (3)$$

σ and x_i^S can be calculated.

Using the thermodynamic data from [3] as well as the density and surface tension for pure metals (In and Sn from this work and Cu from [7, 10]), the surface tension of the Cu–In–Sn alloys was calculated. Figure 9 illustrates the comparison between calculation and experimental measurements. The main reasons for the deviation could be the oxidation reaction during the measurement and the errors of the thermodynamic parameters and of the values of the pure metal used for the calculation.

Conclusions

The density and surface tension of In–Sn and ternary Cu–In–Sn alloys have been measured by the sessile-drop method. The density and surface tension values of all the investigated compositions decrease with increasing temperature. For the ternary Cu–In–Sn alloys, addition of Cu

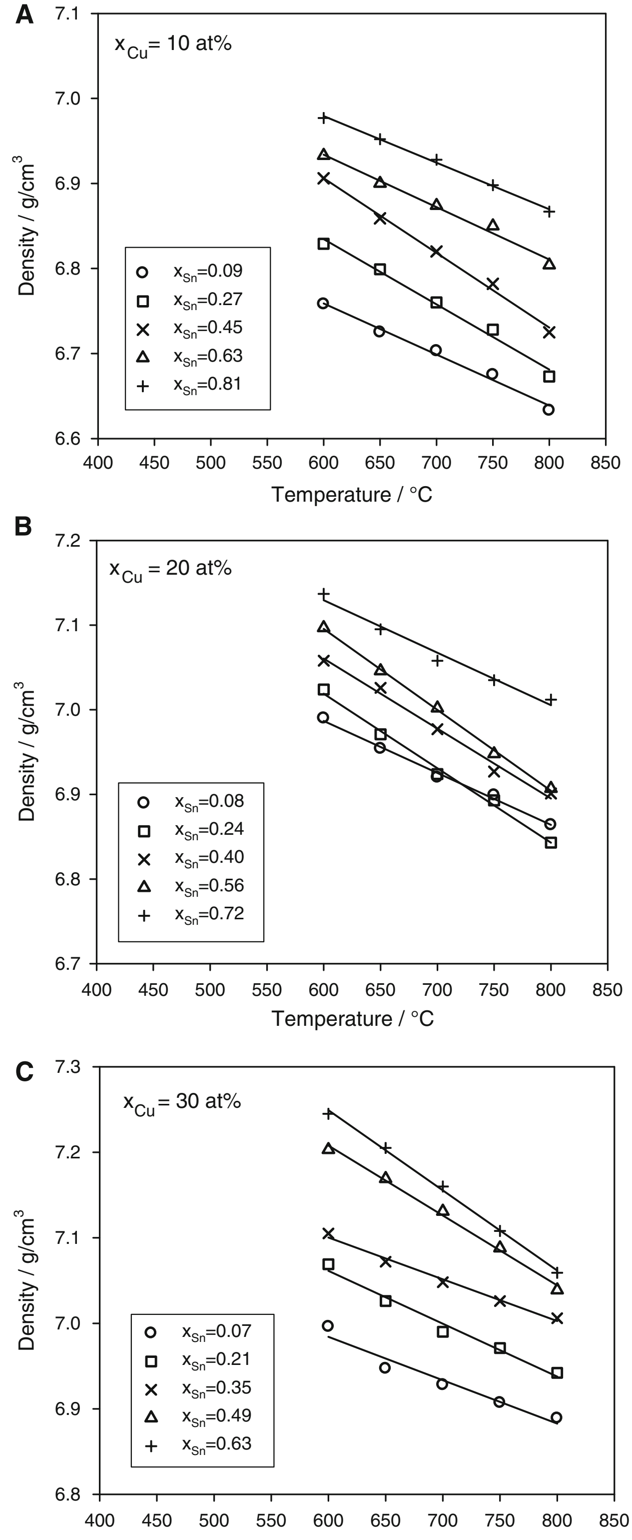


Fig. 6 Temperature dependence of density of the Cu–In–Sn alloys with **a** 10 at%, **b** 20 at%, and **c** 30 at% copper content

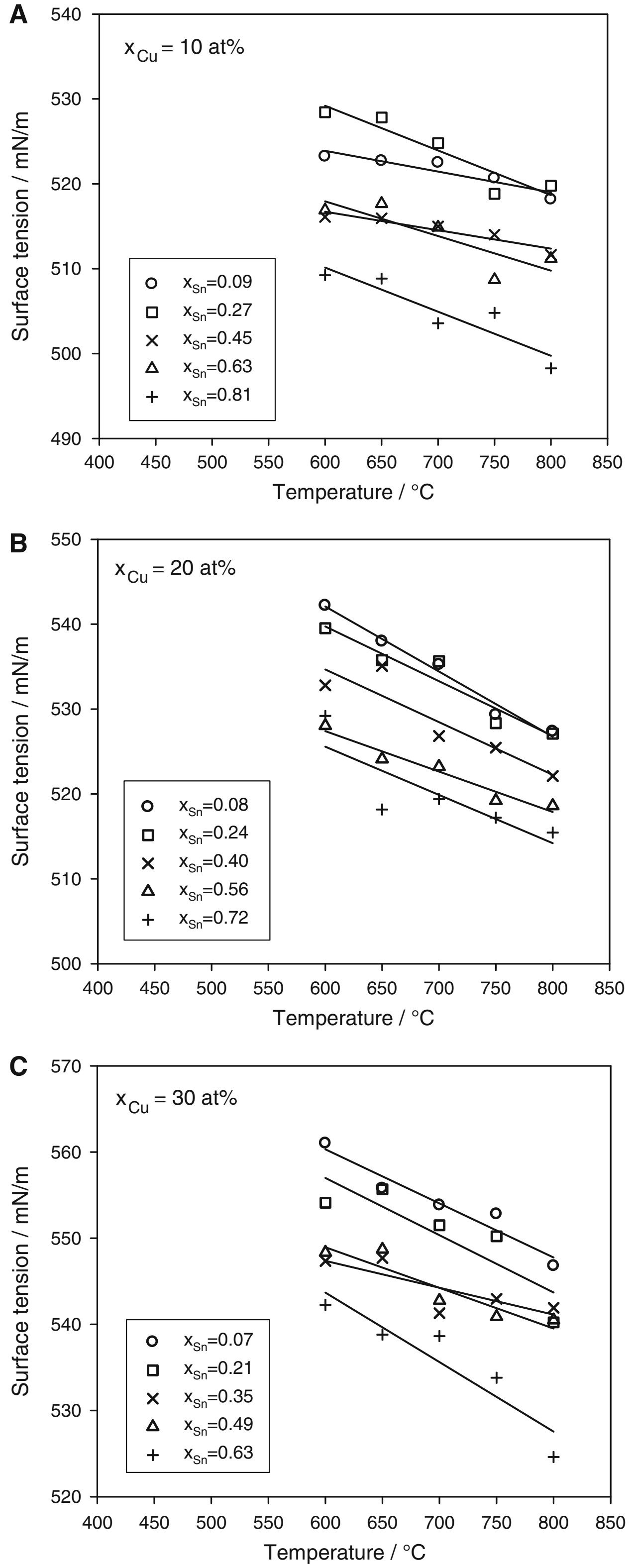


Fig. 7 Temperature dependence of surface tension of the Cu–In–Sn alloys with **a** 10 at%, **b** 20 at%, and **c** 30 at% copper content

Table 2 Density ρ and surface tension σ for Cu–In–Sn alloys

x_{Sn}/x_{In}	$\frac{\rho = A + B \cdot t(^\circ C)}{g\,cm^{-3}}$	R^2	$\frac{\sigma = A + B \cdot t(^\circ C)}{mN \cdot m^{-1}}$	R^2
$x_{Cu} = 0.1$				
1:9	$7.119 - 6.00 \times 10^{-4}t$	0.9885	$538.49 - 0.0243t$	0.8602
3:7	$7.294 - 7.66 \times 10^{-4}t$	0.9878	$560.77 - 0.0526t$	0.8708
5:5	$7.433 - 8.78 \times 10^{-4}t$	0.9948	$529.78 - 0.0218t$	0.8867
7:3	$7.303 - 6.16 \times 10^{-4}t$	0.9864	$542.47 - 0.0409t$	0.7124
9:1	$7.308 - 5.48 \times 10^{-4}t$	0.9966	$541.29 - 0.0519t$	0.8424
$x_{Cu} = 0.2$				
1:9	$7.355 - 6.14 \times 10^{-4}t$	0.9934	$588.11 - 0.0767t$	0.9817
3:7	$7.547 - 8.80 \times 10^{-4}t$	0.9935	$578.43 - 0.0645t$	0.9182
5:5	$7.556 - 8.26 \times 10^{-4}t$	0.9897	$571.87 - 0.0620t$	0.8371
7:3	$7.669 - 9.56 \times 10^{-4}t$	0.9985	$555.97 - 0.0476t$	0.9469
9:1	$7.501 - 6.20 \times 10^{-4}t$	0.9793	$559.73 - 0.0569t$	0.6934
$x_{Cu} = 0.3$				
1:9	$7.289 - 5.08 \times 10^{-4}t$	0.9486	$598.03 - 0.0628t$	0.9334
3:7	$7.432 - 6.18 \times 10^{-4}t$	0.9802	$596.85 - 0.0664t$	0.7543
5:5	$7.393 - 4.88 \times 10^{-4}t$	0.9897	$566.08 - 0.0312t$	0.6533
7:3	$7.699 - 8.18 \times 10^{-4}t$	0.9948	$577.19 - 0.0470t$	0.8614
9:1	$7.812 - 9.38 \times 10^{-4}t$	0.9976	$592.08 - 0.0806t$	0.8645

can increase the values of the density and surface tension. The surface tension of the Cu–In–Sn system was calculated by use of Butler's equation, and the results agree well with the experimental values.

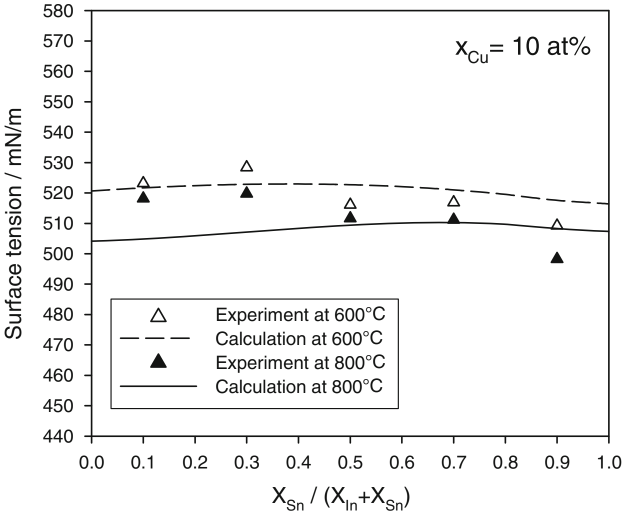


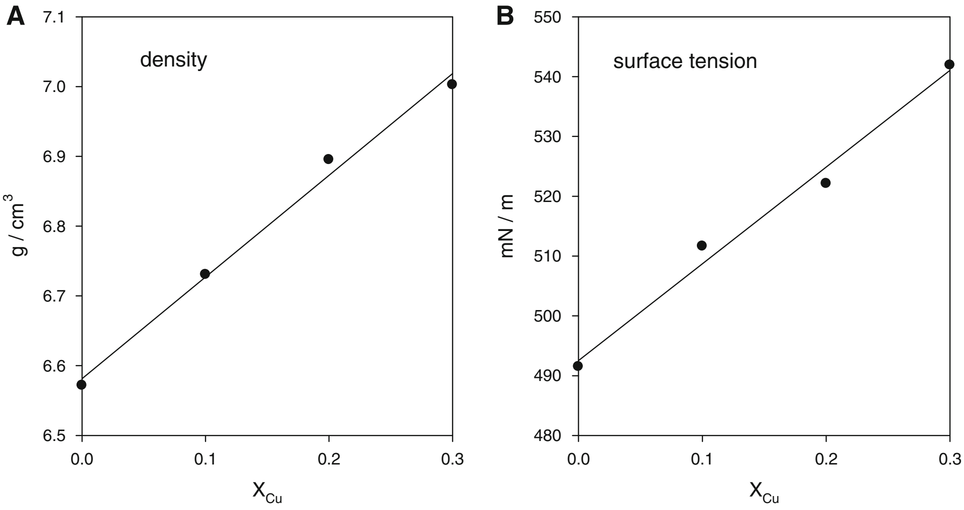
Fig. 9 Calculated surface tension of Cu–In–Sn alloys with 10 at% copper content compared with experimental data obtained in this work

Experimental

All the In–Sn binary and Cu–In–Sn ternary alloys with total weight of 2 g were prepared from high-purity metals (copper wire, purity 99.9%; indium ingots, 99.99%; tin ingots, purity 99.998%). All the metals were products of Johnson Matthey GmbH, Germany. The metals were sealed in quartz tubes under vacuum and melted together at 800 °C for 1 week. Afterwards, the alloys were quenched in ice water, and approximately 70 mg was used for each measurement. For the ternary alloys, differential thermal analysis (DTA) was carried out with a 404S DTA instrument (Netzsch, Germany) to determine the liquidus of the samples.

The sessile-drop method was used to measure the density and surface tension of the alloys. A high-temperature contact angle measuring system from Krüss, Germany was used, consisting of the DSA10HT system (special model) with an integrated high-temperature tube furnace (LORA 1600-40-600-1) from Reetz, Germany. An alumina plate was used as a substrate so that no wetting occurred. The temperature was measured by two K-type thermocouples which were inserted directly into the sample holder to

Fig. 8 **a** Density and **b** surface tension of In/Sn = 1 alloys at 800 °C with different copper content



allow accurate temperature determination of the samples during the measurements. The furnace was evacuated before heating, and argon gas with 5% H_2 was passed through during the measurements to minimize oxidation of the sample surface. Pure In, Sn and In–Sn alloys were heated up to 400 °C (600 °C for the ternary alloys), and the temperature was kept constant for 1 h to make sure the samples were homogeneously liquefied. Measurements were carried out between the heating steps. The temperature was kept constant for 0.5 h at every 50 °C. Images were taken by the camera every 10 s during the whole measurement, and the ones at constant temperature were used for evaluation.

The determinations of the density and the surface tension were both based on the shape of the sample. The shape-analysis program was provided by the Institute of Physics, Chemnitz University of Technology, Germany. Details of the mathematical procedure can be found in [11], where the principle of determining surface tension follows the analysis given by Rotenberg [12].

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