J Mater Sci (2010) 45:2009–2014
DOI 10.1007/s10853-009-3973-y

HTC2009

Effect of metal purity and testing procedure on surface tension measurements of liquid tin

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Received: 26 May 2009 / Accepted: 8 October 2009 / Published online: 23 October 2009

Abstract The surface tension of liquid tin of three different grades of purity (99.85, 99.96, and 99.999%) was measured by the classical sessile drop method over the temperature range 523–1023 K, in heating and cooling regimes. The results obtained show that the metal purity affects the values of surface tension and its temperature dependence. The highest values of surface tension and smooth linear temperature dependence were obtained in cooling regime for tin of the highest purity. With increasing content of impurities, both surface tension and its temperature coefficient decrease while the scatter of the data increases. The surface tension values measured on heating regime show higher scatter, compared to those obtained in cooling regime, and the temperature dependence of the surface tension is curvilinear rather than linear.

Introduction

Capillary phenomena play an important role in joining dissimilar materials by soldering. Therefore, the reliable values of the surface tension of solder alloys are of great practical importance. Despite numerous papers devoted to new generation of Sn-based lead-free solder materials, there is still uncertainty regarding the real value of surface tension of Sn and the reasons that cause significant differences among the data available in the literature [1, 2].

Since the surface tension of liquid alloys can be estimated by thermodynamic calculations [3–6], the reliable reference data of respective pure components are very important for prediction of the properties of solder candidates.

Several attempts have been made to determine the exact value of surface tension of Sn either by experimental investigation in controlled conditions [7–9] or by deriving it from a large collection of literature data [1, 2]. Most of the experimental data have been obtained with either the maximum bubble pressure method or the sessile drop method, both in its classic or large drop variant [10].

The aim of this paper is to examine the effects of metal purity, testing, and data acquisition procedures on the results of surface tension measurements of liquid tin.

Experimental

Experimental setup

The surface tension of tin of three different grades of purity (99.85, 99.96, and 99.999%) was measured with the sessile drop method using the experimental complex for investigation of high temperature capillarity phenomena. The complex, described in detail in [11], consists of a set of chambers allowing one to carry out the tests under ultra high vacuum (up to 10^{-8} mbar) produced by turbomolecular pump. A specimen is heated by Ta heater surrounded by Ta and Mo isolation screens. The temperature of the specimen is automatically controlled and recorded by the thermocouple located beneath the sample. The test chamber is fitted with a gas spectrometer for on-line recording of residual gas analysis. The images of the liquid drop are acquired by high

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resolution monochrome digital camera with a resolution of 1200(H)×960(V) pixels and directly transmitted into the computer system for drop profile processing. A halogen lamp (1000 W) is used as a light source. The magnification factor of the image in this work was found to be 19.5 and no image distortion was observed. Directly before every test, every Sn sample was cut into a cylinder of approximately 5 × 5 mm, ultrasonically cleaned in acetone, dried in air and transferred into the test chamber. The mass of each sample was measured with an accuracy of 0.0001 g before and after each test, and no mass change was observed. Well-polished, high purity, and porosity-free graphite substrates were used as support in the sessile drop tests.

Methodology of measurements

The chemical assay for three different grades of Sn provided by suppliers is presented in Table 1. In order to determine whether the purity of the metal has any influence on its melting point, the samples were tested with digital scanning calorimetry (DSC) technique, two runs each.

The sessile drop experiments were carried out in both heating and cooling regimes, in the temperature range of 523–1023 K, at a vacuum level of 10^{-7}–10^{-6} mbar. First, the Sn sample was heated to melt and reach 523 K. After stabilizing the temperature it was kept at this temperature for 15 min. During that time an image of the droplet was taken every 60 s, resulting in 16 images per specific temperature. Next, the same procedure was repeated in heating regime for each 50 K step until the droplet reached 1023 K. When the measurement at 1023 K was completed, the temperature was lowered by 50 K, and the process was repeated in cooling regime until the sample reached 523 K.

For surface tension estimations the drop images were processed using two distinct data acquisition procedures. The first one [12], further referred to as multi-step procedure, was semi-automatic as it involved the use of separate programs for image analysis and surface tension calculation. The second procedure, further referred to as all-in-one procedure, involved fully automatic computer processing of drop shape profiles using ad hoc acquisition ASTRA software (Automatic Surface Tension Real-Time Acquisition) [13, 14] in a LABView® environment. ASTRA software was developed in Instituto per l'Energetica e le Interfasi, Consiglio Nazionale delle Ricerche, CNR-IENI Genova, Italy. The same density values were used as input parameter for surface tension calculations due to the fact that both procedures are sensitive to density data.

Table 1 The chemical assay for Sn of different purity

Sn (%)	Impurities (ppm)				
	Pb	As	Sb	Cu	Fe
99.85	40	20	40	80	10
99.96	117	10	123	53	43
99.999	1.5	–	–	–	0.25

Results

Table 2 presents the results of melting point measurements for three different grades of Sn purity and the average value is 504.4 K.

For each grade of tin the results of density measurements were analyzed with the least square method. The linear equations obtained are summarized in Table 3 and compared with some literature data in Fig. 1.

The results of surface tension measurements are given in Table 4. Figure 2 illustrates the surface tension temperature dependencies $\sigma = f(T)$ corresponding to different grades of Sn while Fig. 3 presents the results for tin of the

Table 2 The DSC data for Sn of different purity

Sn (%)	T_{melting} (K)		
	1st run	2nd run	Average
99.85	505.8	504.5	505.15 ± 0.65
99.96	505.0	502.6	503.80 ± 1.20
99.999	504.4	504.3	504.35 ± 0.05

Table 3 The linear equations presenting the density (g cm^{-3}) dependence of liquid Sn of different purity on temperature

Sn (%)	$d = A + B \cdot (T[\mathrm{K}] - 505)$	R^2	$d_{723\ \mathrm{K}}$
99.85	6.892–0.0008(T-505)	0.9865	6.74 ± 0.02
99.96	6.861–0.0007(T-505)	0.9849	6.73 ± 0.02
99.999	7.001–0.0010(T-505)	0.9965	6.78 ± 0.01

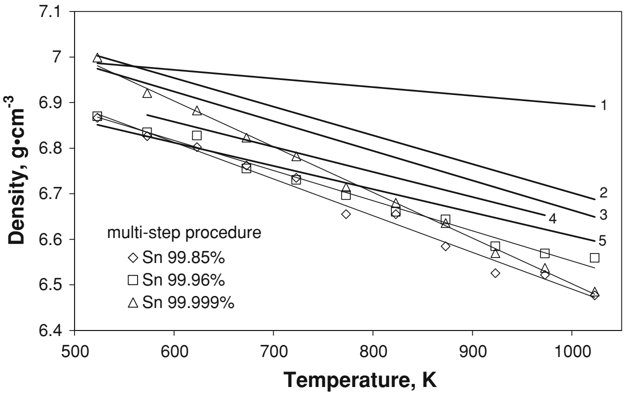


Fig. 1 The density dependence on temperature for different grades of tin (cooling regime, multi-step calculation procedure) compared with literature data: 1 [7], 2–5 [15–18], respectively

Table 4 The linear equations presenting the surface tension (mN m^{-1}) dependence of liquid Sn of different purity on temperature

Sn (%)	$\sigma = A + B \cdot (T[\mathrm{K}] - 505)$	R^2	$\sigma_{723\ \mathrm{K}}$
99.85	519.7–0.0646(T-505)	0.8149	513 ± 13.0
99.96	526.3–0.0659(T-505)	0.9010	513 ± 6.0
99.999	576.7–0.1307(T-505)	0.9869	551 ± 2.8

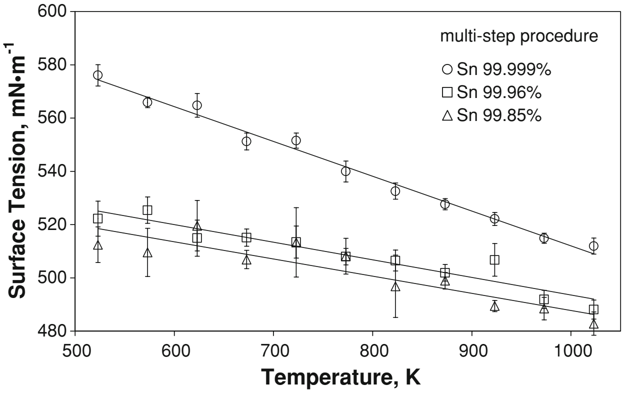


Fig. 2 The temperature dependence of surface tension of different grades of tin (cooling regime, multi-step calculation procedure)

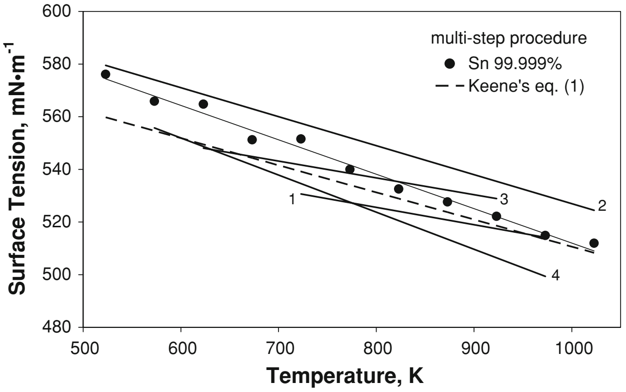


Fig. 3 Temperature dependence of the surface tension of high purity tin (cooling regime, multi-step calculation procedure) compared with literature data: 1 [8], 2–4 [18–20], respectively

highest purity, compared with some recent results of other authors.

Discussion

General

The data given in Table 3 show clearly that the purity of tin has negligible effect on the results of density measurement similarly to the effect on melting temperature. The densities for each grade of tin decrease linearly with the increase of temperature and lie well within experimental data of other authors. It is noteworthy that the correlation coefficient (R^2) for tin of the highest purity is higher than those for other grades of tin. In the case of surface tension, it is much more complicated and aspects that affect on the result of measurement are discussed in the following paragraphs.

Effect of testing procedure

As can be seen in Fig. 4, at low temperature the surface tension measured during heating regime is significantly lower than the values obtained during cooling regime. Also for heating regime, the temperature dependence is curvilinear rather than linear recorded in cooling regime. The most likely explanation for this phenomenon is the coexistence of two chemical and mechanical effects. At low temperatures (near melting point), the surface of molten droplet is, to some extent, covered with a thin oxide film that affects the surface tension measurements. This oxide film is either already present on the sample or might be formed during low-temperature heating due to the oxidation by oxygen adsorbed on its surface or present in the surrounding atmosphere [21–26]. With increasing temperature, the metal evaporation and dissolution of the tin oxide in molten Sn contribute to erosion of this oxide film. At the same time, with increasing volume of the drop its surface area is expanded and this causes cracks in the oxide layer. As both these effects lead to effective de-oxidation, the drop surface gradually gets cleaned, at least partially, and the maximum value of the surface tension is reached around 700 K. Further increase in temperature causes a lowering of surface tension. Thus, it can be assumed that at high temperatures under the experimental conditions of this study, the drop surface is deoxidized and it remains clean during subsequent cooling. Owing to this, the data obtained in cooling regime lie along a straight line.

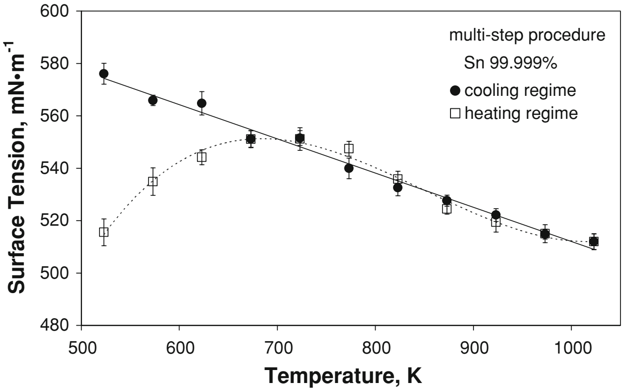


Fig. 4 The surface tension of high purity tin in cooling and heating regimes obtained with multi-step calculation procedure

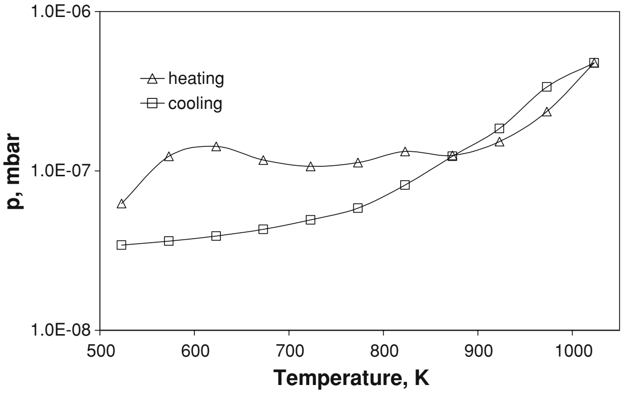


Fig. 5 Vacuum level dependence on temperature recorded in heating and cooling regimes (multi-step calculation procedure)

The curvilinear dependence of surface tension on temperature obtained in heating regime in this study is very similar to that reported by Passerone et al. [21, 23]. The authors observed this dependence in the cooling regime, and found that it is associated with high oxygen partial pressure in the system in low temperature range. Based on experimental results and the thermodynamic–kinetic model of liquid metal oxidation, they demonstrated that oxygen partial pressure of 10^{-11} MPa is sufficient to observe low surface tension of Sn below 700 K, as it is in this case. Yuan et al. [26] also found similar surface tension dependence for Sn for relatively high oxygen partial pressure conditions and explained this dependence by an oxidation of the liquid metal surface during testing at low temperatures. Figure 5 presents vacuum changes with temperature during heating and cooling of high purity tin (99.999%). It can be seen that in heating regime, after an initial increase, the pressure remains almost stable between 573 and 923 K and rises again above 923 K. In cooling regime, however, the pressure decreases gradually with the decreasing temperature. Most importantly, below 873 K it remains lower than it was in heating regime at respective temperatures. As far as the residual gases composition is concerned, these are composed of products from the decomposition of water vapor, oxygen, and carbon oxides, as can be seen in Fig. 6. Consequently, it can be assumed that in cooling regime the drop surrounding is much closer to clean conditions, with respect to oxygen content, than it was in heating regime.

Effect of metal purity

Figure 2 shows the comparison of the surface tension data obtained in this study for tin of differing purity. As could be expected, the purer the metal the higher the surface tension. Similar effects of metal purity were reported earlier for two grades of silver [27] and three grades of zinc [28], showing that at their melting point the highest values of surface tension are associated with samples of the highest purity.

In his review, Keene [1] gave two equations describing the temperature dependence of surface tension of liquid tin. The equations were worked out on the basis of 37 literature data published before 1993. The first equation was based on all of the data in the set, while the second one on the highest 30% values. Keene assumed that the highest values of surface tension (particularly near the melting point) and the greatest slope of the surface tension temperature dependence can be obtained for very pure metals, i.e.,

$$\sigma = 561.6 - 0.103(T[\mathrm{K}] - 505) \qquad (1)$$

$$\sigma = 585.7 - 0.124(T[\mathrm{K}] - 505) \qquad (2)$$

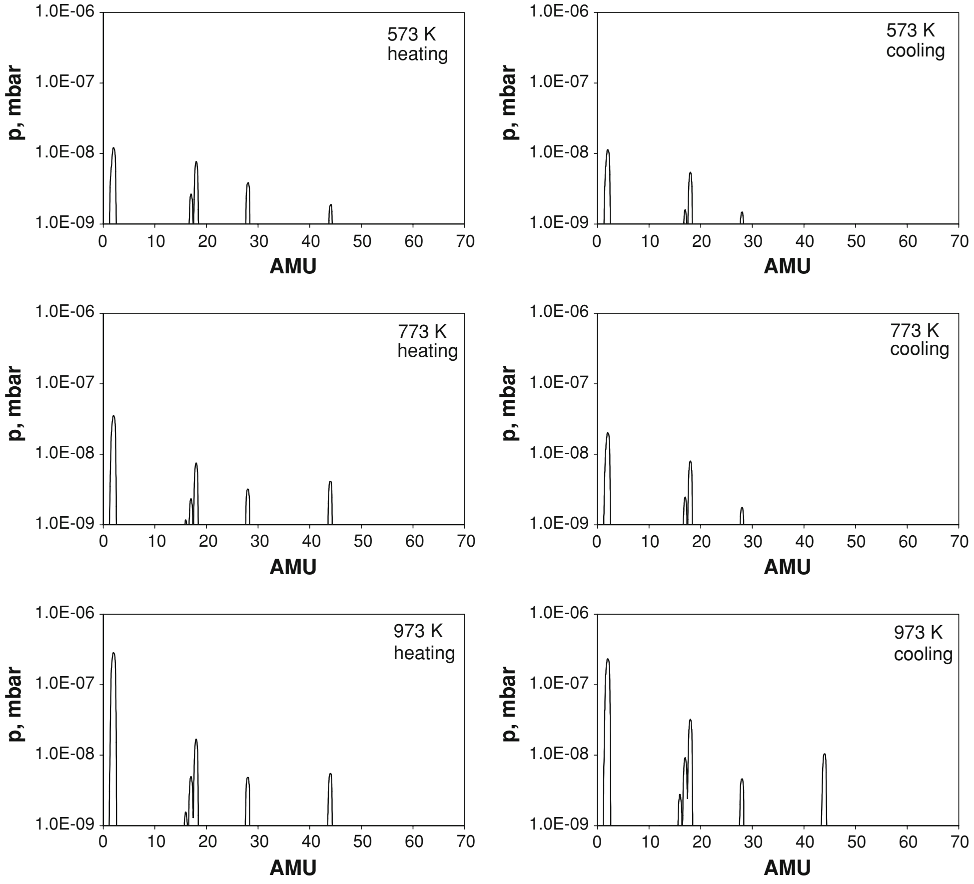
In the case of data shown in Fig. 2 and Table 4, the highest values of surface tension and the greatest slope were obtained for tin of the highest purity, which is in agreement with Keene's assumption. With increasing content of impurities, both surface tension and $d\sigma/dT$ get lower, however, the scatter of the data represented by the correlation coefficient (R^2) gets higher.

Calculation procedure

The results presented in Fig. 2 were obtained using the multi-step calculation procedure described in [12], utilizing a computer program based on the algorithm proposed by Rotenberg et al. [29] for surface tension calculation. This procedure is relatively time consuming as it consists of separate steps with a corresponding use of separate programs. For example, using third party software in the first step the drop images must be binarized in order to obtain the images of required high sharpness, then the coordinates of points on a drop's meridian section can be assigned and, finally, the surface tension is calculated. Different approach to surface tension calculation is used in all-in-one procedure. In this study, a single computer program ASTRA [13, 14] conducts all the steps mentioned above in a few seconds time per each image, in a fully automatic manner, without user's involvement. For surface tension calculation, ASTRA utilizes the improved algorithm proposed by Maze and Burnet [30].

In order to distinguish the difference between the results obtained by these two procedures, the images recorded during cooling regime for tin of the highest purity were processed by both procedures and the results are compared in Fig. 7. As can be seen, both sets of data are very similar, however, the data from the all-in-one procedure are slightly lower at low temperatures (see Table 5; Fig. 7). Consequently, their dependence on temperature seems to be weaker. Also, they have slightly greater scatter than those obtained by the first procedure. The reasons for this

Fig. 6 Residual gases composition at selected temperatures recorded in heating and cooling regimes



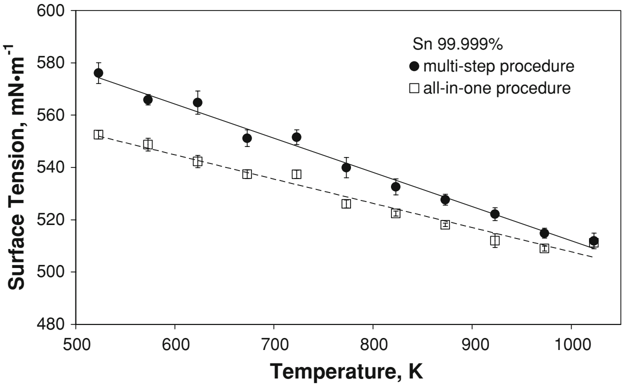


Fig. 7 The surface tension of tin 99.999% calculated using multi-step (*circles*) and all-in-one (*squares*) calculation procedures

Table 5 The surface tension dependence of liquid tin (99.999%) determined using different data acquisition procedures on temperature

Procedure	$\sigma = A + B \cdot (T[\mathrm{K}] - 505)$	R^2	$\sigma_{723\ \mathrm{K}}$
Multi-step	576.7–0.1307(T-505)	0.9869	551 ± 2.8
All-in-one	553.7–0.0927(T-505)	0.9702	537 ± 1.6

discrepancy might be related to differences in image analysis corresponding to each data acquisition procedure, as well as the different algorithms used in calculation software.

Conclusions

The surface tension of tin of three grades of purity was investigated in both heating and cooling regimes. It was found that the metal purity has negligible effect on measurements of both its melting point and density, however, it has influence on the determined surface tension. For tin of the highest purity, both the highest surface tension and its temperature coefficient were obtained. With increasing content of impurities the surface tension of tin decreases, while scatter of the data increases.

It was shown in the example of very pure tin, that the testing procedure has a great influence on measurement of surface tension. The temperature dependence obtained in heating regime is curvilinear contrary to the linear dependence obtained in cooling regime.

The images recoded in cooling regime for tin of the highest purity were processed using two distinct data acquisition procedures, showing the dissimilar values obtained. The reasons behind this discrepancy might be associated with differences in drop profile analysis and the algorithms used in surface tension calculation software.

Acknowledgement This work is sponsored by the Ministry of Science and Higher Education of Poland under the project No. PBZ/MNiSW/07/2006/56.

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