1660 J. Chem. Eng. Data 2009, 54, 1660–1665

Surface Tension of Molten Cu−Sn Alloys under Different Oxygen Containing Atmospheres[†]

Enrica Ricci,*[‡] Donatella Giuranno,[‡] Irene Grosso,[§] Tiziana Lanata,[‡,§] Stefano Amore,[‡] Rada Novakovic,[‡] and Elisabetta Arato[‡,§]

CNR-IENI, Department of Genoa, Via De Marini, 6 - 16149 Genoa, Italy, and DICAT - University of Genoa, Via Opera Pia, 15-16145 Genoa, Italy

The surface tension of the Cu−Sn system has been measured over the whole composition range by using the large drop method over the temperature range $T = (430$ to $1300)$ K. The measurements were carried out at equilibrium and under "oxygen-free" conditions. The results obtained were compared with the available literature data as well as with theoretical values calculated by the compound formation model (CFM) and quasi chemical approximation for regular solution (QCA). In addition, dynamic surface tension measurements have been performed to study the evolution of the molten alloy surface in the presence of trace amounts of oxygen in the surrounding atmosphere. The general physico-mathematical formalism developed by our group to study liquid binary alloys and their oxides has been applied to describe the interactions in Cu−Sn melts under an oxidizing atmosphere. The experimental findings validate the model predicting the oxidation phenomena which contribute to maintain the interface cleanness and to determine the boundary separating oxidation and deoxidation regimes.

1. Introduction

Copper−tin is a basic system of many multicomponent alloys having different important technological applications. These alloys are precipitation hardened and, if containing some surface active elements, such as Ti, exhibit high strength, high resistance to corrosion, and stress relaxation. Depending on the additional elements, they show good performance both at high temperatures and at high pressures, so they can be used for a wide range of applications such as mechanical and micromechanical, chemical, electrical, architectural, as well as soldering materials in microelectronics.[1]

Similar to other complex metal systems,[2] the development of new and improvement of existing, casting technologies require a precise knowledge of the thermophysical properties of the liquid phase as a function of temperature and other parameters. However, most of the multicomponent alloys show a very high chemical reactivity in the liquid state which makes accurate measurements of these properties often impossible. One of the main causes is the presence of reactive elements, such as oxygen, which can dramatically influence the determination of the thermophysical properties.[3,4] In particular, oxygen can strongly affect the surface tension value and its temperature coefficient even if it is present in really small quantities. This fact was experimentally confirmed on both pure metals[5,6] and alloys[7] by using different measurement techniques. An understanding of the factors influencing the composition dependence of the surface tension, as for any other thermophysical property, is important to provide reasonable extrapolations of measured values to a whole range of related alloy compositions.[8] Accordingly, the experimental investigations have to be substantiated by suitable theoretical models able to predict the behavior of the properties for a proper interpretation of the experimental results.

In this work, the surface tension behavior of several Cu−Sn alloys has been investigated both as a function of composition and under variable oxygen content in the surrounding atmosphere. The experimental data have been analyzed together with the corresponding theoretical values calculated by different thermodynamic models (i.e., QCA and CFM)[9] and by applying a physico-mathematical analysis describing the interactions between the oxygen-containing atmosphere and a liquid metal surface.[10]

2. Surface Tension under "Oxygen-Free" Conditions

2.1. Experimental. The Cu−Sn alloys were prepared from the highest purity Sn and Cu shots (99.9999 % Marz-grade) as already described.[11] The surface tension measurements were performed by the variant of the large drop method,[3,12] called pinned drop method.[5] In this case, the solid support is a special circular crucible with sharp edges. The design of the edges of the crucible blocks the triple line at an "apparent" contact angle that is much higher than the real one. A further advantage of the pinned drop method is that the axis-symmetry of the drop can be imposed. In this work, samples of about 3.0 g were contained in a sapphire crucible. The surface tension measurements were carried out in a furnace with a Pt-heating element to ensure the cleanest working conditions. The temperature was decreased from $T = (1300$ to $50)$ K above the liquidus temperature, T_l. A flux of pure argon was kept constant, and the oxygen partial pressure between $pO_2 = (10^{-4}$ and $10^{-2})$ Pa was measured by the electrode (μPOAS Setnag). At each temperature, the real time acquisition of all parameters (surface tension, oxygen partial pressure, temperature, drop size, shape factor, and weight to volume ratio) was done every two seconds for a period of about 20 min with a precision of 0.2 %. The

---

[†] Part of the special section "2008 European Conference on Thermophysical Properties".

* Corresponding author. E-mail: e.ricci@ge.ieni.cnr.it.

[‡] CNR-IENI, Department of Genoa.

[§] DICAT - University of Genoa.

10.1021/je800717a CCC: \$40.75 © 2009 American Chemical Society
Published on Web 03/02/2009

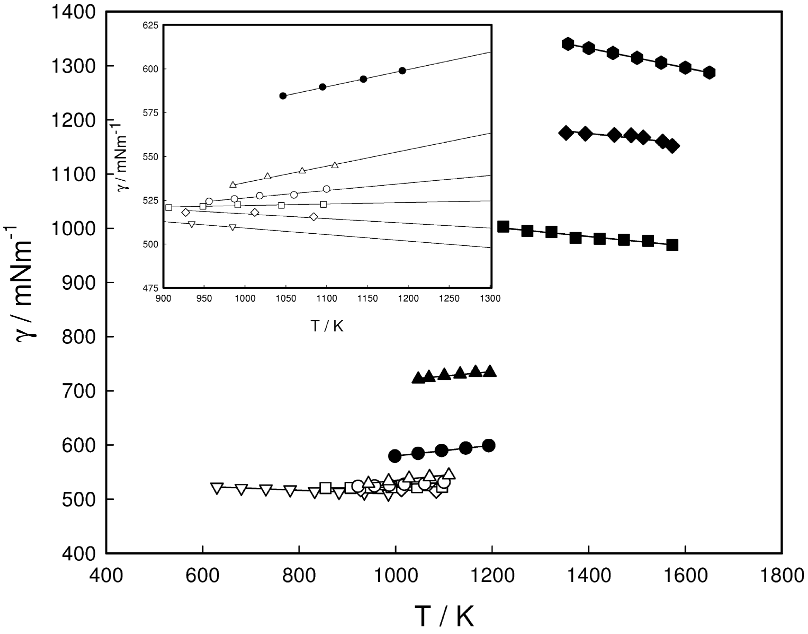

Figure 1. Surface tension as function of temperature of: ⬢, Cu; ♦, $Cu_{95.5}Sn_{4.5}$; ■, $Cu_{90}Sn_{10}$; ▲, $Cu_{80}Sn_{20}$; ●, $Cu_{70}Sn_{30}$; △, $Cu_{60}Sn_{40}$; ○, $Cu_{50}Sn_{50}$; □, $Cu_{30}Sn_{70}$; ◇, $Cu_{15}Sn_{85}$; ▽, $Cu_{10}Sn_{90}$.

final value of the surface tension is a result of the average over all these data: the experimental error of the surface tension measurements was less than 1 %. A detailed description of the apparatus and methodologies used can be found in the literature.[2,5]

2.2. Results. The surface tension experimental data of pure Cu and the Cu−Sn alloys measured in the whole composition range between T = (630 and 1700) K are shown in Figure 1. For the sake of clarity, the surface tension as a function of temperature of Cu−Sn alloys with the Sn content varying between (30 and 90) at % is shown in the inset of Figure 1. Indeed, it is worth noting the presence of both negative and positive values of the surface tension temperature coefficient, $d\gamma/dT$. The results shown in Figure 1 are in good agreement with the experimental and theoretical data on the surface tension of the Cu−Sn system as a function of temperature reported in the literature.[13−16] In particular, in ref 16 the surface tension data of liquid Cu−Sn alloys, measured in the temperature range T = (700 to 1500) K, are shown to have both negative and positive temperature coefficients, similar to the results obtained in this work. Generally, a positive temperature coefficient is observed as a consequence of the presence of tensioactive elements,[16] mainly oxygen, as an effect of the solubility increasing with the temperature decreasing. A positive temperature coefficient has also been observed for liquid alloys having a positive excess free energy.[18,19] The Cu−Sn system exhibits negative excess Gibbs energy in the liquid phase, so the positive temperature coefficient is claimed[16] due to the enhanced surface segregation of Sn caused by the large difference in the surface tension between the two components.

3. Thermodynamic Modeling

The basis of the thermodynamic calculations of the surface properties of Cu-based alloys has been extensively described in our previous work.[20] Since the phase diagram of the Cu−Sn system has been assessed by many authors,[21−23] the optimized data set related to the excess Gibbs energy of mixing, G_M^{xs}, of the Cu−Sn liquid phase[22] together with experimental data on the Gibbs energy of mixing[21] were the input data. The normalized form of the Gibbs energy of mixing, G_M^{xs}, calculated for the equiatomic composition at T = 1423 K, has a value of about −1.06, indicating that the tendency of compound formation in the liquid phase is weak. All thermodynamic data exhibit a minimum around 75 at % of Cu, and thus, the stoichiometry of the Cu_3Sn intermetallic compound, A_3B, was taken in the present calculations as the most probable.[14,24] The mixing behavior of two metals forming binary alloys is the result of the interplay of energetic and structural readjustment of the constituent atoms. The "energetic effect", generally termed as order energy of a system, is the typical combination of interatomic interaction energies of different pairs of nearest neighbors present in the melt. The computed values of the order energy parameters at T = 1423 K are, in k_bT units, $W = -0.071$, $W_{AB} = -3.97$, $W_{AA} = -0.043$, and $W_{BB} = 0.0$. The obtained values are slightly less negative than the corresponding values calculated at T = 1373 K.[14,20]

The Cu−Sn phase diagram[25] and the thermodynamic functions of mixing[21] indicate that the tendency of compound formation in the melts is weak.[26] The surface properties of liquid Cu−Sn alloys have been considered in the framework of the quasichemical approximation for regular solutions (QCA)[27,28] and the compound formation model (CFM) in a weak interaction approximation.[9,26] The theoretical curves, calculated at T = 1423 K, are shown in Figure 2. The surface tension prediction of molten metallic alloys requires reliable reference data for the surface tension of the pure components.[6,17] Surface tension data of pure Cu were obtained by our new measurements. These data are close to that of Lee et al.,[16] while our recently obtained surface tension data on Sn were taken from the literature.[29] It is interesting to notice that for the Sn-rich alloys all experimental sets exhibit a good agreement with the calculated values. On the other hand, for the Cu-rich alloys the disagreement between the measured and calculated values is more evident, and differences up to 180 mN·m^{-1} can be observed in particular with respect to the CFM isotherm (Figure 2). Concerning the alloys with intermediate compositions, our experimental results agree with the literature data,[13,16] while the surface tension data reported by Kawai et al.[15] differ from all experimental sets but

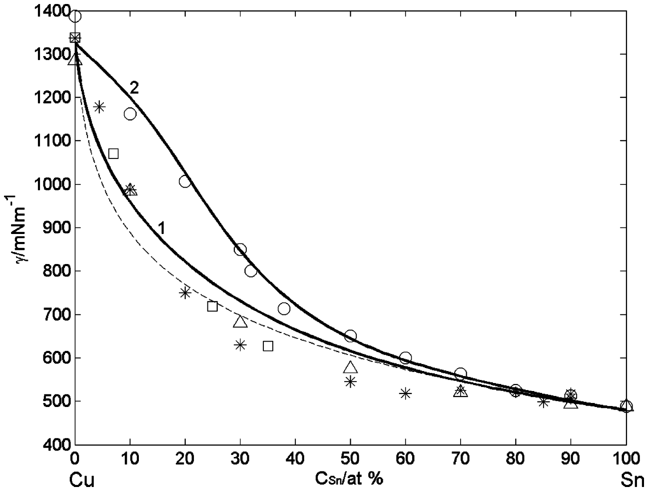

Figure 2. Surface tension isotherms of liquid Cu−Sn alloys at $T = 1423$ K. 1, calculated curve by QCA for regular solution model; 2, calculated curve by CFM; -----, calculated curve by the ideal solution model; *, ref 11; ○, ref 13; □, ref 15; △, ref 16.

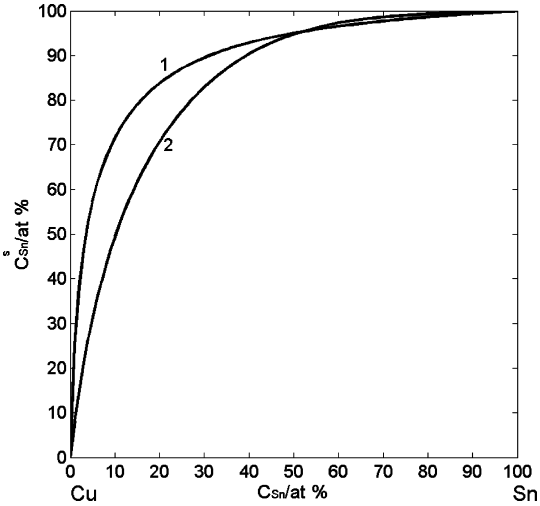

Figure 3. Surface composition ($C_{Sn}{}^s$) vs bulk composition (C_{Sn}) for liquid Cu−Sn alloys at $T = 1423$ K. 1, calculated curve by the QCA for regular solution; 2, calculated curve by the CFM.

exhibit good agreement with the CFM isotherm. All other Cu−Sn surface tension experimental data sets seem to be better described by the QCA for regular solutions than by the CFM (Figure 2). Although Cu−Sn is a weakly interacting system, the effect of the chemical short-range order (CSRO) on its surface tension is more pronounced for the Cu-rich alloys having compositions close to that of an energetically favored intermetallic compound, Cu_3Sn. This theoretical consideration was experimentally confirmed by ref 15.

None of the models[9,27,28] mentioned above take into account the presence of oxygen during the surface tension measurements. However, it is important to underline from the experimental point of view that the surface tension values of pure metals, even if determined under a controlled atmosphere particularly poor in oxygen, can never be considered as "oxygen free". According to Arato et al.,[30] the condition of "clean surface" for a liquid metal or alloy has to be used to define a surface free of oxide but not free of adsorbed oxygen. Small or large discrepancies between the theoretically predicted and experimentally obtained surface tension data can often be explained by an oxidation tendency of a system under so-called "oxygen-free conditions".

The calculated values of surface composition at $T = 1423$ K suggest the segregation of Sn atoms to the surface at all bulk concentrations. To estimate the effects of clustering on the surface segregation in the Cu−Sn system, the CFM has been applied, and the obtained values have been compared with the corresponding results obtained by the QCA for regular solution. The contribution of the short-range order to Sn-surface segregation on liquid Cu−Sn alloys can be estimated by the difference in the surface composition calculated by the two models. As shown in Figure 3, the presence of associates or clusters in the liquid phase slightly decreases the Sn segregation, exhibiting the maximum difference at composition that corresponds to the energetically favored Cu_3Sn intermetallic compound.

4. Interaction with Oxygen-Containing Atmosphere

As previously mentioned, it is impossible to avoid traces of oxygen in the working atmosphere, and so, surface contamination phenomena are of great practical relevance in determining reliable thermophysical properties data such as surface tension, density, etc. In such instances, the evaluation of oxygen−liquid metal interactions can be correctly studied using theoretical approaches based on the study of mass transport phenomena in liquid metal−gas systems.[5]

4.1. Theoretical Achievements. The presence of oxygen and the existence of oxygen fluxes at the liquid metal/gas interface lead to the oxidation phenomena to be taken into account, forming one or more oxides at the interface or inside the gaseous layer close to it. It is required to distinguish between the stable condensed oxides and the volatile oxides in terms of thermodynamic considerations. For those liquid metals that have highly volatile oxides, there are oxide fluxes coming from the metal surface. In these cases, the study of the oxygen exchanges between the gaseous and liquid phases must consider both the molecular oxygen and that linked as oxide. In determining the oxidation conditions of the liquid metal, the equilibrium thermodynamic approach has been shown to be inadequate,[30] and only the consideration of the liquid−atmosphere mass−exchanges under stationary conditions makes it possible to describe the phenomena occurring at the liquid metal/gas interface. The steady state condition leads to the definition of "the effective oxygen pressure": the oxygen partial pressure at which the oxidation of the liquid metal becomes evident. This effective oxygen pressure can be considered as a property of each pure metal, and it can be many orders of magnitude greater than the (thermodynamic) equilibrium pressure.[5,10]

Both the theoretical and experimental aspects of this question have already been discussed for the pure liquid metals.[31,32] Recently, an extension to liquid binary alloys has been proposed,[10] which allows the interpretation of the behavior of the molten Cu−O−Sn system to be described in this work.

For a molten binary alloy, there are two equilibrium reference conditions: one for each component. In fact, each metal is considered as saturated by oxygen, and the equilibrium between the oxidizing atmosphere and the condensed phase, e.g., the metal and its stable oxide, is taken into account. However, in many instances, the existence of a volatile oxide prevents surface oxidation even if the corresponding metal is present in low percentages. The model[10] demonstrates that the behavior of a molten binary alloy to oxidation tends to be similar to that of the "less oxidizable" component also if it is present in a low percentage. The term "less oxidizable" is not used in its strict thermodynamic sense but with the dynamic meaning, particularly allowing for the oxide evaporation phenomena. Following

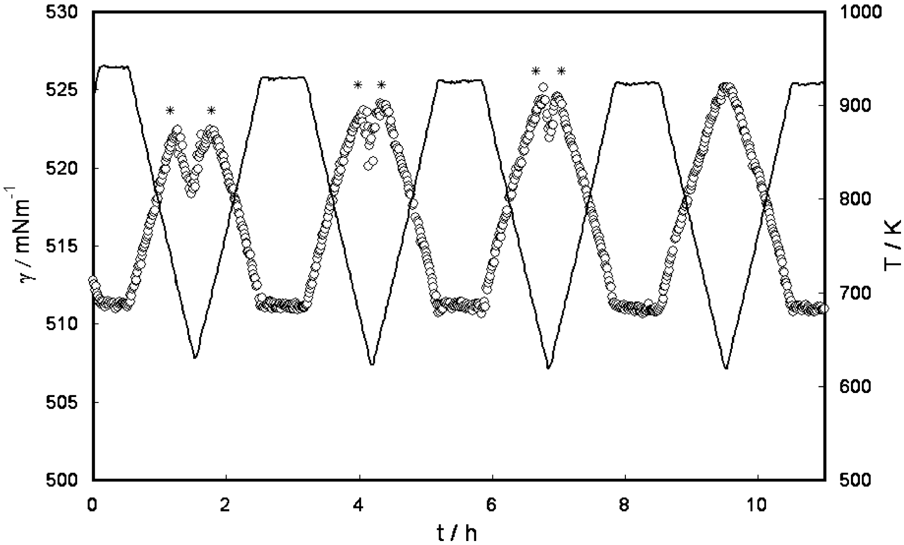

Figure 4. ○, Surface tension γ of the Cu_5Sn_{95} alloy as a function of time t in the temperature (−) range T = (630 to 930) K. *, inversion points.

the theoretical description, when dealing with the Cu−Sn system, there are two equilibrium reference conditions: (1) each metal (Cu and Sn) and its stable condensed oxide (i.e., Cu_2O and SnO_2) and (2) the formation of two other oxides in the gas phase (i.e., CuO and SnO) that play an important role.

From the thermodynamic point of view, Sn segregates over the whole composition range, and it should be more oxidizable than Cu, as the saturation pressure of Sn is some orders of magnitude lower than that of Cu.[33] On the other hand, the vapor pressure of CuO is extremely lower than the vapor pressure of the volatile oxide of Sn (i.e., SnO). In fact, Cu can be mentioned among those metals for which the effective oxygen pressure coincides with the saturation pressure. So, only the evaporation of the tin volatile oxide, SnO, maintains the cleanness of the liquid alloy surface. The theoretical approach predicts that the alloy will behave, over a wide composition range, like Sn, the "less oxidizable" component, according to the definition of the effective oxygen pressure.[10]

4.2. Dynamic Surface Tension Measurements. The behavior of the Cu−Sn system with respect to oxidation phenomena has been determined by dynamic surface tension measurements. To obtain the indication of the oxygen interactions with the liquid metal surface, an experimental isobaric procedure was utilized, where the imposed temperature was changed under constant oxygen partial pressure of the feed gas until the effect of oxygen was found.[5,31,32] The tensioactivity is revealed by the change of the temperature coefficient sign. As saturation conditions strongly depend on temperature, a temperature modulation corresponds to a modulation of the saturation level, and it is then equivalent to a modulation of oxygen concentration in the liquid phase.[34,35] The dynamic surface tension experiments were performed varying the temperature at a rate equal to 5 K·min^{-1}, under a Knudsen regime, over the temperature range T = (630 to 1130) K at one minute intervals. As an example, the test performed on the Cu_5Sn_{95} alloy is shown in Figure 4. The experiment was performed at $P_{tot} \approx 10^{-3}$ Pa (Knudsen regime) and at the constant oxygen partial pressure $pO_2 = 2.6 \cdot 10^{-5}$ Pa. The oxygen partial pressure was continuosly monitored by a solid state oxygen sensor placed close to the sample inside the test chamber. The temperature modulation between T = 630 K and T = 1130 K allowed some significant inversions of the surface tension behavior with the temperature to be revealed (marked with stars in Figure 4). They indicate the temperature value at which the tensioactive effect of oxygen at the surface of the liquid alloy becomes evident. In fact, the surface tension temperature coefficient changes rapidly from negative to positive as a result of a temperature decrease, and vice versa, showing the existence of oxygen adsorption/desorption. However, the surface adsorption is mainly due to the segregation of the oxygen dissolved in the liquid bulk (the consequence of the variation in the temperature), more than the effect of the externally imposed oxygen partial pressure. Moreover, the experimental conditions of the inversion are linked to the tensioactive effect but not necessarily to the formation of stable oxides on the surface, and this effect is identified by the sign inversion of the surface tension temperature coefficient.[34]

In Figure 5, the results of the dynamic surface tension measurements performed on the $Cu_{50}Sn_{50}$ alloy, under the constant oxygen partial pressure $pO_2 = 1.7 \cdot 10^{-3}$ Pa, are shown. This alloy has a positive temperature coefficient, as described in Section 2.2. In this case, the oxygen tensioactive effect was indicated by a slight change of the slope of the surface tension linear behavior with the temperature, instead of a sharp change of it. The oxygen partial pressure values corresponding to the inversion or deviation points of the surface tension with the temperature, together with the calculated effective oxygen pressure, are shown in Figure 6. The values were obtained from the experimental data at T = 1050 K as a function of alloy composition. The difference between the experimental values (circles) and the theoretical predictions (line) is of only 1 order of magnitude. The agreement can be considered very significant in comparison with the difference between the thermodynamic predictions, e.g., the calculated saturation pressures[33] and the experimental data here reported, is more than 15 orders of magnitude.

Moreover, another important point to be mentioned here is that the experimental findings seem not to contradict the substantial invariance in the oxidizability of Cu−Sn alloys with a Cu content up to about 80 %.

5. Conclusions

The surface tension of liquid Cu−Sn alloys has been measured over the whole composition range by the large drop method, at equilibrium, under "oxygen-free" conditions. As is reported in the literature, the alloys with compositions between $Cu_{80}Sn_{20}$ and $Cu_{30}Sn_{70}$ show positive values of the surface

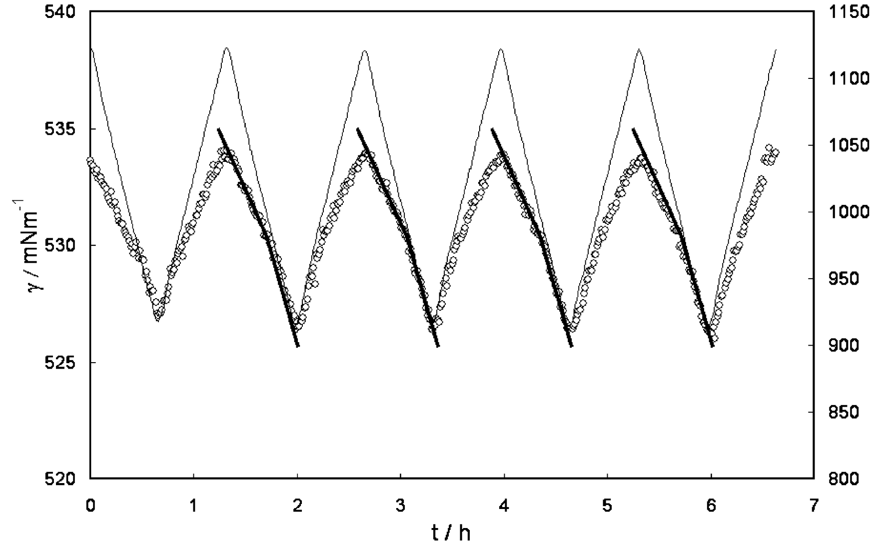

Figure 5. ○, Surface tension γ of the $Cu_{50}Sn_{50}$ alloy as a function of time t in the temperature (−) range T = (900 to 1130) K. The bold lines indicate the change of the slope.

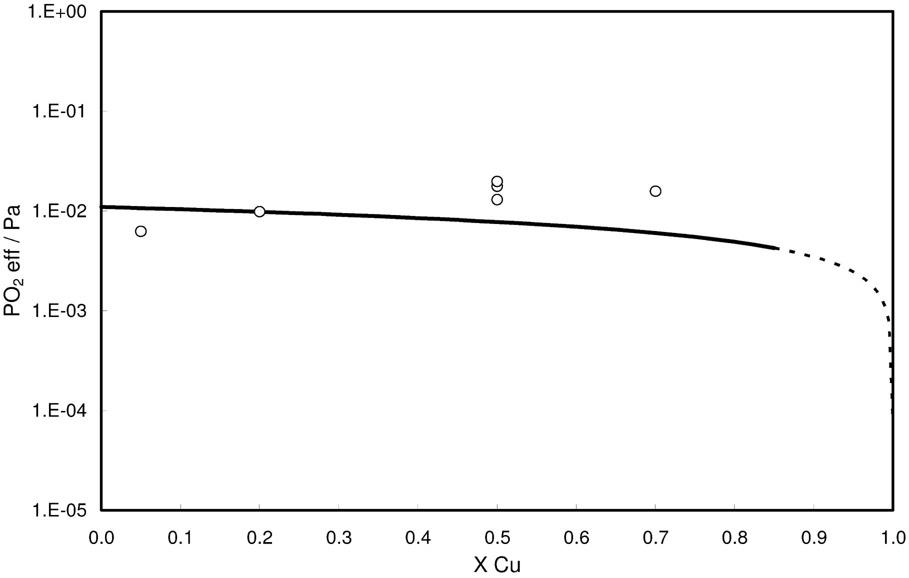

Figure 6. Effective oxygen pressure PO_{eff} for the Cu−Sn alloys at T = 1050 K, as a function of alloy composition at %. Line (−), effective oxygen pressure calculated at T = 1050 K; ○, experimental values obtained from the dynamic surface tension measurements of Cu−Sn alloys at the same temperature T.

tension temperature coefficient. This behavior cannot be justified only by the presence of compounds in that composition range. Accordingly, the specific phenomena can only be partially encoded in terms of the compound formation model (CFM) which, in some cases, has been successfully applied to describe the mixing behavior of Cu−Sn melts. The presence of associates or clusters in the liquid phase slightly decreases Sn segregation, exhibiting the maximum difference at a composition that corresponds to the energetically favored Cu_3Sn intermetallic compound. The surface tension isotherms of the Cu−Sn system computed at T = 1423 K together with the experimental data mainly agree with the surface tension isotherm calculated by the QCA for regular solutions.

The oxygen tensioactive effect on liquid Cu−Sn alloys has been studied both theoretically and experimentally. The application of the theoretical analysis based on the fluid-dynamic model recently extended to liquid binary alloys and their oxides has indicated that the interactions of the alloy and oxygen tend to be similar to that of the less oxidizable component. The assumption of stationary conditions leads to the definition of the effective oxygen pressure: it is a property of the system and it can be many orders of magnitude greater than the equilibrium oxygen pressure due to the existence of volatile oxides preventing the surface oxidation, even if the corresponding metal is present in low percentages. This can be observed performing dynamic surface tension measurements of several Cu−Sn alloys at constant oxygen partial pressure and by modulating the temperature. The very good agreement between the experimental data and the model predictions can be considered as a confirmation that the dependence of the effective oxygen pressure on the composition can really be predicted for the Cu−Sn alloys from the knowledge of the experimental effective oxygen pressures of their pure constituents. Sn maintains the cleanness of the surface under higher oxygen partial pressures; in other words, Sn is in practice less oxidizable than Cu. According to the theory, the effective oxygen pressure of the alloy should be similar to that of pure Sn, even with a Cu content up to about 80 at %.

In agreement with thermodynamic calculations, theoretically supported in the literature, the surface segregation of Sn seems to be the driving phenomenon which can explain the behavior of the surface tension with the temperature of liquid Cu−Sn alloys. The effect of segregation, together with the key role of Sn in the alloy oxidation, should explain the positive surface tension coefficient observed for some alloy compositions.

However, the CSRO effects also have to be encountered even if the thermodynamic functions of mixing indicate that the tendency of compound formation in the liquid is weak.

Depending on the alloy composition, a competition between all these effects can be taken into account, leading to the formation of particular surface structures which could be the main reason of the discrepancy between the experimental surface tension values and the thermodynamic predictions as well as of positive surface tension temperature coefficients. To confirm experimentally the above hypothesis, X-ray and/or neutron diffraction experiments[36] on the liquid metal surface are needed to explain the liquid surface structure.

Acknowledgment

The authors wish to thank Prof. P. Costa for fruitful discussions.

Literature Cited

(1) Abtew, M.; Selvaduray, G. Lead-free solders in microelectronics. *Mater. Sci. Eng.* **2000**, *27*, 95–141.

(2) Ricci, E.; Giuranno, D.; Novakovic, R.; Matsushita, T.; Seetharaman, S.; Brooks, R.; Chapman, L. A.; Quested, P. N. Density, surface tension, and viscosity of CMSX-4 superalloy. *Int. J. Thermophys.* **2007**, *28*, 1304–1321.

(3) Naidich, V. *Progress in Surface and Membrane Science*; Academic Press: New York, 1981.

(4) Eustathopoulos, N.; Nicholas, M.; Drevet, B. *Wettability at high temperatures*; Pergamon Materials Series: Oxford, 1999.

(5) Ricci, E.; Arato, E.; Passerone, A.; Costa, P. Oxygen tensioactivity on liquid-metal drops. *Adv. Colloid Interface Sci.* **2005**, *117*, 15–32.

(6) Keene, B. J. Review of data for the surface tension of pure metals. *Int. Mater. Rev.* **1993**, *38*, 157–192.

(7) Morita, Z.; Kasama, A. Surface tension of liquid copper in dilute oxygen concentration. *J. Jpn. Inst. Met.* **1976**, *40*, 787–795.

(8) Novakovic, R.; Ricci, E.; Gnecco, F.; Giuranno, D.; Borzone, G. Surface and transport properties of Au-Sn liquid alloys. *Surf. Sci.* **2005**, *599*, 230–247.

(9) Bhatia, A. B.; Singh, R. N. Short Range Order and Concentration Fluctuations in Regular and Compound Forming Alloys. *Phys. Chem. Liq.* **1982**, *11*, 285–313.

(10) Arato, E.; Ricci, E.; Costa, P. The effective oxygen pressure of liquid binary alloys. *Surf. Sci.* **2008**, *602*, 349–357.

(11) Amore, S.; Ricci, E.; Lanata, T.; Novakovic, R. Surface tension and wetting behaviour of molten Cu-Sn alloys. *J. Alloys Compd.* **2008**, *452*, 161–166.

(12) Passerone, A.; Ricci, E. *Drops and bubbles in interfacial research: High Temperature Tensiometry*; Elsevier: Amsterdam, 1998.

(13) Lauermann, I.; Sauerwald, F. Oberflaechenspannungsmessungen an geschmolzenen Metallen. *Z. Metallkde* **1964**, *55*, 605–612.

(14) Prasad, L. C.; Mikula, A. Effect of temperature on the surface properties of Cu-Sn liquid alloys. *J. Alloys Compd.* **2001**, *314*, 193–197.

(15) Kawai, M.; Kishimoto, H. T. Surface Tension and Density of Liquid Cu - Sn Alloys. *Nippon Kinz. Gakk.* **1973**, *37*, 668–672.

(16) Lee, J.; Shimoda, W.; Tanaka, T. Surface Tension and its Temperature Coefficient of Liquid Sn-X (*X*=Ag, Cu) Alloys. *Mater. Trans.* **2004**, *45*, 2864–2870.

(17) Iida, T.; Guthrie, R. I. L. *The Physical Properties of Liquid Metals*; Clarendon Press: Oxford, 1993.

(18) Joud, J. C.; Eustathopoulos, N.; Desré, A. Variation of surface tension with temperature for liquid metallic alloys. *J. Chem. Phys. Physico-Chim. Biol.* **1974**, *71* (4), 559–566.

(19) Moser, Z.; Gasior, W.; Pstrus, J. Surface Tension of Liquid Ag-Sn Alloys: Experiment versus Modelling. *J. Phase Equilib.* **2001**, *22*, 254–258.

(20) Novakovic, R.; Ricci, E.; Amore, S.; Lanata, T. Surface and transport properties of Cu-Sn-Ti liquid alloys. *Rare Metals* **2006**, *25*, 1–12.

(21) Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelly, K. K. *Selected values of the thermodynamics properties of binary alloys*; ASM: Metals Park (OH), 1973.

(22) Heuzey, M.-C.; Pelton, A. D. Critical Evaluation and Optimization of the Thermodynamic Properties of Liquid Tin Solutions. *Metall. Mater. Trans. B* **1996**, *27B*, 810–828.

(23) Miettinen, J. Thermodynamic description of the Cu-Mn-Sn system in the copper-rich corner. *Comput. Coupling Phase Diagrams Thermochem.* **2004**, *28*, 71–77.

(24) Prasad, L. C.; Singh, R. N.; Singh, V. N.; Chatterjee, S. K. Compound formation in Sn-based liquid alloys. *Physica B* **1995**, *215*, 225–232.

(25) Massalski, T. B. *Binary Alloy Phase Diagrams*; ASM: Metals Park (OH), 1986; p 965.

(26) Bhatia, A. B.; Singh, R. N. Thermodynamic Properties of Compound Forming Molten Alloys in a Weak Interaction Approximation. *Phys. Chem. Liq.* **1982**, *11*, 343–353.

(27) Singh, R. N. Short-Range order and concentration fluctuations in binary molten alloys. *Can. J. Phys.* **1987**, *65*, 309–325.

(28) Guggenheim, E. A. *Mixtures*; Oxford University Press: London, 1952.

(29) Novakovic, R.; Giuranno, D.; Ricci, E.; Lanata, T. Surface and transport properties of In-Sn liquid alloys. *Surf. Sci.* **2008**, *602*, 1957–1963.

(30) Arato, E.; Ricci, E.; Costa, P. Oxygen transport phenomena at liquid-vapour interface. *J. Mater. Sci.* **2005**, *40*, 2133–2140.

(31) Fiori, L.; Ricci, E.; Arato, E. Dynamic surface tension measurements of molten metals-oxygen systems: validation of the theoretical model on molten tin. *Acta Mater.* **2003**, *51*, 2873–2890.

(32) Giuranno, D.; Ricci, E.; Arato, E.; Costa, P. Dynamic surface tension measurements of aluminium-oxygen system. *Acta Mater.* **2006**, *54*, 2625–2630.

(33) Knacke, O.; Kubashewski, O.; Hesselmann, K. *Thermochemical properties of inorganic substances*; Springer Verlag: Duesseldorf, 1991.

(34) Arato, E.; Ricci, E.; Fiori, L.; Costa, P. Composition transients and saturation phenomena at a liquid metal-vapour interface-an advanced theoretical approach and an application to the oxidation of tin in a vacuum. *J. Cryst. Growth.* **2005**, *282*, 525–536.

(35) Arato, E.; Ricci, E.; Giuranno, D.; Costa, P. Composition transients and saturation phenomena at a liquid metal-vapour interface-the oxidation of tin and aluminium. *J. Cryst. Growth.* **2006**, *293*, 186–192.

(36) Balagurusamy, V. S. K.; Streitel, R.; Shpyrko, O. G.; Pershan, P. S.; Meron, M.; Lin, B. H. X-ray reflectivity studies of atomic-level surface-segregation in a liquid eutectic alloy of AuSn. *Phys. Rev. B* **2007**, *75: 10*, 1–7.

Received for review September 26, 2008. Accepted January 30, 2009. This work has been partially supported by ESA - MAP contract n° AO-99-022 in the framework of the ThermoLab Project.

JE800717A