ELSEVIER
Journal of Alloys and Compounds 452 (2008) 161–166
Journal of ALLOYS AND COMPOUNDS
www.elsevier.com/locate/jallcom

Surface tension and wetting behaviour of molten Cu–Sn alloys

Stefano Amore [a,b,*], Enrica Ricci [a], Tiziana Lanata [a,c], Rada Novakovic [a]

[a] IENI-National Research Council, Via De Marini, 6-16149 Genoa, Italy
[b] DCCI-University of Genoa, and INSTM Via Dodecaneso, 31-16146, Genoa, Italy
[c] DIAM-University of Genoa, Via Opera Pia, 15-16145 Genoa, Italy

Received 18 September 2006; received in revised form 25 January 2007; accepted 30 January 2007
Available online 28 February 2007

Abstract

The surface and interfacial properties of the Cu–Sn system as basic system of the multicomponent alloys proposed as lead-free soldering materials have been studied. The surface tension of the Cu–Sn system has been measured over the whole composition range by using the sessile drop method in the temperature range between 430 and 1300 K. The results obtained are compared with the available literature data and with theoretical values calculated by the compound formation model (CFM) and quasi-chemical approximation for regular solutions (QCA). The study of the wetting behaviour of Cu–Sn on a metal substrate has been performed by measuring the contact angles of four Sn-rich alloys on a pure Ni-substrate and by the metallographic characterization of the solder/Ni interfaces.

Keywords: Surface tension; Wetting; Lead-free solders

1. Introduction

For a long time, the solder used in microelectronic manufacturing and board level packaging was primarily a composition of Sn–37 at.%Pb or Sn–40 at.%Pb, close to the eutectic composition. Nevertheless in the last years some legal, environmental and technological factors were pressing for alternative lead-free soldering materials. For these reasons a large number of Pb-free solder alloys have been proposed [1]. Binary, ternary and quaternary systems have been studied in order to know their characteristics as solder materials. Many of these systems are Sn-based alloys; other constituents are Cu, In, Bi, Au, Ag, Sb, and Mg. In particular the Cu–Sn binary alloys represent a basic sub-system of ternary (Sn–Ag–Cu, Sn–Bi–Cu) and quaternary (Sn–Ag–Cu–Sb, Sn–Ag–Cu–Zn, Sn–Bi–Cu–Zn) systems proposed as alternative solder materials. During soldering, molten alloy (solder) comes into contact and reacts with the metallic pads of the substrate. The nature of this interaction depends on the composition of the solder and on the type of metallic substrate. The most common substrates used in the electronic devices are Cu, Ni, Au and Pd. Among these substrates the electrolytic Ni or Au coatings were commonly used in high-density component assemblies as surface finish on printed wiring boards. Nickel coatings provide desired flat and uniform pad surfaces maintaining a good wettability. Nickel acts as a diffusion barrier layer between Sn-based solders and Cu-conductors and prevents the underlying Cu form reacting with Sn [2].

As mentioned, the solder process consists in the joint formation between the molten solder and a solid metal surface. In the soldering process the formation of a proper metallic bond is a main requirement. The ability of the liquid alloy to flow or spread on the substrate is crucial to the formation of a metallic bond driven by the physical–chemical properties of the system. The interfacial force (surface tension) between molten solder, working atmosphere and substrate influence the degree of wetting and then, the performances of the joints [1,3]. For these reasons the study of the surface tension as well as of the wetting behaviour is an important step in the characterization of solder alloys. In order to understand the behaviour of more complex systems proposed as alternative alloys, the knowledge of the properties of the basic binary system Cu–Sn is needed.

In this work the surface tension of Cu–Sn was measured over the whole composition range (11 different alloys) as a function of temperature. Our experimental results were compared with experimental literature data and with the predictive values

---

[*] Corresponding author at: IENI-National Research Council, Via De Marini, 6-16149 Genoa, Italy. Tel.: +39 010 6475794; fax: +39 010 6475700.
E-mail address: stefano.amore@ge.ieni.cnr.it (S. Amore).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.01.178

obtained by the theoretical models, i.e. regular solution (REG) and compound formation models (CFM). The contact angle of four Sn-rich Cu–Sn alloys on a Ni-substrate was measured as a function of temperature and time. In order to understand the interfacial structures between the drop and the substrate, after each wetting experiment the cross-section of the sample (solder/substrate) was characterized.

2. Experimental

The Cu–Sn alloys were prepared from the highest purity Sn and Cu (99.9999%, Marz-grade). The pure metals were encapsulated in a quartz tube evacuated to high vacuum conditions (10^{-4} Pa), and then molten in a high-frequency generator furnace under pure Argon. The composition of each alloy was checked by using Energy Dispersion Spectroscopy (EDS).

The surface tension as well as the contact angle measurements were performed by the sessile drop method [4]. The drop profile of the sample was acquired using a CCD camera aligned with the sample and a backlighting source. The images were processed by ad hoc acquisition software (ASTRAView) [5,6] in a LABView® environment. This software allowed a very fast automatic acquisition of the drop profile and the elaboration of surface tension, contact angles and other drop parameters in real time during the experiments.

2.1. *Surface tension measurements*

The surface tension of Cu–Sn alloys was measured over the whole composition range. The experiments were carried out in a furnace with Pt as heating element in order to assure the cleanest working conditions. The temperature was checked by a S-type thermocouple placed very close to the specimen and a solid-state electrode (μPOAS Setnag®) allowed the control of the oxygen partial pressure inside the working chamber. All details about the experimental apparatus are reported in our previous works [7,8].

The alloy samples of about 3.0 g were mechanically cleaned by scratching, then chemically rinsed with pure acetone in an ultrasonic bath. The working chamber was evacuated to a total pressure of 10^{-4} to 10^{-5} Pa, then a constant flux of pure Argon (ArN60) was maintained by means a micro-leak precision valve: under these conditions an oxygen partial pressure between 10^{-4} and 10^{-2} Pa was measured by the electrode. During the test the alloy sample was placed in a sapphire crucible ad hoc designed to maintain the axial symmetry of the liquid metal drop. The surface tension measurements were made by decreasing the temperature from 1300 down to 50 K above the liquidus temperature, T_l. At each temperature the acquisition of all parameters (surface tension temperature and oxygen partial pressure) was done every 2 s for a period of about 30 min. The final value of the surface tension is a result of the average over all data with an accuracy less than 1%.

2.2. *Wetting*

The contact angle of four Sn-rich alloys (Cu–70 at.%Sn, Cu–80 at.%Sn, Cu–90 at.%Sn, Cu–95 at.%Sn) was measured on a Ni-substrate under pure Argon (ArN60) in a temperature range from the liquidus temperature up to 900 K. Under the same conditions the contact angle of Cu–80 at.%Sn was measured on a round plate of monocrystalline alumina (sapphire cut along to [0 0 0 1], average roughness $R_a \approx 0.01$ μm, Ø = 15 mm, supplied by R.S.A. le Rubis, France). The experiments were carried out in an horizontal furnace heated by an 800 kHz high-frequency generator coupled to a graphite heater. Before the tests the furnace was heated and degassed under high vacuum conditions (10^{-4} Pa), then pure inert gas was introduced. The resulting oxygen partial pressure was evaluated to be around 10^{-6} Pa. The mass of each alloy sample was around 0.1 g. The substrate was a Ni-square plate (Marz-grade, 13 mm × 13 mm × 1 mm, 99.9999%) metallographically mirror polished ($R_a < 0.05$ μm). During each test the temperature was driven in order to maintain the isothermal conditions for 600 s at different temperatures. The heating rate was around 0.2 K/s, while the cooling rate was 1 K/s.

After the experiment, each sample was metallographically characterized by using optical microscopy, scanning electron microscopy and EDS analysis. Two types of characterizations were performed: on the top of the drop and on the cross-section. The cross-sections were prepared by the usual metallographical method of mirror polishing.

3. Theory

The generalised CFM formalism treats an alloy as a pseudo-ternary mixture of A atoms, B atoms and $A_\mu B_\nu$ (μ and ν are small integers) groups of atoms or clusters with the stoichiometry of the intermetallics present in the solid state, all in chemical equilibrium with one another [9–11]. The absence of clusters in the melt reduces the model to the quasi-chemical approximation (QCA) for regular solutions [11,12]. Butler's concept of a layered interface structure and the relationship between the component's activity in the bulk and the surface phase are basic hypotheses of both models [13]. The CFM formalism in the weak interaction approximation has been successfully applied to the Cu–Sn system to describe the mixing properties in the liquid state with respect to Cu_3Sn, taken as energetically favoured intermetallic compound. Many details of the calculations of thermodynamic and surface properties of liquid Cu–Sn alloys in the framework of the CFM have been reported [14,15]. In the present work only two basic equations used for the calculation of the surface tension isotherms are given. The surface tension for compound forming alloys can be expressed as

$$\sigma = \sigma_A + \frac{k_B T}{\alpha}\ln\frac{C^s}{C} + \frac{W}{\alpha}[p(f^s - f) - qf] + \sum_{i,j=A,B}[p(f_{ij}^s - f_{ij}) - qf_{ij}] \tag{1a}$$

$$\sigma = \sigma_B + \frac{k_B T}{\alpha}\ln\frac{(1-C^s)}{(1-C)} + \frac{W}{\alpha}[p(\phi^s - \phi) - q\phi] + \sum_{i,j=A,B}\frac{\Delta W_{ij}}{\alpha}[p(\phi_{ij}^s - \phi_{ij})] \tag{1b}$$

where σ_A and σ_B are surface tensions of the components A and B, respectively, C and C^s are bulk and surface concentration of A, while W and ΔW_{ij} are interaction energy parameters. k_B, T, p and q are Boltzman's constant, absolute temperature and surface coordination fractions, respectively. α is the mean surface area of the alloy.

The equations for surface tension derived by the CFM (Eqs. (1a) and (1b)) include the concentration functions ϕ, f, ϕ_{ij}, f_{ij}, ϕ^s, f^s, ϕ_{ij}^s and f_{ij}^s [10].

The surface tension of a regular solution described by the QCA, is

$$\sigma = \sigma_A + \frac{k_B T(2-pZ)}{2\alpha}\ln\frac{C^s}{C} + \frac{Zk_B T}{2\alpha}\left[p\ln\frac{(\beta^s - 1 + 2C^s)(1+\beta)}{(\beta - 1 + 2C)(1+\beta^s)} - q\ln\frac{(\beta - 1 + 2C)}{(1+\beta)C}\right] \tag{2a}$$

$$\begin{aligned}\sigma = \sigma_{\mathrm{B}} + \frac{k_{\mathrm{B}}T(2-pZ)}{2\alpha}\ln\frac{(1-C^{\mathrm{s}})}{(1-C)} + \frac{Zk_{\mathrm{B}}T}{2\alpha}\\ \left[p\ln\frac{(\beta^{\mathrm{s}}+1-2C^{\mathrm{s}})(1+\beta)}{(\beta+1-2C)(1+\beta^{\mathrm{s}})} - q\ln\frac{(\beta+1-2C)}{(1+\beta)(1+C)}\right] \quad \text{(2b)}\end{aligned}$$

where β and Z are an auxiliary variable and the coordination number, respectively [11]. In all equations the superscript 's' indicates the surface phase. The application of both models, the CFM and the QCA for regular solutions, make possible to estimate the effect of short range order phenomena on the surface tension, expressed by the difference between two models.

4. Results and discussion

4.1. Surface tension

In the literature some experimental and theoretical data on the surface tension of the Cu–Sn system as function of temperature are reported. Prasad and Mikula [14] as well as the present authors [15] have theoretically investigated the temperature dependence of the surface tension of liquid Cu–Sn alloys. The theoretical studies are in good agreement with the experimental data [16,17] only for Sn-rich alloys containing up to 40 at.%Cu. Recently, Lee et al. [18] have measured the surface tension of liquid Cu–Sn alloys in the temperature range 700–1500 K over the whole composition range. Their experimental results showed the presence of both negative and positive values of the surface tension temperature coefficient (dσ/dT). Our results reported in Table 1 are in good agreement with the works cited above [17,18]. In particular, as reported by Lee et al. [18] we also found both negative and positive temperature coefficients, although we noticed the inversion of slope in a larger composition range. All experimental data of the surface tension of liquid Cu–Sn alloys are shown in Fig. 1. The theoretical curves were calculated at 1373 K applying the compound formation model (CFM) (Eq. (1a) and (1b)) and the QCA for regular solutions (REG) (Eq. (2a) and (2b)). For these calculations the experimental surface tension of pure Cu [19] and pure Sn [20] were taken as reference data. It is interesting to notice that for Sn-rich alloys all experimental sets exhibit a good agreement with the calculated values. In the case of Cu-rich alloys the deviation is pronounced and differences up to 100 mN/m can be observed in particular with respect to the CFM isotherm (Fig. 1). Moreover, as concerns the alloys with intermediate compositions, our experimental results agree with the literature data [17,18], while the surface tension data reported by Kawai et al. [16] differ from all experimental sets. The surface tension of Cu–Sn system seems to be better described by the QCA for regular solutions than by the compound formation (CFM) model. The Cu–Sn phase diagram [21] and the thermodynamic functions of mixing indicate that the tendency of compound formation in the liquid is weak [14,15]. This fact could explain the disagreement of the experimental data with the CFM surface tension isotherm.

Table 1
Surface tension of liquid Cu–Sn alloys (T_{m} melting temperature; σ_{m} surface tension at the melting point; dσ/dT temperature coefficient)

Alloy composition (at.% Sn)	T_{m} (K)	σ_{m} (mN/m) (±2)	dσ/dT (mN/m K)
4.5	1303	1184	−0.094
10	1233	999	−0.089
20	1033	720	0.085
30	993	585	0.119
50	893	521	0.05
60	853	508	0.019
70	813	518	0.012
80	743	539	−0.03
85	703	542	−0.065
90	653	535	−0.04
95	583	524	−0.01

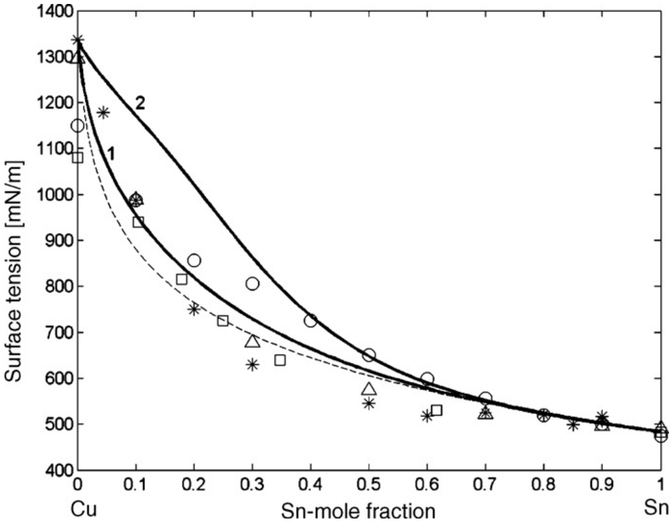

Fig. 1. Surface tension of liquid Cu–Sn alloys at 1373 K: (1) QCA model; (2) CFM model; (- -) the ideal solution model; (*) our results; (◯) Kawai [16]; (□) Drath [17]; (△) Lee et al. [18].

4.2. Wetting

Only few experimental works on the wetting properties of the Sn-based alloys (Sn–Pb, Sn–Bi, Sn–Ag, Sn–In, Sn–Au) on copper substrates are reported in the literature [22,23]. In particular, Arenas and Acoff [22] have measured the contact angle of Sn–0.7 wt.%Cu on a Cu substrate and obtained a value around 35° at 513 K. Although there no experimental data on the contact angle of Cu–Sn alloys on Ni-substrates, the literature reports some works about the interfacial reaction between Sn-based alloys and Ni [24–27]. The growth of the ε-Ni_3Sn intermetallic compound at the interface between Bi–42 at.%Sn and the Ni-substrate was observed by Lee [27]. The presence of $(Cu,Ni)_6Sn_5$ at the interface between a near-eutectic Ag–Cu–Sn and Ni(P) was observed by Vuorinen et al. [3]. However, Hwang et al. [28] have suggested that this phase could be Ni_3Sn_2 with Cu being dissolved into the Ni-sublattice. The Cu–Ni phase diagram presents complete solubility [21] suggesting that Ni and Cu could form the same type of intermetallics with Sn [26,29]. As a consequence, a reactive wetting should be expected to occur when a pure Ni-substrate and Sn-rich alloys are brought into contact.

Table 2
Contact angle values of liquid Cu–Sn alloys on a Ni-substrate (T_l temperature of liquidus; θ_0 contact angle at the melting point; T_f final temperature; θ_f final contact angle; t_f time to reach equilibrium)

Alloy composition (at.%)	T_l (K)	θ_0 (°) (±1)	T_f (K)	θ_f (°) (±1)	t_f (s)
Cu–70Sn	813	31	910	26	2600
Cu–80Sn	743	51	910	25	3100
Cu–90Sn	653	108	910	10	5500
Cu–95Sn	583	140	910	4.5	4250

In order to obtain a preliminary reference parameter for non-reactive wetting, the contact angle of the Cu–80 at.%Sn alloy on a sapphire substrate was measured. At 910 K the contact angle was $\theta_f = 140°$. From this value and from the surface tension of Cu–80 at.%Sn (Table 1), by applying the Young–Duprè equation [28,30] the work of adhesion (W_A) and the interfacial tension (σ_{SL}) of the system could be calculated. The resulting values were $W_A = 1.251\ \text{J/m}^2$ and $\sigma_{SL} = 1.449\ \text{J/m}$.

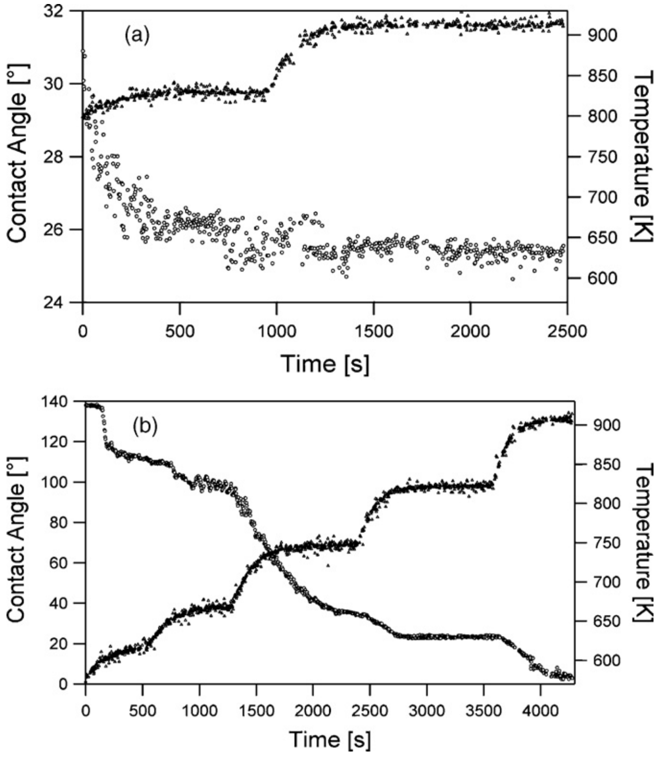

Fig. 2. Contact angle (○) and temperature (△) as function of time of (a) Cu–70 at.%Sn, (b) Cu–95 at.%Sn on a pure Ni-substrate.

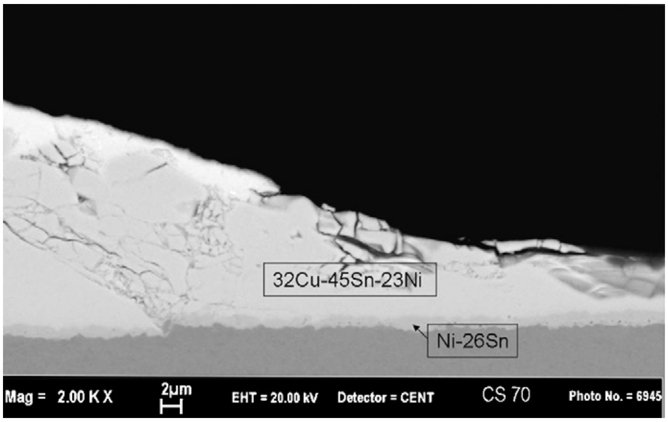

Fig. 3. SEM micrographs of a cross-section of Cu–70 at.%Sn on a pure Ni-substrate. Spot on the interface reaction layer.

Under the same working conditions the contact angles of four Sn-rich Cu–Sn alloys were measured on Ni-substrates as function of temperature and time. The results are reported in Table 2 where the initial composition of the alloy, the liquidus (T_l) temperature, the initial contact angle at the melting point (θ_0), the final contact angle (θ_f) are listed together with the corresponding temperature (T_f) and time (t_f). The results clearly show that, as expected, the degree of wettability increases with an increase of the Sn-content in the alloys. The contact angle of the Cu–70 at.%Sn alloy, as shown in Fig. 2a, after the melting point quickly reaches a final constant value at around 800 K and remains almost constant increasing the temperature up to 900 K. It was observed that the increase of the Sn-content from Cu–70 at.%Sn to Cu–80 at.%Sn did not strongly affect the final contact angle. A remarkable effect of Sn-content was observed between Cu–80 at.%Sn and Cu–90 at.%Sn. A similar behaviour was observed for Cu–90 at.%Sn and Cu–95 at.%Sn for which the contact angle decreases with increasing temperature. In Fig. 2b the behaviour of the contact angle versus time and the corresponding temperature of Cu–95 at.%Sn are shown. Starting from the initial value of $\theta_0 = 140°$ at 583 K, the Cu–95 at.%Sn alloy reached total spreading at 900 K. After the wetting experiments, the cross-section of all samples were analyzed by optical microscope and SEM-EDS. The main results of the interface analysis are reported in Table 3. In all samples an interface layer near the substrate was observed. Figs. 3 and 4 show the micrographs of the interface of Cu–70 at.%Sn and Cu–95 at.%Sn alloy on Ni substrate, respectively. In all cases the interface layer has a composition very close to the Ni_3Sn. The thickness of this layer slightly increases with an increase in Sn-content (Table 3). An erosion of the substrate creating a crater under the drop was also observed for all samples, as shown for Cu–70 at.%Sn in Fig. 5. The depth of this crater decreases with an increase of Sn-content (Table 3). In addition, the presence of a “foot” at the

Table 3
Summary of the results obtained by the SEM-EDS characterization of the Cu–Sn/Ni interface

Alloy composition (at.%)	Interface composition (at.%)	Layer thickness (μm)	Crater depth (μm)	Bulk-phase compositions (at.%)
Cu–70Sn	Ni–26Sn	1	9	32Cu–45Sn–23Ni
Cu–80Sn	Ni–26Sn	2	5	25Cu–45Sn–30Ni
Cu–90Sn	Ni–27Sn	2	4	20Cu–44Sn–36Ni
Cu–95Sn	Ni–27Sn	3	3	4Cu–42Sn–54Ni

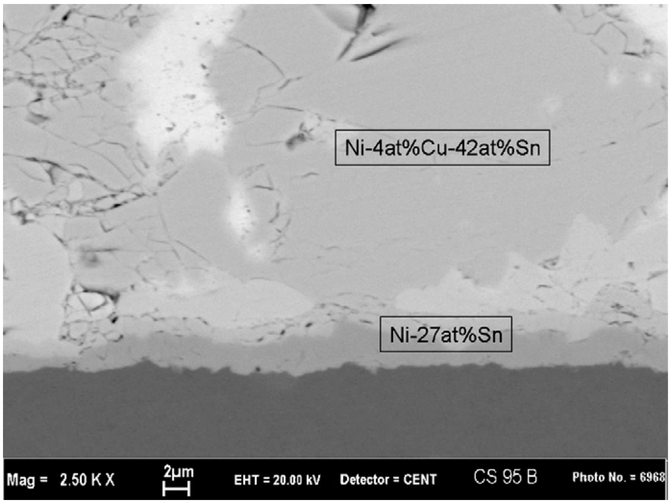

Fig. 4. SEM micrographs of a cross-section of Cu–95 at.%Sn alloy on a pure Ni-substrate. Spot on the interface reaction layer.

edge between the drop and the substrate has also been observed (Fig. 5). The width of this foot is around 80 μm, the same as the rim around the drop. On the other hand, the compositions of a ternary phase $Ni_xCu_ySn_z$, with different x, y, z, detected in the bulk of the drop are given in Table 3. However, the presence of Ni inside the drop is in agreement with the formation of a crater under the drop. The ternary bulk phase has a composition very close to $(Cu,Ni)_6Sn_5$ and in all samples the Sn-content is constant, while the ratio between Cu and Ni increases with an increase of Cu-content in the alloy (Table 3). This is in agreement with the complete solubility in Cu–Ni [21] suggesting that Cu and Ni could replace each other.

The information obtained by the characterization of the cross-section suggests that a part of Sn present in the alloys diffused into the solid substrate forming the interface layer and the “foot” at the edge as first step during the experiment. This hypothesis is supported by higher diffusion coefficient ($A = 0.83\ cm^2/s$) and lower activation energy ($Q = 243$ kJ/mol) of Sn in Ni as compared to Cu in Ni ($A = 0.27\ cm^2/s$, $Q = 255$ kJ/mol) [31]. Accordingly, liquid Sn diffuses in a Ni-substrate faster than Cu. A three-step wetting mechanism can be supposed: the spreading of the liquid phase on the formed layer (Ni_3Sn) which acts as a precursor, the diffusion of Ni inside the drop and the formation of the $(Cu,Ni)_6Sn_5$ ternary phase in the bulk. To validate the hypothesis of such behaviour the study of the kinetics of wetting is in progress.

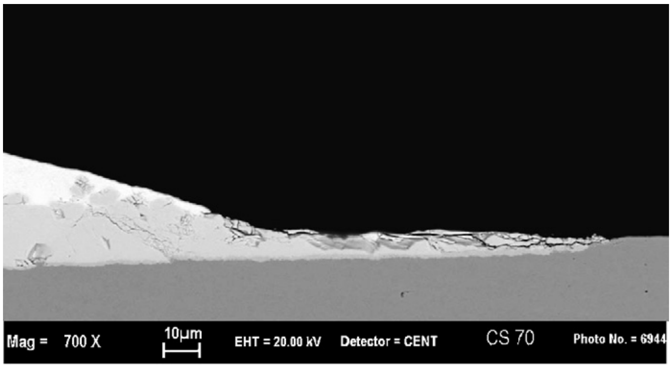

Fig. 5. SEM micrographs of a cross-section of Cu–70 at.%Sn alloys on a pure Ni-substrate.

5. Conclusions

The surface tension of Cu–Sn liquid alloys has been measured over the whole composition range as a function of temperature. Our experimental results are in good agreement with the literature data and show an increase of the surface tension with an increase of the Cu-content as well as a change of sign of $d\sigma/dT$ for intermediate alloy compositions. The comparison with the theoretical curves indicates a good agreement with the regular solution model. An exception is alloys with intermediate compositions where deviations with respect to the regular solution isotherm can be observed.

The wetting behaviour of four Sn-rich Cu–Sn alloys in contact with a Ni-substrate was analyzed. The contact angle decreased with an increase of Sn-content starting from $\theta_0 = 26°$ at 900 K for Cu–70 at.%Sn and reaching the spreading conditions with $\theta_f = 4.5°$ for Cu–95 at.%Sn at the same temperature. From the analysis of the sample cross-sections the formation of an interface layer of Ni_3Sn with a thickness ranging from 1 to 3 μm was detected. Furthermore, an increase of the substrate erosion was also observed which decreased with the Sn-content in the alloy. Hence the growth of an interface layer with a thickness of some microns is desirable for the formation of a good solder joint. The results obtained in this work encourage the study of the surface properties and the wetting behaviour of more complex Cu–Sn-based systems, as candidate materials for lead-free alloys.

Acknowledgements

This work was performed in the framework of the E.C. action COST 531 project: “Lead-free solder materials” and financially supported by INSTM-PRISMA. The authors would like to thank THERMOLAB-ESA MAP PROJECT, Contract no. AO-99-022 for a part of financial support. The authors would like to thank Dr. Ing. Alberto Passerone, IENI-CNR Genoa and Prof. Gabriella Borzone, University of Genoa, for helpful discussion on this subject; also Mr. C. Bottino, IENI-CNR Genoa, for performing the Optical Microscope and EDS analysis and Mr. Roberto Minisini, IENI-CNR Genoa, for technical support.

References

[1] M. Abtew, G. Selvaduray, Mater. Sci. Eng. 27 (2000) 95–141.
[2] N. Eustathopoulos, M.G. Nicholas, B. Drevet, Wettability at High Temperatures. Pergamon Materials Series, vol. 3, Pergamon Press, Oxford, 1999.
[3] V. Vuorinen, T. Laurila, H. Yu, K. Kivilahti, J. Appl. Phys. 99 (2) (2006) 23530(1:6).
[4] A. Passerone, E. Ricci, Drops and Bubbles in Interfacial Research, Elsevier, Amsterdam, 1998, p. 475.
[5] L. Liggeri, A. Passerone, High Technol. 7 (1989) 82.
[6] M. Viviani, ICFAM-CNR Technical Report, CNR Genoa, 1999.
[7] L. Fiori, E. Ricci, E. Arato, Acta Mater. 51 (2003) 2873–2890.

[8] D. Giuranno, F. Gnecco, E. Ricci, R. Novakovic, Intermetallics 11 (2003) 1313–1317.

[9] A.B. Bhatia, R.N. Singh, Phys. Chem. Liq. 11 (1982) 285–313.

[10] A.B. Bhatia, R.N. Singh, Phys. Chem. Liq. 11 (1982) 343–353.

[11] R.N. Singh, Can. J. Phys. 65 (1987) 309–325.

[12] E.A. Guggenheim, Mixtures, Oxford University Press, London, 1952.

[13] J.A.V. Butler, Proc. R. Soc. A 135 (1932) 348–375.

[14] L.C. Prasad, A. Mikula, J. Alloys Compd. 314 (2001) 193–197.

[15] R. Novakovic, E. Ricci, S. Amore, T. Lanata, Rare Met. 25 (5) (2006) 1–12.

[16] Y. Kawai, M. Kishimoto, H. Tsuru, Nippon Kinz. Gakk. 37 (6) (1973) 668.

[17] G. Drath, F. Sauerwald, Z. Anorg. Chem. (1927) 162–301.

[18] J. Lee, W. Shimoda, T. Tanaka, Mater. Trans. 45 (2004) 2864–2870.

[19] R. Novakovic, E. Ricci, D. Giuranno, A. Passerone, Surf. Sci. 576 (1–3) (2005) 175–187.

[20] L. Fiori, E. Ricci, E. Arato, P. Costa, J. Mater. Sci. 40 (2005) 2155–2159.

[21] T.B. Massalski, Binary Alloy Phase Diagrams, vols. 1, 2, ASM, Metals Park, OH, 1986.

[22] M.F. Arenas, V.-L. Acoff, J. Electron. Mater. 33 (2004) 1452.

[23] M.J. Rizvi, J. Electron. Mater. 34 (8) (2005) 1115–1122.

[24] P.T. Vianco, D.R. Frear, JOM 45 (1993) 14–19.

[25] K.J. Rönkä, F.J.J. Van Loo, J.K. Kivilahti, Scripta Mater. 37 (10) (1997) 1575–1581.

[26] B.-J. Lee, N.M. Hwang, H.M. Lee, Acta Mater. 45 (5) (1997) 1867–1874.

[27] M.S. Lee, J. Electron. Mater. 28 (1) (1999) 57–62.

[28] C.W. Hwang, K. Suganuma, M. Kiso, S. Hashimoto, J. Mater. Res. 18 (2003) 2540–2543.

[29] F. Gnecco, E. Ricci, S. Amore, D. Giuranno, G. Borzone, G. Zanicchi, R. Novakovic, International Journal of Adhesion & Adhesives 27 (2007) 409–416.

[30] R. Novakovic, E. Ricci, M.L. Muolo, D. Giuranno, A. Passerone, Intermetallics 11 (2003) 1301–1311.

[31] Smithels, Metals Reference Book, 5th ed., Butterworths, London/Boston, 1976, p. 876.