Structural investigation in Cu-In-Sn alloys around 60 at.% Cu for Pb-free transient liquid phase bonding

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Abstract. The study of the Cu-Sn-In ternary system has acquired in recent years a great importance, due to new environmental regulations forcing to eliminate the use of Pb in bonding technologies for electronic devices, such as Transient Liquid Phase Bonding. There is a lack of basic information on this system regarding some intermetallic phases, which grow in the bonding zone, particularly the so-called η-phase (Cu3In or Cu6Sn5) that exists in both the binary and the ternary phase. In this work, preliminary data are presented obtained for a series of six alloys with about 60 at.% Cu and with In and Sn contents ranging from 0 to 20 at.%, quenched from 300ºC. The alloys were characterized using differential scanning calorimetry, electron probe microanalysis and neutron diffraction. The modiffraction experiments were performed and the temperature scans indicate a relation between the phase transitions observed in the calorimetry curves with structural modifications of the intermetallic phases. Neutron data also suggest the formation of superstructures in the η-Cu6Sn5 phase and even for the ε-Cu3Sn, pointing to the need of further investigation to clarify the present findings.

1. Introduction

The new environmental regulations for electronics devices require avoiding the Pb-based solders. Therefore, large efforts are being devoted to the study of Pb-free alternative alloys [1]. In addition, the high performance of electronic devices involves high current densities, increasing the working temperatures which have to be withstood by bondings. The conventional soldering method is not able to fulfill this aspect, since bonds can only afford working temperatures below the processing temperature. Therefore, new joining methods are being explored, in particular the Transient Liquid Phase Bonding (TLPB) family of methods, which can produce joints capable of operating at higher temperatures [2]. The TLPB method, also called diffusion soldering, promotes the total consumption of the filler or solder alloy by diffusion-reaction with the contact material, thus leading to the formation of new phases which determine the working conditions of the bonds. Sn-based alloys are one of the favorite Pb-alloy substitutes in bonding technology because of their low melting temperature, good wettability, low cost, etc. In particular, the In-Sn system presents an eutectic point at 120ºC which lowers the processing temperature in TLPB.

On the other hand, in the electric and electronic industry Cu is the most popular material. Therefore, a deep understanding of the Cu-In-Sn ternary system is required. However, the equilibrium phase diagram for this system is still in evaluation and there exist certain disagreements between the...
experiments reported and the available assessment of the phase diagram [3]. In fact, there is just one fully experimental work devoted to the Cu-rich region and only above 400ºC [4]. The Cu-In-Sn ternary system presents a large variety of intermetallic phases (IPs).

As part of a long-term project focused on studying the thermodynamic, kinetic, structural and technological development of the so-called diffusion soldering bonds [5], a systematic study of the IPs structure of the η-phase (Cu$_2$In or Cu$_6$Sn$_5$) is being conducted, since this IP is present in the interconnection zone of bonding and its description has been so far confusing and ambiguous [1,3].

2. Experimental

Six ternary alloys were prepared by melting high purity elements (4N) in electric furnaces under a reducing Ar atmosphere. The alloys were annealed for 3 weeks at 300ºC to promote homogenization and rapidly quenched to 0ºC. The compositions of the alloys determined by the electron probe microanalysis (EPMA) technique are indicated in Table 1. There is no available isothermal region at 300ºC for this system, so in Fig. 1 we have marked the present alloys in a 400ºC isothermal section of the equilibrium phase diagram to highlight the proximity to the η-phase region.

| Table 1. Ternary Cu-In-Sn alloys composition close to the η- region. |
| Sample | Cu (at.%) | Sn (at.%) | In (at.%) |
|--------|-----------|-----------|-----------|
| S1     | 53.90     | 46.00     | 00.10     |
| S2     | 54.30     | 44.50     | 01.10     |
| S3     | 53.90     | 43.00     | 03.10     |
| S4     | 55.60     | 39.40     | 05.00     |
| S5     | 58.10     | 29.70     | 12.20     |
| S6     | 61.20     | 18.40     | 20.40     |

Figure 1. Isothermal section at 400ºC of Cu-In-Sn equilibrium phase diagram indicating the position of the alloys on the η- region [4]

Cross-sections of the cylindrical bulk material were prepared by metallographic techniques and examined by optical and electronic microscopy. Additional bulk material was milled to obtain a powder suitable for differential scanning calorimetry (DSC) and for neutron diffraction (ND). ND experiments at room temperature (RT) and in situ thermodiffraction experiments were performed in the D1B instrument at the Institute Laue-Langevin. Silicon and alumina standards were used to calibrate the neutron’s wavelength, yielding the value $\lambda = 2.523$ Å. Thermodiffractions were collected on warming up to 450ºC, recording one diffractogram every 2 min with a heating/cooling rate of 1.6º/min in a furnace under a vacuum of $10^{-4}$ mbar. Calorimetric curves were obtained under nitrogen flow, on warming and cooling with a rate of 10-15º/min.

3. Results

From the composition of our alloys, the presence of the η IP was expected. Given that the alloys had been quenched from 300ºC, the high-temperature (HT) modification of this phase (SG P6/mmc) should be observed, although the low-temperature (LT) modification (SG C2/c) may also appear during quenching. These two polymorphs, together with the so-called η° and η¹ superstructures are documented in the crystallographic databases (ICSD). All these IPs yield very similar diffraction patterns in particular using a long wavelength, with a strong overlap between them. The differences among them correspond to very low intensity Bragg reflections at low angles.

Although with diffraction patterns resembling those of the hexagonal HT η-phase, none of the RT diffractograms for the series of samples could be unambiguously related to any of the reported structures, showing additional low-intensity reflections highlighted by the long wavelength used in the
experiment. In addition, for samples S1 and S2, there appears an additional set of reflections consistent with the minority presence of the ε-phase (Cu₃Sn). Apparently, the metastable HT η-phase was retained at RT during quenching from 300ºC. For the In-poor samples, the single-phase η-region in the equilibrium diagram at 300ºC seems to be slightly shifted from the 400ºC isothermal section but there is no 300ºC isothermal section available in the literature to contrast this. However, there still remains the identification of the structure of η compatible with the observed additional reflections.

In order to study the stability of the η-phase and to identify phase transitions, sample S4 was subjected to thermal treatments in situ at D1B in an adapted furnace under vacuum. The thermodiffractogram collected for sample S4 during its first heating ramp is shown in Fig. 2, where the nucleation of the ε-phase can be detected almost at the end of the heating ramp. The projection in the 2θ-T plane (see inset) indicates that the transformation η→ε starts at 445ºC. This transition can be correlated to the peak observed in the DSC curve obtained for the first heating of the as-quenched S4 alloy, occurring at 467.1ºC as shown in Fig. 3 (solid line). The small peak observed at 216ºC could be due to a small amount of the low-temperature modification of η transforming to the HT hexagonal structure, reported at 186ºC for the binary Cu₆Sn₅ but not reported for ternary alloys. A closer inspection of the first heating thermodiffractogram indicates, indeed, that a structural transition occurs in the sample, as evidenced by some reflections disappearing on warming (Fig. 4). It is also interesting to note that the DSC peak at 216ºC is drastically increased in the second heating cycle (dashed curve in Fig. 3), indicating that the DSC ramp velocity has probably allowed the retransformation to the LT η-phase during the cooling process so that the first and second cycles have different starting points. On the other hand, during the ND thermodiffraction experiment, a fraction of the HT ε-phase is retained during the cooling ramp. For this reason, data collected on warming during the first and second heating at D1B are different, as shown in Fig. 5(a) and (b) respectively. During the second heating ramp a structural transition occurs between 150-200ºC, which still needs to be clarified.

**Figure 2.** Thermodiffractogram of sample S4 during the first heating ramp in the range 400ºC < T < 450ºC. The gradual growth of the ε-phase reflections is indicated with arrows. The inset shows the projection on the 2θ-T plane for a low-angle Bragg reflection, the arrow indicates the beginning of the transformation at 445ºC (b)

**Figure 3.** DSC curves collected on warming for sample S4. The first heating corresponds to the as-quenched sample, while the second heating is already in another initial state. The curves were obtained under N flow for a heating/cooling rate of 10-15ºC/min.
4. Conclusions
The ND technique has been applied to the study of stable and metastable phases in the Cu-In-Sn ternary system. Thermodiffraction in situ experiments have proven to be a powerful tool to follow phase transitions in alloys [6-9]. However, given the extreme complexity and subtle differences between the IPs, which can crystallize in this system, further studies are necessary to arrive to a consistent picture. High resolution diffraction experiments are under progress to properly identify the IPs, since the present results do not completely agree with the reported structures for \( \eta \) and \( \varepsilon \), probably due to superstructure formation as suggested by a number of low angle additional reflections. The quenching from 300°C seems to have avoided almost completely the formation of the stable LT \( \eta \)-phase favoring the HT \( \eta' \)-phase. For the In-poor samples S1 and to a less extent S2, the \( \varepsilon \)-Cu\(_3\)Sn is also retained during quenching from 300°C, and becomes stable during heating: DSC curves for samples S1 to S4 all show the \( \eta \rightarrow \varepsilon \) transition to occur between 420 and 470°C.

Figure 4. Projections to the 20-\( T \) plane of the thermo-diffractograms for sample S4 during the first heating ramp showing a structural transition in the \( \eta \)-phase between 150-200°C.

Figure 5. Projections to the 20-\( T \) plane of the thermodiffractograms for sample S4 for the first (a) and second (b) heating ramps showing a structural transition between 150-200°C, which can be possibly related to the first peak in the DSC curves (Fig. 4).

References
[1] COST Action 531- Atlas of Phase Diagrams for Lead-Free Soldering 1. A T Dinsdale, A Watson, A Kroupa, J Vřeštál, A. Zemanová, J. Vízdal. 2008, 289 pp.
[2] W F Gale, D A Butts. Sci. and Tech. of Welding and Joining. 9-4, 283 (2004).
[3] T Velikanova, M Turchanin, O Fabrichnaya. Index of Selected Soldering and Brazing Systems. G Effenberg, S Ilyenko (ed.) Springer Materials – The Landolt-Börnstein Database, URL: www.springermaterials.com, DOI: 10.1007/978-3-540-47004-5_2. pp 249-273
[4] W Köster, T Gödecke, D Heine, Z. Metallkd. 72, 802 (1972).
[5] S Sommadossi, A Fernández Guillermet, Intermetallics 15-7, 912 (2007).
[6] G M Benites, A Fernández Guillermet, G J Cuello, J Campo, J Alloys Comp. 299, 183 (2000).
[7] G M Benites, G Aurelio, A Fernández Guillermet, G J Cuello, F J Bermejo, J Alloys Comp. 299, 183 (1999).
[8] G B Grad, A Fernández Guillermet, J J Pieres, G J Cuello, Z. Metallk. 87, 721 (1996).
[9] G B Grad, J J Pieres, A Fernández Guillermet, G J Cuello, R E Mayer, J R Granada, Z. Metallk. 86, 395 (1995).