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Liquidus determination in the Cu–Sb–Sn ternary system

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ABSTRACT

In this study the liquidus temperature in the ternary Cu–Sb–Sn system was determined by using DTA/DSC experimental technique. Experiments were carried out along three sections of the ternary system assuming $x_{Cu} = 0.8$; $x_{Cu}/x_{Sn} = 1.22$ and $x_{Sb}/x_{Sn} = 1$, respectively. The liquidus temperatures obtained in this study were compared with calculated liquidus lines. Muggianu approximation method was used to predict respective isopleths along chosen cross-sections. It was found that measured liquidus temperatures are lower than those calculated from respective binary systems using CALPHAD formalism.

1. Introduction

The aim of this study was to conduct thermal analysis on ternary Cu–Sb–Sn alloys in order to obtain more information about the liquidus surface of this system. In addition to the thermodynamic data of the Cu–Sb–Sn system, information about the topology of this system is needed for its thermodynamic assessment. For this purpose it is necessary to study the invariant reactions as well as solidus and liquidus surfaces as a function of composition and temperature. Thus, data from differential thermal analysis (DTA) can be used as the input for the optimization of the ternary phase diagram together with thermodynamic parameters.

Previous investigations of the Cu–Sb–Sn phase relations were recently summarized by Ghosh [1]. It is clear from his survey that our knowledge of the phase equilibria in this system is based on the results that are mostly about eighty years old. The first systematic study of ternary Cu–Sb–Sn alloys was carried out by Bonsack [2], who used metallography and thermal analysis to determine parts of the liquidus surface and twelve isopleths at constant Sb contents. Next, extended study was carried out by Tasaki [3] who investigated phase equilibria in the entire system. Investigations of the phase equilibria in the Sn-rich corner were then repeated by Harding and Pell-Walpole [4] who, on the basis of thermal analysis and metallography, reported isopleths of the phase diagram (for 0.5–3 at.% Cu, 2–14 at.% Sb) and ternary isothermal sections in the temperature range from 20 to 240 °C. Recently, an isothermal section at 260 °C was established by Lee et al. [5] from electron probe microanalysis (EPMA) and X-ray diffraction (XRD) measurements on annealed samples. These experiments showed no evidence of the existence of ternary compounds in this system, but confirmed the existence of the region of mutual solubility between the two isomorphous binary phases Cu_3Sn and Cu_4Sb (denoted as δ). Solubility of antimony in Cu_6Sn_5 (up to 6.5 at.%), of tin in Cu_2Sb (up to 6.2 at.%) and of copper in (Sb) and SbSn (low solubility limit) was also observed, although to a smaller extent. Only Sb_2Sn_3 was reported as a stoichiometric phase (line compound). Also, Lee et al. [5] showed five three-phase fields in their isothermal section of the system: [$\delta + Cu_2Sb + SbSn$], [$(Sb) + Cu_2Sb + SbSn$], [$\delta + SbSn + Cu_6Sn_5$], [$Cu_6Sn_5 + SbSn + Sb_2Sn_3$], and [$Cu_6Sn_5 + Sb_2Sn_3 + L$] at 260 °C.

However, the most extensive study made so far is still that of Tasaki [3]. Needless to say, since then there has been a big change in thermal analysis instruments [6]. Nowadays, DTA/DSC equipment enables precisely controlled experiments to be run during heating and cooling cycles [7]. In particular DSC allows the quantitative determination of the heat turnover in a system, giving various types of information about melting and solidification of alloys. The most common measurements involve the determination of liquidus and solidus temperatures as well as detection of invariant reaction temperatures and their characters (eutectic and peritectic), i.e. the thermal behavior of a substance during melting and

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freezing. For phase diagram research in ternary and higher-order systems, information may be sought regarding additional thermodynamic transitions with one or more degrees of freedom. In order to provide input data for the thermodynamic optimization of the ternary Cu–Sb–Sn system, the liquidus temperatures along three sections were determined by DTA/DSC in this work.

2. Experimental

Samples for DTA/DSC investigations were chosen along three sections:

(1) $x_{Cu} = 0.8$ and x_{Sn} variable in the range 0.05–0.15.
(2) $x_{Cu}/x_{Sn} = (0.55/0.45) = 1.22$ and x_{Sb} variable in the range 0.1–0.8.
(3) $x_{Sb}/x_{Sn} = 1$ and x_{Cu} variable in the range 0–0.65.

The ternary alloy samples were prepared from pieces of pure elements: Cu (99.99%, Aldrich, USA), Sn (99.99%, POCh, Poland) and Sb (>99.5%, Fluka AG, Switzerland). After melting in evacuated quartz tubes, all samples were held at 300 °C for one month to obtain thermodynamic equilibrium.

For the DTA measurements, the samples were sealed under vacuum in specially designed quartz ampoules. Before sealing, all tubes were flushed with high purity argon and evacuated. The total weight of the samples used for the DTA experiments was about 320 mg.

The measurements of samples selected from cross-sections 1 and 2 were performed on DTA 404 NETZSCH apparatus in the temperature range from 150 to 1200 °C. The DTA instrument consists of a single furnace and a symmetrical sample carrier with positions for sample and reference. A piece of nickel, also sealed in an evacuated quartz crucible, was used as reference material. Calibration was done using the melting points of the high purity metals, Al, Au, Ni and Sn to establish an internal calibration file.

The total experimental error of the method has been estimated to be ±2 °C. Generally two heating and cooling cycles were recorded for each sample. The starting temperature was chosen to be equal to the annealing temperature of the sample, i.e. 300 °C. The minimum temperature between the cycles was 150 °C in order to allow for possible supercooling. The heating/cooling rate was 5 K/min for both cycles. Liquidus temperatures on heating were evaluated from the peak maximum, those on cooling from the corresponding onset (cf. Fig. 2). The obtained values, both for heating and cooling, are listed in Table 1 and shown in Figs. 2 and 5–7. Although it was demonstrated by Boettinger et al. [7] that for multicomponent alloys the peak maximum may (depending on a number of parameters, including the heating rate) yield temperature values somewhat higher than the true liquidus temperature this evaluation is still considered a very good approximation, especially with heating rates of 5 K/min or less.

Samples in cross-section 3 ($x_{Sb}/x_{Sn} = 1$) were investigated using a DSC111 Setaram apparatus, a heat-flux calorimeter working up to 830 °C with heating and cooling rates of 0.5 °C/min. The DSC samples were prepared separately by sealing from 500 to 700 mg of the alloys under Ar in quartz crucibles. The calorimeter was calibrated by comparison of the melting temperatures of metallic In, Sn, Pb and Zn (99.999 mass% purity) with tabulated values with an accuracy of the melting temperature of ±0.5 °C. The liquidus temperatures reported in Table 1 represent the average values of the thermal effects detected during first and second heating. Usually, pronounced supercooling effects were observed for all investigated alloys, and the relevant phase diagram information was therefore taken from the heating curves.

Table 1
Liquidus temperatures of ternary Cu–Sb–Sn samples on heating and cooling.

No. of sample	Composition (molar fraction)			Liquidus effect, °C	
	x_{Cu}	x_{Sb}	x_{Sn}	Heating	Cooling
1	0.800	0.150	0.050	676	659
2	0.800	0.100	0.100	699	687
3	0.800	0.050	0.150	725	695
$x_{Cu}/x_{Sn} = 0.55/0.45$					
4	0.500	0.100	0.400	593	571
5	0.440	0.200	0.360	533	500
6	0.385	0.300	0.315	475	477
7	0.330	0.400	0.270	498	458
8	0.275	0.500	0.225	477	466
9	0.220	0.600	0.180	496	461
10	0.165	0.700	0.135	539	497
11	0.110	0.800	0.090	575	541
$x_{Sb}/x_{Sn} = 1$					
12	0.082	0.457	0.461	399	397
13	0.178	0.405	0.417	424	418
14	0.264	0.355	0.381	458	450
15	0.372	0.312	0.316	484	480
16	0.468	0.264	0.268	554	532
17	0.501	0.248	0.251	564	551
18	0.569	0.217	0.214	595	582
19	0.643	0.181	0.176	623	615
20	0.478	0.257	0.265	547	530
21	0.338	0.335	0.327	474	467

Before performing thermal analysis, the initial state of the prepared samples was examined by metallographic and EPMA (electron probe microanalysis), also to recognize and/or confirm the subsequent crystallization steps. Samples subjected to DSC measurements were also re-examined afterwards by the same techniques. An electron microscope (Zeiss EVO-40) equipped with an OXFORD INCA Energy 300 analyzer, which allowed local chemical analysis by energy dispersive X-rays method (EDS), was employed. For quantitative EPMA, the samples were analyzed using an acceleration voltage of 20 kV with cobalt as calibration standard for the beam current, gain and resolution of the spectrometer. The X-ray intensities were corrected for ZAF (Z absorption fluorescence) effects using pure elements as standards. All samples resulted on the section $x_{Sb}/x_{Sn} = 1 \pm 0.03$ with the exception of sample no. 14 for which a ratio of $x_{Sb}/x_{Sn} = 0.93$ was obtained.

The samples were also observed by means of a back-scattered electron detector (BSE). Microanalysis (EPMA) was used to check the overall composition of the samples, the uniformity of chemical composition and the composition of the coexisting phases.

3. Results

A total of 21 samples were analyzed by DTA/DSC measurements and the experimental results are collected in Table 1 together with the nominal compositions, while the respective cross-sections investigated in this study are shown in Fig. 1.

A typical DTA curve of one cycle obtained for sample 1 ($Cu_{0.80}Sb_{0.15}Sn_{0.05}$) is shown as an example in Fig. 2. As an example of the microstructure change taking place in the alloy, the structures of two samples before and after experiments are shown in Figs. 3 and 4.

Fig. 3 shows the metallographic appearance of sample no. 21 (in Table 1) in as cast condition (SEM image, BSE mode) with big primary crystals of Cu_2Sb and the formation of the phases Cu_6Sn_5 and SnSb following the U-type reaction $L + Cu_2Sb \leftrightarrow Cu_6Sn_5 + SbSn$.

In turn, Fig. 4 shows an SEM image (BSE mode) of sample no. 19 (in Table 1) after DSC measurements. The products of two different reactions may be observed: a mixture of the two phases Cu_2Sb and Cu_3Sn formed during the reaction $L + Cu(Sb, Sn) \leftrightarrow Cu_2Sb + Cu_3Sn$ as well as the phases formed during the reaction $L + Cu_3Sn \leftrightarrow Cu_2Sb + Cu_6Sn_5$. The small quantity of SbSn phase (white phase) is due to an excess of liquid coming from

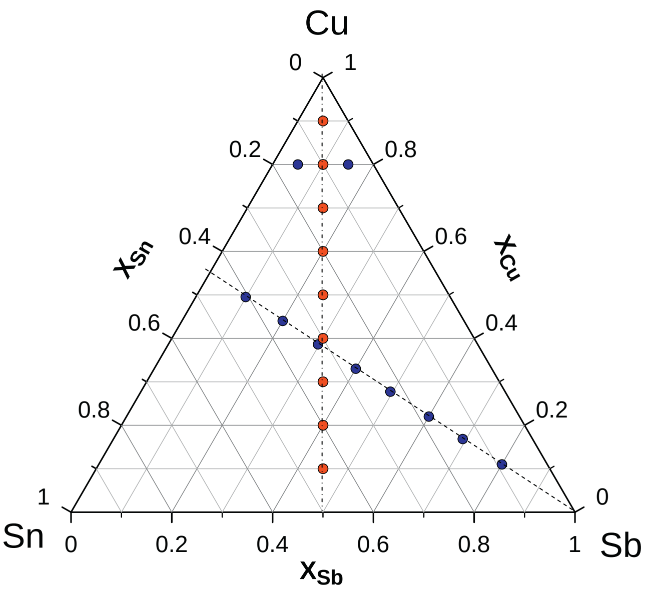

Fig. 1. Schematic presentation of sample compositions along three different isopleths: $x_{Cu} = 0.8$, $x_{Cu}/x_{Sn} = 1.22$ and $x_{Sb}/x_{Sn} = 1$.

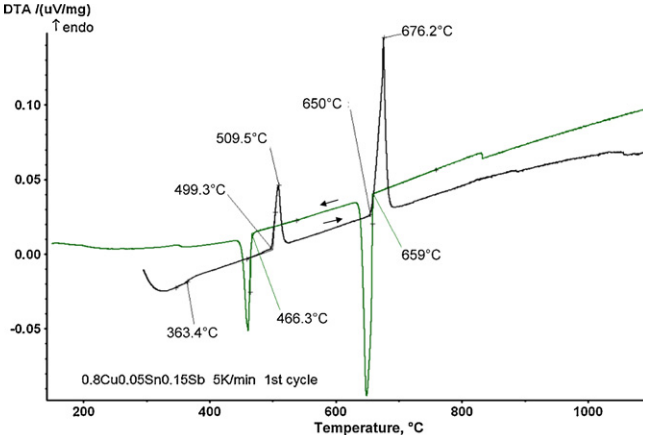

Fig. 2. DTA analysis of sample no. 1 (first cycle).

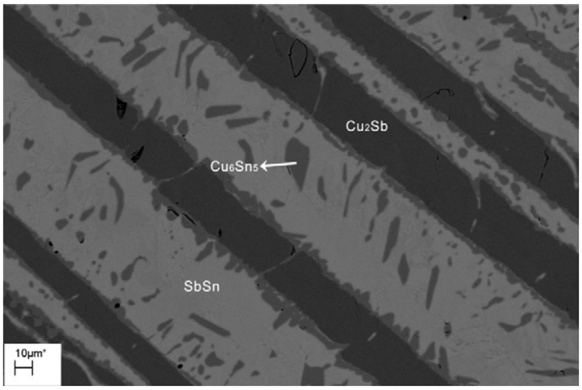

Fig. 3. SEM image (BSE mode) of a sample $Cu_{0.34}Sb_{0.33}Sn_{0.33}$ (no. 21 in Table 1) as cast: big dark crystals of Cu_2Sb surrounded by Cu_6Sn_5 and a matrix of the phase SbSn (light-grey).

the small quantity of liquid phase remaining from the unfinished U-type reactions.

Both characteristic heat effects recorded for heating and cooling (melting and beginning of crystallization, respectively) were recorded. It can be seen that the temperatures obtained from cooling are clearly lower due to supercooling so that the values from heating should be taken as the liquidus temperature. Nevertheless, both temperatures for the respective alloy compositions are shown in Figs. 5–7. They are superimposed on isopleths along chosen cross-sections which were predicted by the CALPHAD method. These predictions were performed by extrapolating the thermodynamic information from the respective binary systems by Muggianu extrapolation. No ternary parameters were assessed. All parameters necessary for thermodynamic calculations were taken from the COST531 database (version 3) [8]. The obtained results are shown in Figs. 5–7. The very short horizontal line around 500 °C close to pure Sb in section 2 (see Fig. 5) is due to an invariant reaction liquid + η-CuSb ↔ β-Cu(Sb, Sn) + (Sb) and is connected with a reduced copper solubility in (Sb). Moreover, calculated by the binary approximation method β-Cu(Sb, Sn) phase field [8] spreads between CuSb bcc phase denoted as β-$D0_3$ and CuSn bcc phase (denoted as Bcc_A2). It should be remembered that the real range of existence of these phases and/or $D0_3$-Bcc order-disorder transition are not exactly known.

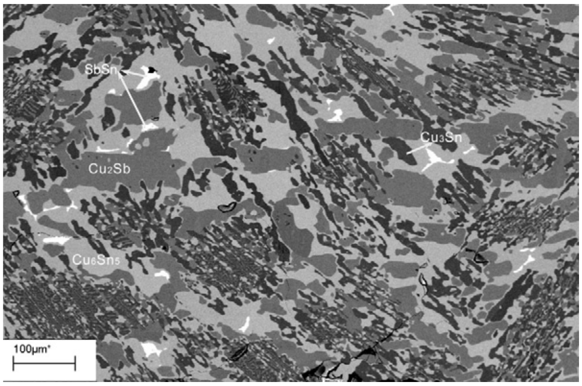

Fig. 4. SEM image (BSE mode) of a sample $Cu_{0.64}Sb_{0.18}Sn_{0.18}$ (no. 19 in Table 1) after DSC: a small quantity of the phase SbSn (white) may be observed (see text).

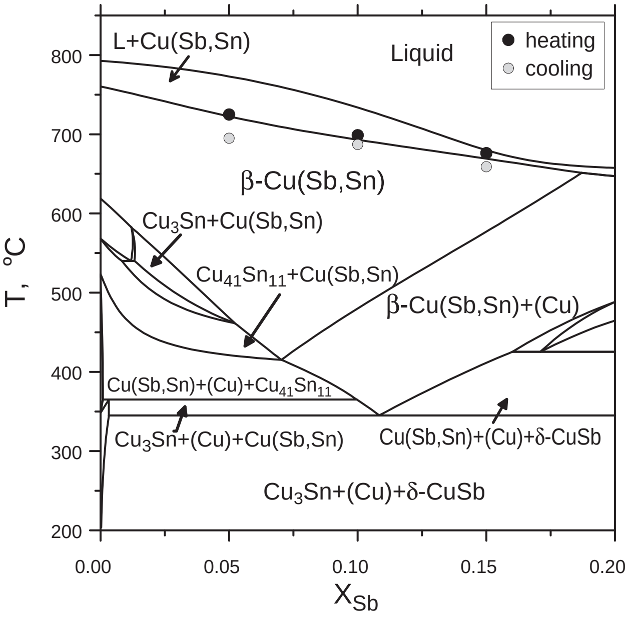

Fig. 5. The results of DTA measurements in the Cu–Sb–Sn system for the $x_{Cu} = 0.8$ isopleth superimposed on the ternary isopleth calculated by the binary approximation method.

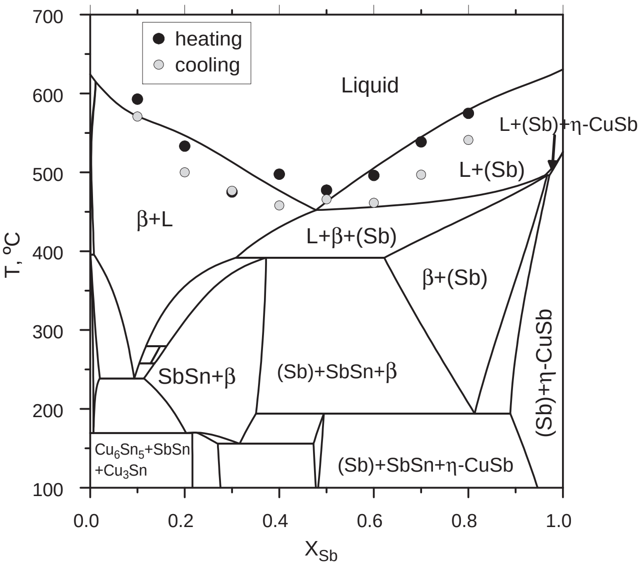

Fig. 6. The results of DTA measurements in the Cu–Sb–Sn system for the $x_{Cu}/x_{Sn} = 1.22$ isopleth superimposed on the ternary isopleth calculated by the binary approximation method. The very short horizontal line around 500 °C close to pure Sb in section 2 (see Fig. 5) is due to an invariant reaction liquid + η-CuSb ↔ β-Cu(Sb, Sn) + (Sb) and is connected with a reduced copper solubility in (Sb).

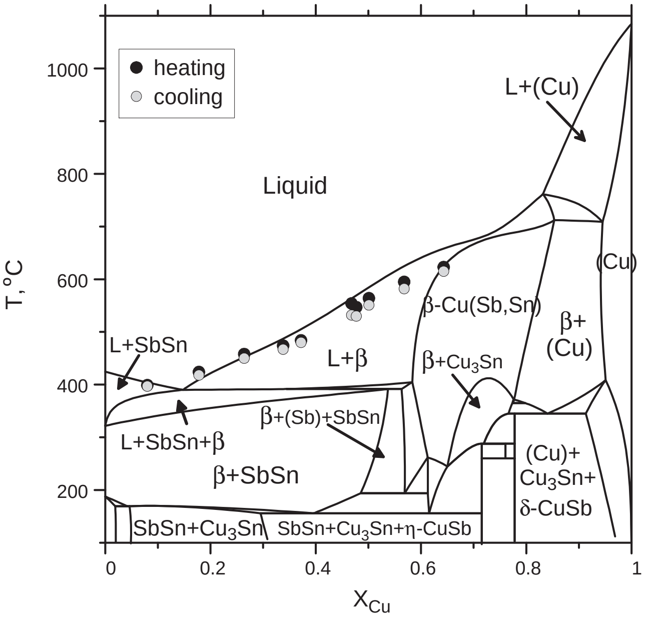

Fig. 7. The results of DTA measurements in the Cu–Sb–Sn system for the $x_{Sb}/x_{Sn} = 1$ isopleth superimposed on the ternary isopleth calculated by the binary approximation method.

4. Conclusions

The analysis of the obtained results and their comparison with the calculated cross-sections of the ternary system leads to the following conclusions:

(1) It seems that the real liquidus surface (at least in certain part of the ternary system) is located at lower temperatures than the one calculated by a binary approximation method.

(2) It is seen from the results obtained for the cross-sections $x_{Sb}/x_{Sn} = 1$ and $x_{Cu} = 0.8$ (Figs. 6 and 7) that the liquidus temperatures are 30–50 °C lower comparing with calculated from binary formalism, narrowing the field of stability of the β-Cu(Sb, Sn) phase. This observation is also supported by the peak detected around 500 °C (see Fig. 2) which is found in a phase field calculated as β-Cu(Sb, Sn) + (Cu) equilibrium. More studies under isothermal conditions are needed to resolve this discrepancy.

(3) Since the displayed isopleths were calculated from the thermodynamic description of the binary systems, probably the ternary interaction parameters determined from DTA data are needed to describe the liquid phase. But only the proper description of the involved solid phases enforced by solubility of the 3rd component in the binary intermetallic phases and the simultaneous change in the thermodynamic description of liquid solution can improve the calculated liquidus and solidus surfaces.

Taking into account the facts mentioned above, new results obtained in this work should improve the optimization process of the ternary Cu–Sb–Sn system.

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