COST531 PROJECT - STUDY OF THE ADVANCED MATERIALS FOR LEAD FREE SOLDERING

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Abstract

The COST 531 [1] project runt in the years 2002-2007, and dealt with the materials suitable for lead-free soldering. The main aim was to increase the basic knowledge on possible alloy systems that were used or planned to be used as lead-free solder materials and offer scientific information about these materials in order to replace the currently used lead-containing solders. The databases of materials and thermodynamic properties are one of the expected results and the basic features and properties of the thermodynamic database, allowing to model phase diagrams in multicomponent systems, are described in following paper.

Keywords: Lead-free solders, Thermodynamic database, Calphad method

1. Introduction

Public awareness of environmental issues including the use and disposal of potentially toxic materials is increasing and lead is one of subjects involved. Lead containing materials are among the most important threatening human life and the environment.

The main reason is the ability of lead to accumulate in the human body, leading to damage in the nervous and reproductive systems. It may cause behavioural problems and anaemia and hypertension. Currently, lead poisoning is assumed to have occurred if the level of lead in the blood exceeds 500 μg/ml, but recent studies have found that

such limit is still above safe dose for the child's neurological and physical development.

There is now increasing pressure to eliminate lead containing materials, which is significantly supported by the legislative process in the EU. Despite the fact that the electronics industry is not the largest user of lead and lead containing chemicals (the electronics industry uses only very small fraction of the overall consumption of lead but 80% of its consumption is in solders), electronic products and processes were (and still are) significant sources of lead contamination, both through occupational exposure and through waste disposal of electronic assemblies, causing e.g. the contamination of underground water sources.

Recent EU legislation (DIRECTIVE WEEE (Waste from Electrical and Electronic Equipment) and DIRECTIVE 2002/95/EC, Restriction of the use of certain Hazardous Substances (RoHS) in electrical and electronic equipment) prohibited the use of lead containing solders in many industries from July 1st, 2006.

It is clear that there is no immediate alternative for the standard lead-tin solders (mostly Sn37Pb and Sn40Pb), but a range of possible alternatives has been developed. Most frequently, one family of alloys based on tin, silver, and copper is used, especially by the telecommunications industry: possible candidates are alloys Sn3.5Ag, Sn0.7Cu, or Sn3.8Ag0.7Cu with melting points (around 220°C) more than 30 degrees higher than their lead-containing predecessor. Nevertheless, the choice of a solder material will depend on planned application, i.e. factors like temperature compatibility and/or cost might make also other alloys more useful for automotive, telecommunications,

consumer, military and aerospace industries. The current situation can be described in such a way that it is generally acknowledged that lead-free soldering is technologically possible, but many key issues have still to be solved, both scientifically and industrially.

Among the crucial properties of the perspective lead free solders belong the melting temperature and the precipitation of intermetallic phases on the interface. Knowledge of the phase equilibria that occur in the solder/substrate alloy systems, can be gained by the application of thermodynamic modelling based on self-consistent and reliable thermodynamic database together with appropriate software (MTDATA [2], Pandat [3], ThermoCalc [4], Factsage [5]). By this way, it is possible to obtain important information concerning the interaction of solders with substrates underlying intermetallic phase formation and solidification properties, such as solidification paths, liquidus surface and Scheil solidification simulation. The thermodynamic database can also be part of larger software packages that model physical properties, e.g. surface tension using the Butler equation [6,7].

2. The CALPHAD approach in alloy thermodynamics

The modelling of thermodynamic properties and consequently the calculation of phase diagrams and the prediction of phase transformations in complex systems is based on semi-empirical approach, which combines experimental observation with theoretical modelling based on the thermodynamic laws. Therefore, it is significantly dependent on the amount and quality of experimental data available. The

CALPHAD approach [8], which is the most widely used method of this type in use, is based on the bottom-up approach to the modelling of chemical systems, starting from binary phase diagrams and adding additional elements. The thermodynamic properties of a binary system can be calculated using the Gibbs energy expressions for both elements in each of the phases existing in the system. It is possible to model such a system with high precision if reliable experimental data describing both the thermodynamic properties of the phases (e.g. specific heat, enthalpies of formation or mixing, activities) and their phase data (e.g. invariant temperatures, compositions and amounts of phases) are available. By combining correct descriptions of binary and ternary alloy systems, it is possible to predict phase equilibria in higher order systems. The deviation of the real behaviour of the system from the prediction can be minimised by adding new parameters (usually ternary parameters are enough), but they must not influence the modelled thermodynamic properties and calculated phase diagrams of the lower order systems.

For successful using of mentioned description of phases in practical calculations, the thermodynamic databases can be used. They contain the results of assessments of thermodynamic parameters for expressing of Gibbs energies of individual systems. The assessed Gibbs energy parameters are then collected in databases that are often oriented towards particular specialised groups of materials. The COST 531 database [9] for lead-free solders is typical example. Quite valuable overview of rules for creating correct and reliable assessment were recently proposed by Schmid-Fetzer [10] et al.

3. The COST 531 thermodynamic database [9]

The consistent database is not just a collection of thermodynamic assessments for a number of binary and higher order systems. Even if individual assessments reproduce their respective phase diagrams and thermodynamic properties well, a collection of such assessments in the form of a database may contain problems and discrepancies. Several important rules have to be respected when such database is compiled. These rules and its application for the COST 531 thermodynamic database for lead-free solders will be described in following paragraphs.

3.1. Content of the database

11 elements were included in a database for lead-free solders. Cu and Sn (Cu is a substrate material as well) along with Ag have already been identified as component elements for lead-free soldering material. Low melting point elements such as In and Bi have been added to the list, along with possible substrate materials Ni, Au and Pd. Elements Sb, Zn are also included. Lead was included so as to be able to model equilibria relating to repairs of old electrical components using the new materials. The following elements are in the database: Ag, Au, Bi, Cu, In, Ni, Pb, Pd, Sb, Sn and Zn.

The database currently holds thermodynamic descriptions for 53 of the 55 binary systems associated with 11 elements in scope of the database. Added to these are assessed data for 20 ternary systems, which are listed in Table 1.

Table 1. *Assessed ternary systems in the COST 531 thermodynamic database*

Ag-Au-Bi	Ag-Cu-Ni	Ag-Ni-Sn	Bi-In-Sn	Cu-Ni-Pb
Ag-Au-Cu	Ag-Cu-Pb	Au-In-Sb	Bi-Sb-Sn	Cu-Ni-Sn
Ag-Au-Sb	Ag-Cu-Sn	Au-In-Sn	Bi-Sn-Zn	In-Sb-Sn
Ag-Bi-Sn	Ag-In-Sn	Au-Ni-Sn	Cu-In-Sn	In-Sn-Zn

3.2 The creation of consistent thermodynamic database

To verify the reliability and consistency of the database we employ three approaches to the testing. Firstly, each assessment, integrated into the database, was tested to ensure that the typographical errors and omissions are excluded. The aim was to obtain correctly reproduced phase diagram and thermodynamic properties as given in the source of the data.

The second approach arises from the fact that several software packages for the modelling of phase diagrams are currently in use. The assessments from different sources were checked using three different currently available software packages for computational thermodynamics: MTDATA, Pandat and Thermo-Calc [2-4]. The result of calculations using each of the software packages has to be identical.

The third approach stems from the fact, that the consistent database is not just a collection of thermodynamic assessments for a number of binary and higher order systems. Even if individual assessments reproduce their respective phase diagrams and thermodynamic properties well, a collection of such assessments in the form of a database may contain problems and discrepancies. Several important rules have to be respected when such database is compiled.

3.2.1. First condition of database consistency

A reliable thermodynamic database has to be consistent with respect to the models used for the expression of Gibbs energy functions of the elements and their mutual interactions in the system.

The total molar Gibbs energy of a phase f is given by the sum of a number of different contributions, (e.g. G^f_{ref} - the reference state of the molar Gibbs energy of the phase, G^f_{id} - the contribution resulting from ideal mixing of the component atoms, G^f_E - the excess Gibbs energy, which describes the influence of non-ideal behaviour of the thermodynamic properties of the phase, G^f_{mag} - the magnetic contribution). Standardised polynomials are used for the expression of G^f_{ref} and G^f_E. The excess Gibbs energy term is described using thermodynamic interaction parameters [11] and is expressed by an appropriate polynomial. The most frequently used is the Redlich-Kister formalism, which was extended for ternary systems by Muggianu [12]. Nevertheless, other formalisms can be also used, e.g. the T.A.P (**T**hermodynamic **A**dapted **P**ower Serie) polynomial [8], but it has to be checked (by program package) to ensure that it is the same in all cases or at least that proper polynomial is taken for calculations.

3.2.2. Second condition of database consistency

A reliable thermodynamic database has to be consistent with respect to the models and names used for the description of equivalent phases existing in different systems, which have to be the same throughout the database.

It is not easy to fulfil this condition, as the assessor can select the model for the description of a particular phase and to allocate any name to it. The sublattice model [11], which has been widely used for metallic systems gives the authors complete freedom in the selection of the number of sublattices, their site ratios and occupancies, usually based on existing experimental information mainly concerning the crystallography of the phase. The ordering behaviour in some phases represents further phenomenon which can be described with the application of different models [13]. As the same systems have often been modelled several times in the past, it is very important to identify carefully the models used in these assessments.

The consistency in the phase names is also important to allow for the possibility of mixing in higher order systems. To enable this mixing, it is important to have the same thermodynamic model for the phases, which occurs in more binary or ternary systems and complete solubility exist in higher order system. Where conflicts occur in the modelling of a binary phase, a decision has to be made on which model to choose, often based on ternary information. As an example, combining Cu-In system with Sn, the CuIn-η phase, existing in the whole concentration range in Cu-In-Sn system, has to have the same name and the same thermodynamic model in both Cu-In and Cu-Sn systems. In next example, in the Cu-In system, Cu_2In phase has the same crystal structure (γ-brass) as Ag_2In phase. It is modelled as stoichiometric phase in Ag-In system by Moser [14] but as solution phase with three sublattices in Cu-In system by Liu et al [15]. Although the two binary phases are stable over different temperature ranges in the binary systems, the phase does exist in very wide temperature and concentration region in the ternary Ag-Cu-In system, which requires the same model for the Ag_2In-phase so that the ternary extension of this phase can be modelled. This phase is now described with three sublattices model under one phase name and one set of parameters in the COST531 database.

3.2.3. Third condition of database consistency

The same description of the Gibbs energy (including the numerical values) for an element or compound (species) in a given crystallographic structure, has to be used throughout a consistent thermodynamic database. Using the same set of thermodynamic parameters for the calculation of Gibbs energies of any species for every system included in the database (not only the type of polynomial description as mentioned in the first condition of consistency) is therefore very important. This is essential even for the pure elements. In particular, the Gibbs energy description for crystallographic structures in which the element does not exist in nature, may differ significantly not only between different authors, but also in various versions of the database from the same source [16,17].

The thermodynamic properties for such unstable structures cannot be measured and therefore the parameters are either estimated

(traditionally) or modelled during the assessment of higher order systems where such a structure exists and the element dissolves into it. Recently, the energy difference of such hypothetical phases at 0 K with respect to stable phases has been calculated by ab-initio methods.

The Cu-Ni-Sn system is very important system in lead free soldering and therefore, it is important to have its reliable description. Unfortunately, this system can be also used as illustration of many of the inconsistency problems of the type 2 and 3.

The thermodynamic data for the Cu-Sn system were taken from X.J. Liu et al. [15], the liquid and FCC_A1 phase data were modified to take into account new experimental data obtained in the scope of COST 531 Action. A high temperature BCC region exists in this system at around 700 C and 25 wt% of Sn that exhibits complex ordering behaviour of the type $A2 \rightarrow B2 \rightarrow D03$. As there is not enough experimental information about this region, it was modelled as single BCC_A2 phase [15].

Condition of consistency between the thermodynamic data for the different binary systems enforces modification of the data for the Ni-Sn system [18]. The high temperature Ni_3Sn phase having the $D0_3$ structure has been observed in Ni-Sn system. In the ternary Cu-Ni-Sn system, a continuous solubility region is observed between the high-temperature BCC_A2 phase originating in the Cu-Sn binary and this Ni_3Sn phase. Therefore, it was necessary to unify the models used for both phases to model that region as a single phase. It was therefore decided to remodel the Ni_3Sn phase as the BCC_A2 structure. Re-optimisation of the Gibbs energy parameters for Ni-Sn system

yields the result shown in Fig. 1, which is in very good agreement with the previous assessment and experimental data.

For the database, the reassessment of the ternary Cu-Ni-Sn system was based on the work of Miettinen [19] along with experimental results obtained mainly as part of the COST 531 Action. Miettinnen was primarily concerned with Cu-Ni rich part of the diagram at high temperatures in his partial thermodynamic assessment of the Cu-Ni-Sn system. Apart from different unary data, different descriptions of the relevant binary systems were used in his study [19]; the high-temperature Ni_3Sn- γ phase was modelled as D03 and the ordering reaction in the Cu-Sn system was modelled in simplified form as BCC_A2$\rightarrow$ D03. Therefore, it was necessary to reassess this system to ensure compatibility with the adopted unary and binary data in the COST 531 thermodynamic database. Figure 2 shows an example of a comparison between measured and calculated enthalpies of mixing of liquid Cu-Ni-Sn alloys at 1303° C. Selected isopleth is shown in Fig. 3 at constant nickel content of 2 wt %.

4. Applications of the database

The main benefit of thermodynamic database developed in the COST531 project is in the prediction of phase equilibria. Therefore, the database can be used to investigate the way in which changes in composition will affect properties such as the liquidus temperature and solidus temperature. Moreover, the CALPHAD concept is based on use of reliable, well tested models for extrapolating the thermodynamic properties into multicomponent systems allowing to make
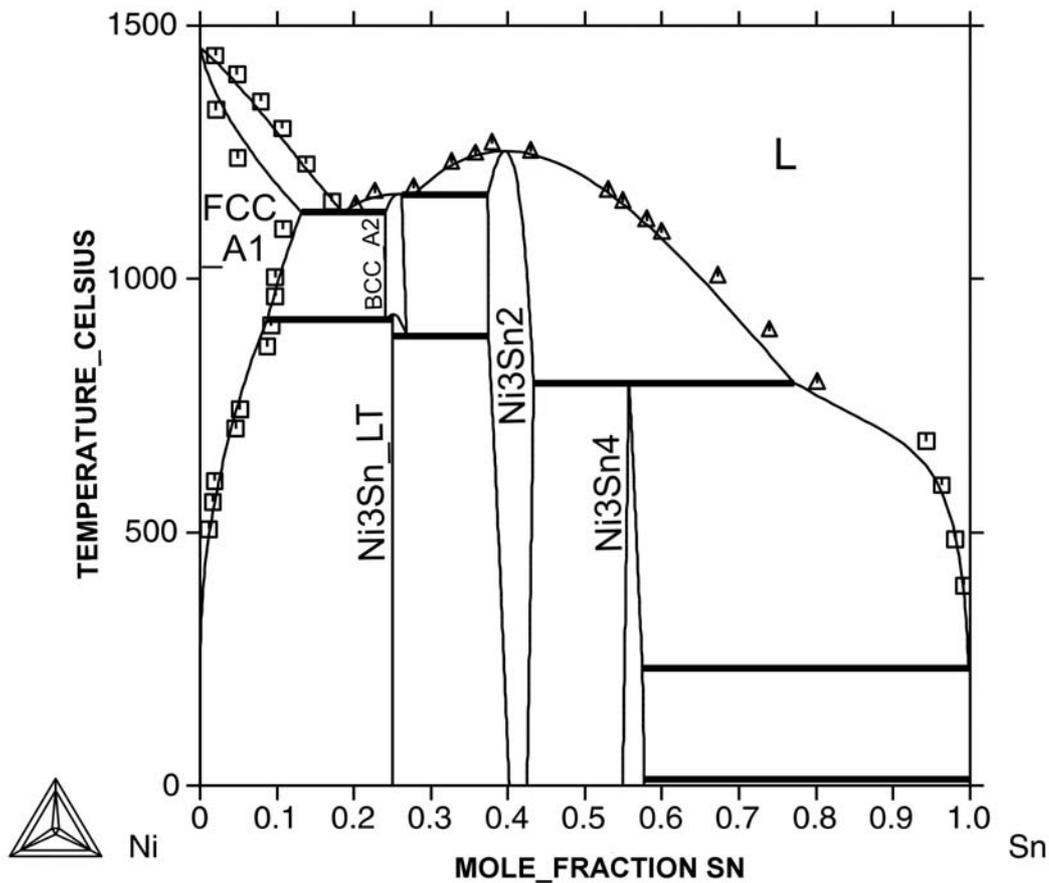
*Fig. 1. The calculated Ni-Sn phase diagram after re-optimisation, together
with experimental data [33,34]*

prediction of influence of further components to phase equilibria. This allows e.g. to perform calculations not just for the systems for which critically assessed data are available but also, for example, to study the effect of impurities e.g. Pb, on phase equilibria in assessed systems. An example of the database application for important lead-free solder system is shown in next paragraph for the Ag-Cu-Sn system.

4.1. Ag-Cu-Sn system

Great deal of research in lead-free solders has been carried out into useful replacements

of Pb-Sn solder which has largely been centred on tin rich alloys (>90% Sn by mass) in the Ag-Cu-Sn system. Such alloys have good thermal resistance, mechanical strength and creep resistance. A knowledge of the phase diagram and thermodynamic properties of this system and with the addition of substrate elements such as nickel, is important for understanding the factors associated with use of these solders. In the Sn rich region of the phase diagram, there is a ternary eutectic at 217.2ºC with the composition approximately 3.6% Ag, 1%Cu by mass.
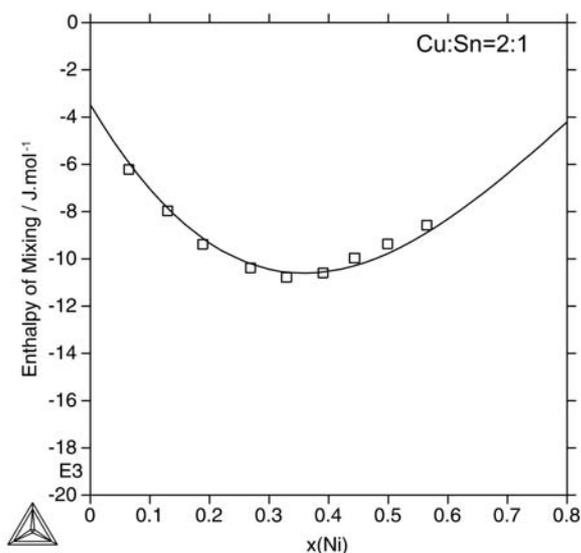
The thermodynamic properties of the Ag-

Figure 2. The calculated enthalpy of mixing in liquid Cu-Ni-Sn alloys at 1303 °C, together with experimental data points [35]. The reference states used are pure liquid components.

Cu-Sn have not, until recently, been studied experimentally in great detail. The enthalpies of solution of Ag and Cu in Sn rich Ag-Cu-Sn alloys were determined by Shen and Spencer [20,21] at 720 K by solution calorimetry. More recently, the enthalpies of mixing for a much wider range of compositions between 500 and 900ºC have been studied by Luef et al. [22] and this has been complemented by recent emf studies by Zabdyr et al. [23], both in the frame of COST531 Action.

The thermodynamic and phase diagram data prior to 2000 were critically assessed by Lee et al. [24,25] and Ohnuma et al. [26], and more recently by Gisby and Dinsdale [27]. The liquidus projection of the system Sn-Ag-Cu calculated using the data of Gisby and Dinsdale [27] is presented in Fig. 4 and liquidus lines projected onto the T- x(Ag)

plane are shown in Fig. 5. This rather unusual type of liquidus lines presentation allows easy identification of the lowest melting temperature and the character of invariant points. It offers, together with standard liquidus projection, complex information about the liquidus properties of the system.

The data stored in the database relate to equilibrium properties, but it is possible to use them also for the calculation of non-equilibrium properties e.g. to apply kinetic models to show how the equilibrium assemblage of phases might evolve during solidification or through chemical reaction. A good example of this is through the use of Scheil simulation to model the solidification of a solder. In the Scheil simulation, it is assumed that the diffusion of atoms is rapid in the liquid and extremely slow in crystalline phases. This means that any solid phases predicted to precipitate from the liquid solder will not equilibrate with any other solid material.

Huang et al. [28] have handled the kinetics in a more detailed way by coupling chemical diffusion data to thermodynamic properties for detailed modelling of microstructure evolution using MATLAB™ to examine how solder bump geometries can influence the kinetics of dissolution of a Au surface finish metal into a liquid solder.

Similar calculations can be used to study the effects of changes of temperature on various thermophysical properties. Molar volume, playing the role in pressure dependence of Gibbs energy, has been included in the NPL thermodynamic database for solders [29] and used for calculations to demonstrate the possible effects of "tin pest". All tin rich solders are in principle prone to the precipitation of the α-Sn based on the DIAMOND_A4 structure at
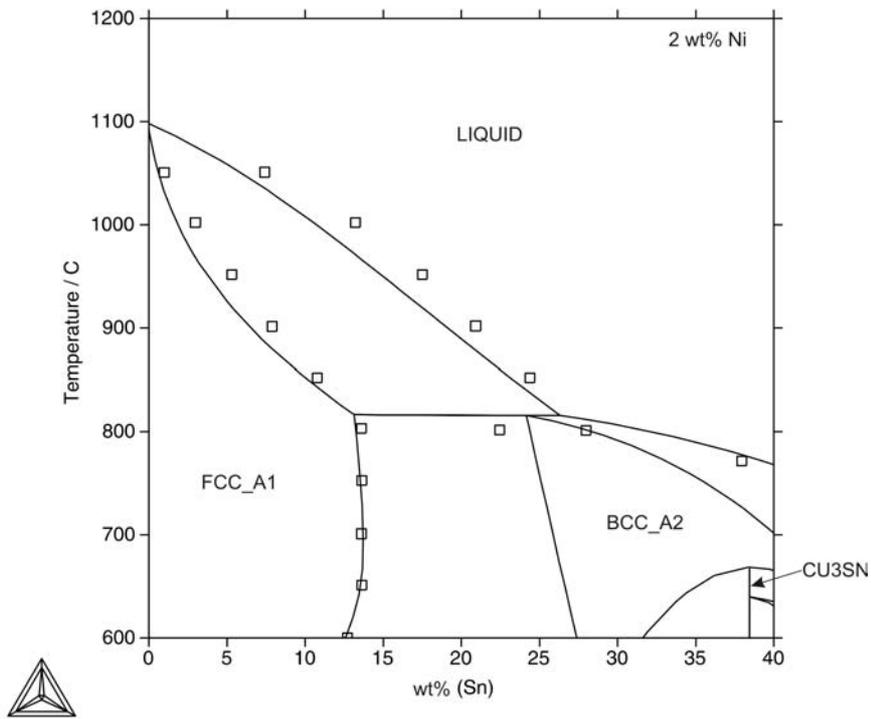
Figure 3. The calculated isopleths at 2 wt% Ni in the copper-rich part of the Cu-Ni-Sn system, together with experimental data [36]
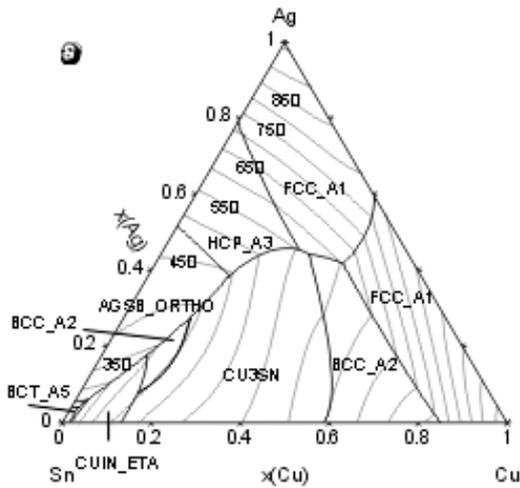

Figure 4. Calculated liquidus projection of the Ag-Cu-Sn system using the data of Gisby and Dinsdale [27]
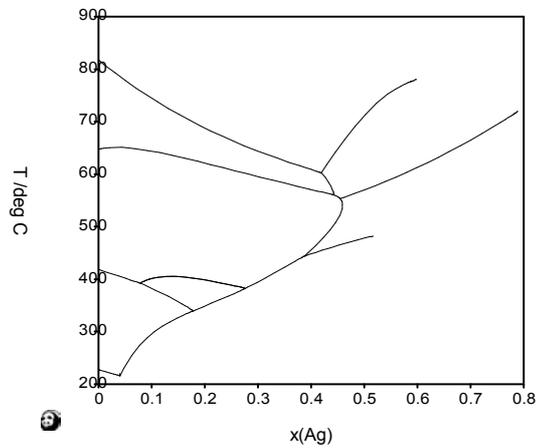
Figure 5. Liquidus lines projected onto the T-x(Ag) plane in the Ag-Cu-Sn system using the data of Gisby and Dinsdale [27]

temperatures below 13ºC. This phase has a much high molar volume than the BCT_A5 structure of β-Sn, and its formation would lead to rapid degradation of the solder joint. In the event, its formation seems to be kinetically inhibited for most alloys.

Surface tension, although, not formally a bulk thermodynamic quantity is a closely related thermophysical property of importance to the electronics industry. In a series of papers, Tanaka [30] has explored the use of the Butler equation [31] in order to predict surface tension data from bulk thermodynamic properties. The basis behind the approach is that the surface monolayer (whose thermodynamic properties can be estimated from those of the bulk) is in equilibrium with the bulk liquid material. By solving for equilibrium conditions it is possible to estimate both the surface tension of the liquid alloy and the composition of the surface monolayer. This approach has been used by Ohnuma et al. [32] and Picha et al. [6] as a basis for the prediction of surface tension of lead free solders.

Acknowledgement

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