

THE THERMODYNAMIC DATABASE COST MP0602 FOR MATERIALS FOR HIGH-TEMPERATURE LEAD-FREE SOLDERING

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Abstract

The current state of thermodynamic modelling in the field of high-temperature lead-free soldering is presented. A consistent thermodynamic database, containing 18 elements (Ag, Al, Au, Bi, Co, Cu, Ga, Ge, Mg, Ni, P, Pb, Pd, Sb, Sn, Ti and Zn) has been created. The thermodynamic data for the most of the important binary and selected ternary systems were checked and included into the database. The database was tested using major commercial software packages. Such reliable and sophisticated software coupled to reliable thermodynamic databases are necessary prerequisites for application of thermodynamics in advanced alloys design.

Keywords: CALPHAD method, lead-free solders, thermodynamic database

1. Introduction

Lead containing materials and especially solders have been used for many years in all kinds of industry, and their properties have been utilised very successfully in the electronics industry and also e.g. in plumbing. Nevertheless the toxicity of lead has recently been identified as a possible source of danger for human health, mainly adversely affecting the development of children and young people. Lead extracted from materials exposed to the environment (e.g. in landfill) has the tendency to accumulate in the human body, and it can lead to disorders of the nervous and reproductive systems and delays in neurological and physical development. It can also cause cognitive and behavioural changes, anaemia and hypertension. Even small amounts of lead can be dangerous to human health (500 µg/ml), but it was found that even smaller levels could be hazardous to a child's neurological and physical development [1].

The use of lead in the electronics industry is regulated by two EU directives, RoHS Directive 2002/95/EC (Restriction of Hazardous Substances in electrical and electronic equipment) and its recast version RoHS 2 2011/65/EU which must be implemented within national legal frameworks by January 2, 2013 within the European Union. The

management of its use, availability, disposal and waste treatment is regulated by the WEEE Directive 2002/96/EC (Waste Electrical & Electronic Equipment). There is also other legislation [REACH Regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals), EC/1907/2006], which regulates the use and exploitation of chemicals in industry in general. More details about the content, scope and validity of these directives and regulations are available in [2].

2. Current situation in high-temperature lead-free soldering

Extensive research has been carried out in the last decade on the development of new lead-free soldering materials especially for mainstream applications. New promising materials, e.g., Sn-Ag-Cu or Sn-Zn based alloys were reviewed recently by Zhang et al. [3]. These alloys already have replaced the (near-)eutectic Sn-Pb solders for mainstream applications (with melting temperatures of approximately 220°C), but there are still no universal alternatives suitable for all applications.

However, there are no viable alternatives at all at the moment for the high-temperature, high-lead containing alloys, where the lead levels can be above

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85 wt.%. The range of desired melting points for such alloys is between 250 and 350°C. These materials are therefore currently exempt from the valid RoHS legislation [2]. Such types of solders are used in the electronics industry typically for advanced packaging technologies, such as die-attach and Ball Grid Array (BGA) solder spheres and chip-scale packages (CSP). High-lead alloys are also exploited in power circuits in the automotive industry for under bonnet applications and in multichip module (MCM) technologies, where the so-called step-soldering approach is employed. Various solder compositions with different liquidus temperatures are employed during a typical step-soldering process. In order for the high-lead alloys to be replaced by new high-temperature lead-free solders for a broad range of melting temperatures, a good understanding of the melting behaviour is paramount. The upper limit of these process temperatures is defined by the polymer materials used in the substrate and is around 350°C. Subsequent process temperatures have to be lower than the melting point of previously used solders.

3. Tools for the new materials development

One very useful and increasingly exploited approach for the development of new materials of any kind is through the use of theoretical methods for the modelling of phase diagrams and phase equilibria. An understanding based on reliable phase diagrams of multi-component materials allows the material designer to avoid dangerous phases with known deteriorative influence on material properties, or to search for compositions with specific physical or chemical properties defined beforehand by the needs of intended application. The request for a specific melting point of an alloy is a typical example of such a condition. Examples of the use of thermodynamic modelling for the development of new solders can be found in [4,5]

With current software and thermodynamic databases, phase diagrams and thermodynamic properties of complex systems corresponding to real advanced materials can be modelled using the CALPHAD method [6,7] which is based on the accurate representation of the Gibbs energies of all phases existing in the chemical system under consideration, followed by the minimization of the total Gibbs energy of the system. The Gibbs energies of phases are obtained by deriving coefficients to pre-defined polynomials in order to reproduce the experimental phase equilibrium data (the positions of phase boundaries, compositions of phases in equilibrium, etc.) and thermodynamic quantities (e.g. heat capacities, enthalpies of mixing, activities) within the limits of experimental uncertainty. It means that the CALPHAD method is dependent on a certain

amount of robust experimental data for simpler, especially for binary and ternary systems. Such binary and ternary assessments subsequently allow the prediction of behaviour of more complex systems. The reliability of such predictions is of course increased if more information about the system is available.

The parameters of such polynomials describing the Gibbs energies as a function of temperature, pressure and composition for the different phases in the simpler binary and/or ternary systems are stored in the form of thermodynamic databases. Good and reliable databases are crucial for successful modelling of the phase equilibria of complex systems, corresponding to real materials; nevertheless it is important to point out that a thermodynamic database is not merely a collection of such coefficients. The thermodynamic database must be consistent with respect to the polynomials used, phase models and names allocated to them and the Gibbs energies of the pure elements. The management of such databases is a major task in its own right. A detailed description of these conditions is given elsewhere e.g. in the reference [8].

Thermodynamic databases for lead-free soldering have been developed by several research teams over the last decade. The earliest, unmaintained database was developed by the National Institute of Standards and Technology (NIST) [9]. Currently, there are other commercial databases for mainstream soldering application, the ADAMIS database developed in Japan [10], database offered by ThermoCalc AB [11] and the SOLDERS database developed by the authors of this paper within the scope of the COST531 project [12,13,14]. The SOLDERS database covers the 11 elements considered to be most important for lead-free soldering (Ag, Au, Bi, Cu, In, Ni, Pb, Pd, Sb, Sn, and Zn). Of these the elements Ag, Bi, Cu, In, Sb, Sn and Zn are possible candidates for lead-free soldering while Au, Ni, Pd appear in the surface metallisation of the electronic components. The necessity to model the interaction of new lead-free and “old” lead containing solders is the reason why Pb has been included in the database. The SOLDERS database contains assessments of all but one binary system (Pd-Sb) and 20 important ternary systems.

4. The thermodynamic database for high-temperature lead-free solders

The SOLDERS database was used as the basic resource for further database development for high-temperature lead-free solders (HT solders) carried out within the scope of the COST MP0602 Action [15]. New elements, identified as offering potential for the HT solders development, were added to the database.

Current research in the field of HT solders

suggests that it may not be possible to find a new single alloy, which would fulfil, even partially, the versatile requirements from the industry as provided by SAC solders for mainstream applications, not to mention the old lead-containing solders. It is unlikely that traditional Sn-based soldering technology will be applicable for this high temperature range. With the exception of additions of Sb, attempts to increase and vary the melting temperature of Sn-based solders by the use of appropriate alloying elements have not been successful, and even Sb can be used for temperatures up to 250°C only. Therefore, other categories of materials have been studied worldwide and several possibilities have been identified. Hypo-eutectic Bi-Ag alloys are promising in view of the range of liquidus temperatures available. Their mechanical properties are comparable to those of Pb-based solders, and are affordable. Other materials under development are Zn-Al eutectic systems alloyed with Mg, Ge, Ga, Sn or Bi, Sb-Sn, and Au-Sn-X or Au-Ge-X systems. Au based solders are already in use [16], but, because of their high price, for very specific purposes only. A typical example is in the space industry, where the cost is not one of the key issues.

The problems associated with the development of substitute materials were discussed e.g. in papers [4,5,17,18]. Some of the elements mentioned above are therefore obvious candidates for inclusion into a thermodynamic database for HT solders.

Furthermore the number of barrier metals used in Si device manufacturing is increasing. Multilayered metallizations (e.g., Ag, Ti, W, Cu, Ni, V) are used in high-end technology for miniaturized devices, such as in flip chip technology. In these instances, the interaction of solders with such materials results in complex interactions during soldering and operational life, leading to galvanic corrosion and destruction of the interconnections [19]. Knowledge of phase equilibria in such complex systems obtained by theoretical modelling can be very useful for the prediction of the behaviour of joints and selection of key experiments to verify the component design and solder selection. On the other hand, these elements again increase the scope of the new database.

Therefore the scope of the thermodynamic database for high-temperature lead-free soldering was broadened to cover the key elements: Ag, Al, Au, Bi, Co, Cu, Ga, Ge, Mg, Ni, P, Pb, Pd, Sb, Si, Sn, Ti and Zn. In-containing systems were removed from the database because it was thought unlikely that a low-melting element such as indium would be used in HT solders. Al, Ga, Ge and Mg were added as possible solder components, Ti, Si, and Co may exist in metal barriers and their interactions with the solder are important. Phosphorus is always present in the Ni-containing systems. Barrier layers of Ni are used because of their good solderability, corrosion

resistance, and uniform deposition. The P content is the result of the Ni deposition procedure and it can be present from between 5 to 15 wt%. Theoretical and experimental studies of P-containing systems are unfortunately sparse and therefore there is a significant lack of theoretical thermodynamic assessments of Metal-P systems.

Theoretical assessments from the literature and also those generated in the scope of COST 531 [14] and COST MP0602 Actions [15] were stored in the database. The assessments were carefully tested for consistency using the rules described in [8], and modified when necessary. Because of the number of elements included into the database, it is a huge task to collect the thermodynamic descriptions of all binary systems associated with 18 elements, as in the case of previous SOLDER database involving 11 elements [13] and this is also not necessary. The content of the database has been limited to just those binary and ternary systems important for High-temperature lead-free soldering. All alloy systems included in the database were tested using the ThermoCalc [20], MTDATA [21] and Pandat [22].

5. Examples of thermodynamic modelling

Several examples of the use of the thermodynamic database will be demonstrated in this section. The phase diagrams of some systems involving the key elements identified earlier, as well as the possibility of exploitation of the database for practical applications will be shown.

5.1 Bi-based systems

Bi-Ag-X systems have been studied as possible candidates for soldering at higher temperatures. The phase diagram of binary Ag-Bi system [23] is shown in Fig. 1. The near eutectic alloys with e.g. 0-11 wt. % Ag are considered as candidates [24]. The phase diagram of the ternary Ag-Bi-Sn system (reassessed in scope of [14]) is shown in Figs. 2 and 3. The liquidus projection, which is very important for the determination of melting point of particular alloy composition, can be calculated routinely as shown in Fig. 2. A table of invariant reactions can be also obtained from the software packages (Table 1). Fig. 3 shows an isopleth for this system for the molar ratio of alloying elements Ag/Sn=1. The equivalence between the database names and common names of some phases is given in the figure captions. The database names are in some cases based on the relevant prototype of the crystallographic structure. This is because the same models have to be used for crystallographically identical or related phases in order to be able to model the complete solubility between them in higher order systems.

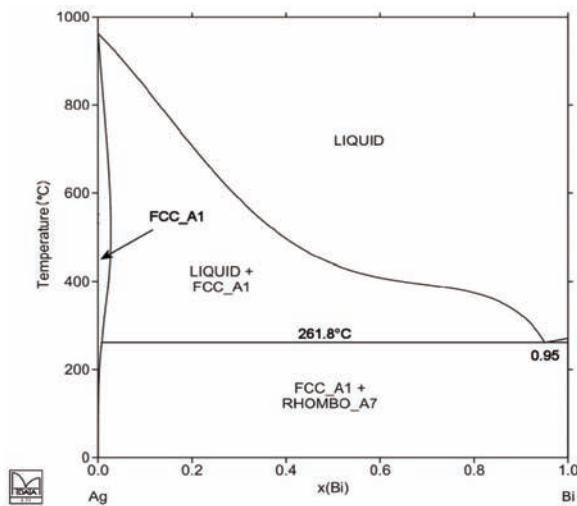


Figure 1. Phase diagram of the Ag-Bi system calculated using the thermodynamic database for HT solders (RHOMBO_A7=(Bi), FCC_A1=(Ag))

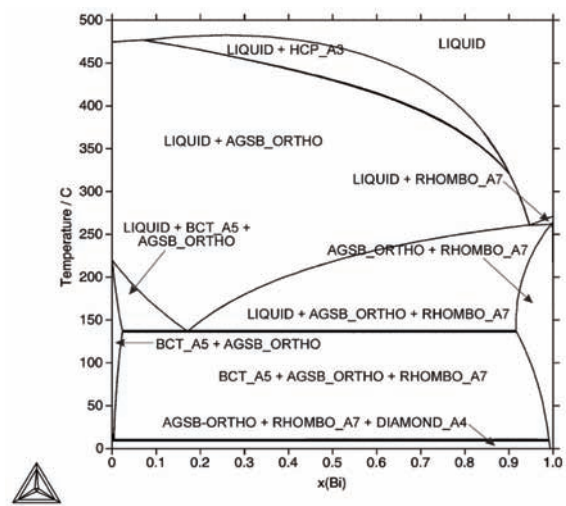


Figure 3. Isoleth of the Ag-Bi-Sn system with the molar ratio Ag:Sn of 1:1 (from [25], RHOMBO_A7=(Bi), AGSB_ORTHO= ϵ (Ag-Sn), HCP_A3= ζ (Ag-Sn), FCC_A1=(Ag), BCT_A5=(β Sn), DIAMOND_A4=(aSn))

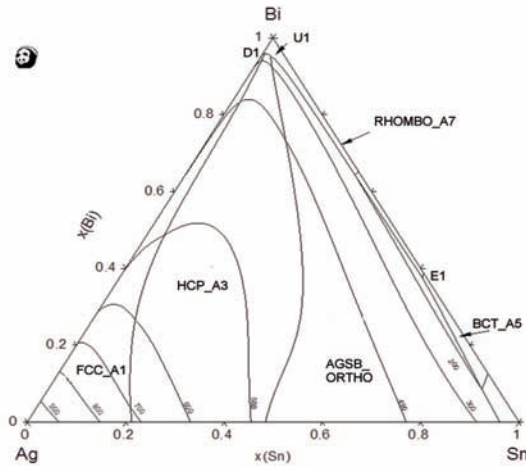


Figure 2. Liquidus surface for the Ag-Bi-Sn system (from [25], RHOMBO_A7=(Bi), AGSB_ORTHO= ϵ (Ag-Sn), HCP_A3= ζ (Ag-Sn), FCC_A1=(Ag), BCT_A5=(β Sn))

Table 1. Table of invariant reactions for the Ag-Bi-Sn system (from [25])

T / °C	Reaction type	Phases	Compositions		
			x_{Ag}	x_{Bi}	x_{Sn}
263.2	D1	LIQUID	0.038	0.958	0.004
		HCP_A3	0.895	0.003	0.102
		RHOMBO_A7	0	1	0
		FCC_A1	0.913	0.002	0.085
262	U1	LIQUID	0.03	0.952	0.018
		HCP_A3	0.859	0.002	0.139
		RHOMBO_A7	0	0.998	0.002
		AGSB_ORTHO	0.75	0.091	0.158
136.9	E1	LIQUID	0.009	0.376	0.615
		RHOMBO_A7	0	0.97	0.03
		AGSB_ORTHO	0.75	0.002	0.248
		BCT_A5	0	0.063	0.936

5.2 Au-Sn based systems

Au-Sn-X and Au-Ge-X alloys are also suitable candidates for high temperature soldering thanks to their relatively simple phase diagrams and the existence of a eutectic reaction in the appropriate temperature region. On the other hand, the price of such alloys is very prohibitive and therefore these materials are suitable just for very specific niche applications, where the cost can be justified. A typical example is the space industry [16, 26]. Calculations using a suitable thermodynamic database can be used to design the composition which would e.g. decrease the content of expensive elements and, at the same time, suppress the presence of phases with poor mechanical properties. Au₃Sn is an example of such a phase in these systems. These systems were studied in detail by Leinenbach et al. [26-29] and Chidambaram [30, 31] who used theoretical modelling techniques to develop a solder for heated conversion surface assemblies for the ESA/JAXA Mission Bepi Colombo, which will be launched in 2014 to Mercury [26].

The binary phase diagrams for the Au-Sn (assessed by [32], and reassessed in the scope of [15]) and Au-Ge system, assessed by [29], are shown in Figs. 4 and 5. Again, the equivalence between the database names and common names of some phases is given in the figure captions. The NIAS_TYPE phase is a typical case of the name based on crystallographic prototype, as it covers the thermodynamic model for phases with the crystallographic structures *hP4* and *hP6* [8].

The liquidus surface of the ternary Au-Ge-Sn system [29] is shown in Fig. 6 and isopleth for 11 at.%

Sn in Fig. 7. The concentration and temperature ranges of stability of the undesirable phase Au_5Sn can be clearly seen.

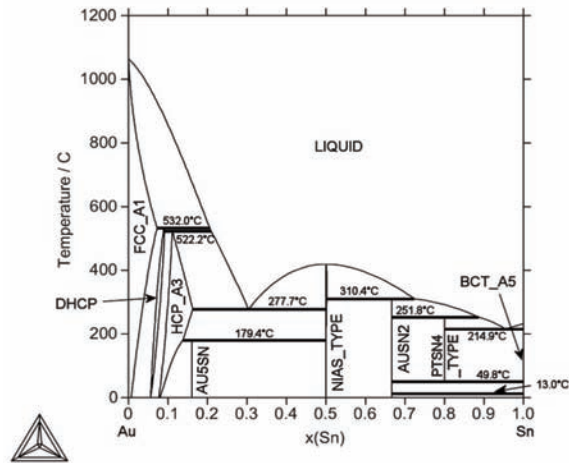


Figure 4. Phase diagram of the Au-Sn system (NIAS_TYPE=AuSn/ δ , DHCP= $Au_{10}Sn/\beta$, FCC_A1=(Au), BCT_A5=(Sn), HCP_A3= ζ , PTSN4_TYPE=AuSn $_4$)

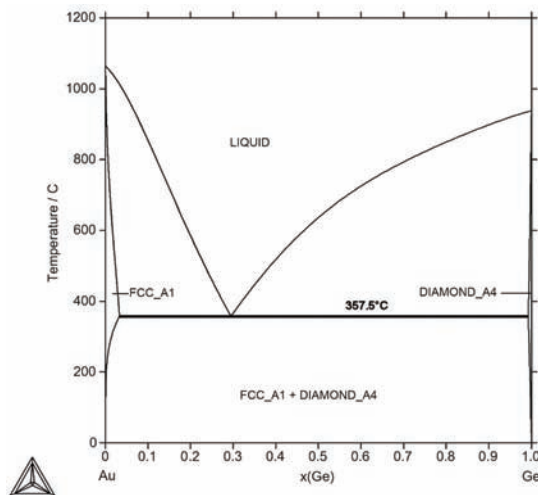


Figure 5. Phase diagram of the Au-Ge system (DIAMOND_A4=(Ge), FCC_A1=(Au)).

5.3 The Al-Zn based system

The Al-Sn-Zn system [33] is representative of Al-Zn based systems for high-temperature lead-free soldering. It is a relatively simple system with no ternary phases and also the solubility of the third elements in binary subsystems is very low. The isopleths of the Al-Sn-Zn system for 10 at.% of Sn is shown in Fig. 8 and the liquidus projection of this system in Fig. 9.

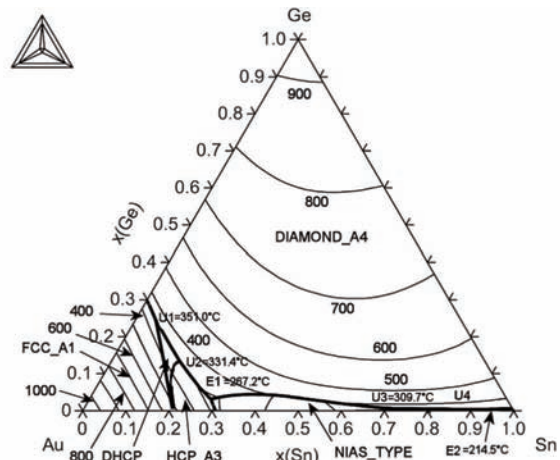


Figure 6. Liquidus projection of the Au-Ge-Sn system (NIAS_TYPE=AuSn/ δ , DHCP= $Au_{10}Sn/\beta$, FCC_A1=(Au), BCT_A5=(Sn), HCP_A3= ζ , DIAMOND_A4=(Ge), PTSN4_TYPE=AuSn $_4$)

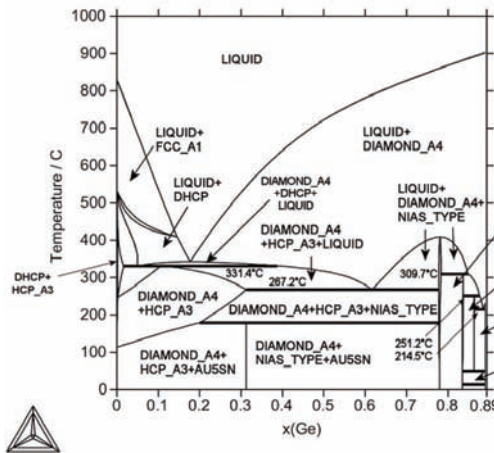


Figure 7. Isopleth of the Au-Ge-Sn system for 11 at% Sn (NIAS_TYPE=AuSn/ δ , DHCP= $Au_{10}Sn/\beta$, FCC_A1=(Au), BCT_A5=(Sn), HCP_A3= ζ , PTSN4_TYPE=AuSn $_4$)

5.4 Liquidus projection with temperature as an ordinate

Computational thermodynamics is an immensely powerful technique. Once a self-consistent database of thermodynamic parameters has been created, it is then possible to represent phase equilibria or thermodynamic properties in many different ways leading to insights that might otherwise lie hidden. A particularly good example is the alternative way of looking at a liquidus projection where the ordinate is temperature.

The traditional view of a liquidus projection is where features of a liquidus surface of the 3-dimensional temperature/composition space diagram

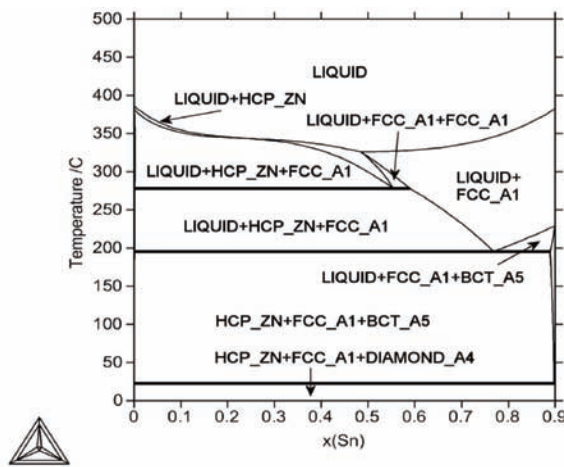


Figure 8. Isopleth of the Al-Sn-Zn system for 10 at% Sn (FCC_A1=(Al), HCP_ZN=(Zn), BCT_A5=(β Sn), DIAMOND_A4=(α Sn))

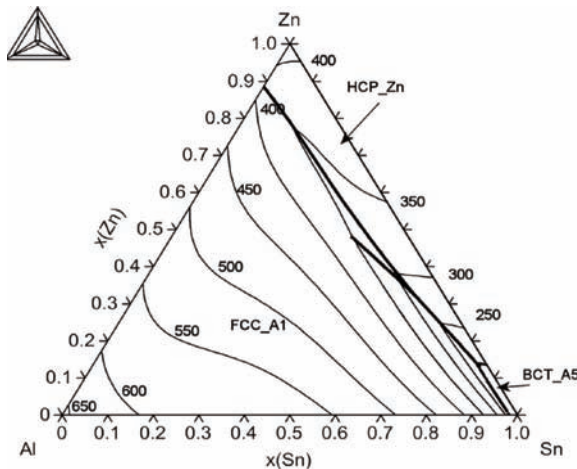


Figure 9. Liquidus projection of the Al-Sn-Zn system (from [25], (FCC_A1=(Al), HCP_ZN=(Zn), BCT_A5=(β Sn)).

is projected on to the base; the Gibbs triangle, as in Fig. 9, for example. Temperatures on the surface are given as contours (isotherms) and univariant lines appear as valleys between primary phase surfaces. This is directly analogous to a map showing the terrain of hills, valleys and so-forth. However, with this projection, the nature of invariant points is not always obvious, and from this point of view, recalculating the liquidus projection onto a T - x plane clearly reveals how the univariant lines rise and fall with temperature. Figure 10 shows the Al-Sn-Zn liquidus surface projected on to the T - x (Sn) plane. The lines on the projection are the univariants and it is now clear that there is a ternary eutectic at approximately $x(\text{Sn})=0.84$ and 195°C. Of course, the precise values of the eutectic temperature and composition are easily found in the calculation, but nevertheless it is a useful alternative visualisation of the liquidus surface.

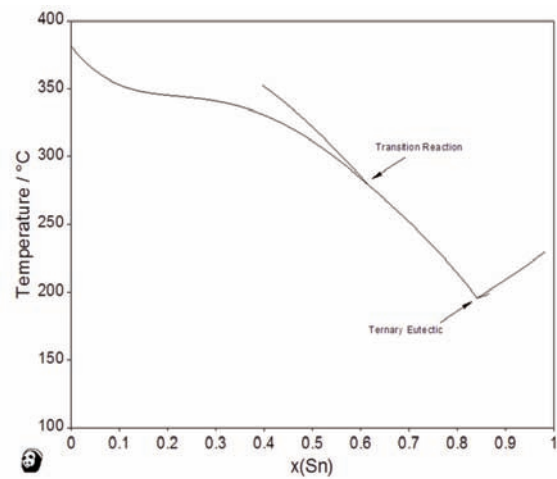


Figure 10. Liquidus projection on on to the T - x plane for the Al-Sn-Zn syste

5.5 Practical use of thermodynamic modelling

Computational thermochemistry also provides an easy way to investigate the potential effect of contamination of the newer lead free solders by relatively small amounts of lead from existing solder joints and component terminations. Computational thermochemistry can be used to investigate the phases formed in a lead-contaminated solder and the microstructure that could be expected as such a contaminated solder solidifies [34, 35].

One way to explore the liquidus temperature, the phases that might form and their range of stability, is by calculating a cut or an isopleth through a multicomponent phase diagram.

Figure 11 shows such an isopleth between an electrician's solder (a eutectic lead-tin alloy) and the standard Sn-Ag-Cu lead-free solder using the

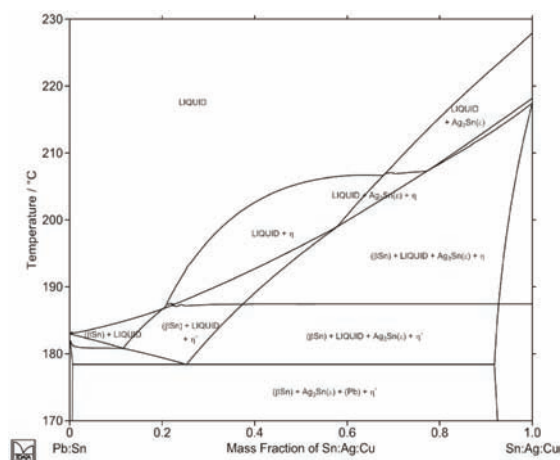


Figure 11. Calculated isopleth between compositions corresponding to an electrician's solder and a 'SAC' lead free solder

SOLDERS database [12]. It shows that, as the lead-free solder becomes more and more contaminated by the lead solder, the liquidus temperature drops and also the range over which the liquid phase is stable, either on its own or in combination with other phases, becomes very much larger. This could lead to unreliability and increased porosity of the solder joint.

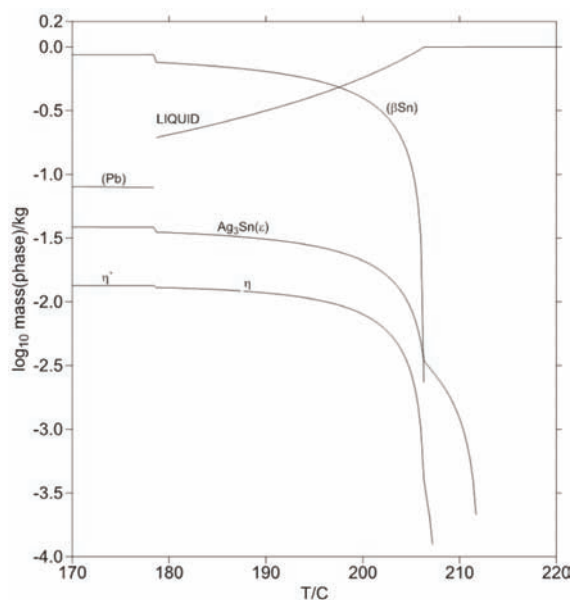


Figure 12. Calculated mass of phases formed on solidification of a mixture of a lead-free solder and a Pb-Sn 'electrician's solder' assuming equilibrium is maintained during solidification

The isopleth, Fig. 11, shows which phases are predicted to appear on cooling down and the appropriate temperature ranges, but it gives no indication of how much of the phase can be expected to form. This, however, can also be calculated, as shown in Fig. 12. The first phase to appear as the liquid is cooled down is the Ag_3Sn phase, which in this case refers to an intermetallic phase based mainly in the Ag-Sn system. Initially, the amount of this phase is very small and does not seem to affect the total amount of the liquid phase. The next crystalline phase to appear is Cu_6Sn_5 (η), followed by the Sn-based solid-solution phase, BCT_A5. Finally, all the liquid disappears at about 178°C with the formation of the Pb(FCC) phase.

An analysis of such plots can lead to an understanding of the microstructure of the solidified material, its strength and brittleness.

6. Conclusions

The possible applications of thermodynamic modelling in the field of high-temperature lead-free

soldering has been demonstrated in this paper. A consistent thermodynamic database has been created, containing 18 elements (Ag, Al, Au, Bi, Co, Cu, Ga, Ge, Mg, Ni, P, Pb, Pd, Sb, Si, Sn, Ti and Zn). Thermodynamic assessments for the most important binary and selected ternary systems were included in the database and it was tested for the use with major commercial software packages.

The theoretical modelling of phase diagrams and thermodynamic properties is a powerful tool, allowing materials scientists to limit the extent of their experimental work, shorten the time and expense required for the development of new and advanced materials. Good software and reliable thermodynamic databases are nevertheless necessary in order to apply such an approach.

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