THE COST 531 LEAD-FREE SOLDERS THERMODYNAMIC DATABASE[1]

Andy Watson[2]
Alan Dinsdale [3]
Ales Kroupa[4]
Jirí Vízdal[4]
Jan Vrestal[5]
Adéla Zemanová [5]

Abstract
Owing to impending European legislation, lead will no longer be used in the fabrication of electrical and electronic materials within Europe. COST 531 is a European action on the study of new lead-free materials suitable for use in the electronics industry. One of the objectives of the action is the provision of a self-consistent thermodynamic database for lead-free solder materials and substrates. Assessed thermodynamic parameters for more than 50 binary systems have been collected from the literature or have been provided directly by a programme of experimental and assessment work as part of the COST action. These data have been supplimented by parameters for ternary systems to provide a self-consistent thermodynamic database. The database has been tested thoroughly using proprietry software to ensure its portabiltiy.
Key words: Lead-free solders; Thermodynamics; Phase diagrams.

[1] *Technical Contribution to the 61st International Congress of the ABM, January 24-27th 2006, Rio de Janeiro – RJ – Brazil.*
[2] *IMR/SPEME, University of Leeds, UK*
[3] *National Physical Laboratory, Teddington, UK*
[4] *Institute of Physics of Materials, AS CR, Brno, Czech Republic*
[5] *Institute of Theoretical and Physical Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic*

INTRODUCTION

Lead has been used in soldering materials for electronic applications for very many years. Lead, with its low melting point and soft, malleable nature, when combined with tin at the eutectic composition gives an alloy which flows easily in the liquid state, solidifies over a very small range of temperature and is at the heart of the electronics industry. Present-day society is totally dependent on this industry; through domestic appliances, telecommunications, transport, and so on. Electronic devices now pervade every aspect of life, and with an increasing reliance on mobile devices, such as telephony and computing, the number of components manufactured, and probably more importantly, discarded, is increasing dramatically. For example, for the period 1992-1997, there was a three-fold increase in the number of printed circuit boards manufactured in Europe, worth 9.7 billion USD. This is a huge industry that is growing, year on year.

The problem with lead, however, is one of health and the environment. Lead can accumulate in the body, leading to many adverse health effects, such as disorders of the nervous and reproductive system, delays in neurological and physical development. Many countries have now banned the use of lead in petrol. The worry over lead in electronic components stems mainly from discarded electronic equipment, much of which ends up in land-fill, with the fear, then, of the contamination of ground water. The decision to remove lead from electronic equipment has been taken by many countries, and in Europe, new legislation will be brought into force in July 2006 banning the use of lead in electrical and electronic equipment – The RoHS directives. The search for a replacement solder material has been underway for some time and a number of formulations are already in use, notably in Japan. However, it is now an accepted fact that there is no ideal 'drop-in' replacement for the traditional lead-tin solder. One particular formulation, Sn3.8Ag0.7Cu, has a melting point of around 220°C, which is about 30°C higher than that of traditional lead-tin solder. This has a number of implications, not least the increase in energy costs associated with using this material. There are then compatibility issues relating to components and their termination finishes, all of which can have an affect on the reliability of the electronic device.

It is clear that knowledge of the phase equilibria involved in the solder-component termination alloy system is crucial in the design of new soldering materials. Traditional methods of experimentation involving trial and error methods for the choice of appropriate compositions are both costly in terms of time and money. Over the past 30 years or so, the construction of thermodynamic databases for the calculation of complex phase equilibria have become more important.[1] Along with appropriate software,[2] it is possible to predict the likely phase equilibria in multicomponent alloy systems as a function of temperature, pressure and composition. This has obvious implications with respect to saving time, not only by reducing the number of experiments that need to be performed to fully understand the chemistry of an alloy system, but also by being able to predict likely scenarios whilst kinetic constraints may mask the true nature of the equilibrium.

In 2002, European COST action (European CO-operation in the field of Scientific and Technical research, which facilitates and encourages networking between nationally funded research) 531 was initiated to study the basic science of lead-free solder alloys and to provide a basis for deciding which alloy to chose for each application. The COST action involves a number of different aspects of lead-free solder alloys; phase equilibria, thermodynamic properties, physical properties such as wetting

behaviour and surface tension, and mechanical properties. This work is on going, and currently, laboratories in 22 different European and associated states are involved. One particular aspect of the whole COST action is the construction of a self-consistent thermodynamic database for the calculation of phase equilibria in lead-free solder alloys and their interaction with substrates, and lead. An important consideration is how lead-free solder alloys will perform during the repair of older electronic equipment that may have been assembled using traditional lead-tin solder. The database can also be used to study intermetallic formation – critical to the strength of a soldered joint, and also solidification paths and for the modelling of surface tension.

Other thermodynamic databases are available. For example, The NIST database for lead-free solder alloys covers the elements Ag, Bi, Cu, In, Pb, Sb & Sn enabling calculation of all of the binary systems plus the Ag-Cu-Pb, Ag-Cu-Sn and Ag-Sb-Sn ternary systems.[3] The ADAMIS database[4] covers thermodynamic properties for binary and ternary systems involving the same elements plus Zn.

An advantage of working under the COST action is that there is sufficient effort available to bring breadth to the research. One of the working groups of the action (there were six in total at the start of the action) is involved solely in the provision of experimental phase equilibrium and thermodynamic property data. A second working group is involved in carrying out the thermodynamic modelling. The interaction between these working groups is crucial to the success of the action.

Scope of the Database

There are a number of obvious choices for the elements that should be included in the database. Cu and Sn (Cu is a substrate material as well) along with Ag have already been identified as components for a lead-free solder material. Alloys such as Sn3.5Ag, Sn0.7Cu, or Sn3.8Ag0.7Cu have melting points of around 220°C, but this is still more than 30 degrees higher than their traditional lead-containing counterparts. Low melting point elements such as In and Bi are added to the list, as well as termination materials such as Ni and Pd. Figure 1 shows a reduced portion of the periodic table comprising the candidate elements for the solder and those for the substrates.

			Al		P
Ni	Cu	Zn	Ga	Ge	As
Pd	Ag	Cd	In	Sn	Sb
	Au	Hg	Tl	Pb	Bi

Figure 1. Elements chosen for inclusion in the thermodynamic database

In order to reduce the total number of systems that needed to be assessed and entered into the database, some elements were removed from the list. In the case of Cd, Hg and Tl, this was owing to toxicity issues. However, it is necessary to include P as it is an impurity associated with Ni, which is of course a substrate material.

The database is based on version 4.4 of the SGTE unary database. As a starting point, two databases already under construction by members of the action were combined. These were the NPL Solders database[5] and the Brno Solders database,[6] the latter having been developed jointly by workers at the Masaryk

University and the Institute of Physics of Materials of the Czech Academy of Sciences at Brno in the Czech Republic. The combination process first involved checking that the type of model and model name were consistent for each phase. Also, each binary system had to be checked to ensure that the better version was accepted in the first version of the COST database and that using v4.4 of the SGTE unary database had no effect on the calculated diagram.
At each stage in the development of the database, it was thoroughly tested with 3 of the most popular software packages used for thermodynamic calculations, namely MTDATA,[7] Thermo-Calc[8] and Pandat.[9] This ensured portability of the database between the different packages.

MODELS

It was decided at an early stage not to include the gas phase in the database. It was recognised that the main application of the database would be for calculations relating to solidification and the creation of intermetallic phases.
The temperature dependence of the Gibbs energy was described by Dinsdale.[10]
$G(T) = A + BT + CT\ln T + \Sigma DT^n$
.where *A-D* are adjustable coefficients. The composition dependence of solution phases was described by

$$G^{\varphi}(x_i x_j) = x_i {}^{\circ}G_i^{\varphi} + x_j {}^{\circ}G_j^{\varphi} + RT(x_i \ln x_i + x_j \ln x_j) + {}^{E}G$$

where the first two terms are the lattice stabilities of the pure components in that phase, the third term is the ideal solution term and the final term is the excess Gibbs energy which is described by the 'Redlich-Kister' expression: [11]

$$^{E}G = x_i x_j \sum_{k=0}^{n} {}^{k}L(x_i - x_j)^k$$

where the adjustable L parameters have temperature dependence of the same form as above. The liquid phase is modelled this way, but more complex phases are modelled using the compound energy formalism,[12] where the crystal structure can be considered as comprising a number of sublattices, which may exhibit preferential occupancy by one or more elements. For a two sublattice structure, for example, the compositional dependence of the Gibbs energy is given as

$$G_m^{\phi} = \sum y_j^1 \sum y_k^2 {}^{\circ}G_{jk} + RT \sum_s a^s \sum_i y_i^s \ln y_i^s + {}^{E}G$$

where the y terms are the site fractions of each component on each sublattice. The first set of terms represent the Gibbs energies of formation of the 'virtual compounds' where each sublattice is occupied by just one component, the second term is the ideal mixing term and the third term is the excess Gibbs energy, given by

$$^{E}G = y_A^1 y_B^1 (y_A^2 L_{A,B:A} + y_B^2 L_{A,B:B}) + y_A^2 y_B^2 (y_A^1 L_{A:A,B} + y_B^1 L_{B:A,B}) + y_A^1 y_B^1 y_A^2 y_B^2 L_{A,B:A,B}$$

for components A and B. This model was used extensively for the intermetallic compounds present in the database. Table 1 gives examples of the modelling used for some of these phases. The binary phases are listed with the number of sublattices and their constituents. Some of the sublattices have three or more constituents indicating dissolution of a third element as the phase extends into multicomponent systems.

In order to maintain the scope of the database and to keep the work involved at a manageable level, it was decided not to include ordering in the modelling of the solution phases, e.g. the $L1_2$ and $L1_0$ phases in the Au-Cu system are not distinguished from the fcc-phase.

Table 1. Solid phases in the COST 531 Database for Lead-free Solder Materials

Phase Name	Number of sublattices	Stoichiometry				Constituents			
AUZN_GAMMA	4	0.15385	0.15385	0.23077	0.46153	Au, Zn	Au	Au,Zn	Zn
CUIN_GAMMA	3	0.654	0.115	0.231		Ag, Cu	Ag,Cu ,In	In,Sn	
BETA_INPD2	2	0.34	0.66			In	Pd		
INNI_CHI	3	1	1	1		Ni, Va	Ni	In,Ni	
IN3PD2	2	0.6	0.4			In	Ag,Pd		
LAVES_C15	2	2	1			Cu, Zn	Cu,Zn		
NI3SN2	3	0.5	0.25	0.25		Ni, Sn	Au,Ni	Au,Ni	
PDZN_GAMA	2	2	9			Pd, Zn	Pd,Zn		
SBSN	2	1	1			Bi,Pb, Sb,Sn	Sb, Sn		
ZETA_AGZN	2	1	2			Zn	Ag, Zn		

BINARY SYSTEMS

At present, the database contains thermodynamic data for 52 binary systems, based on the elements Ag, Au, Bi, Cu, In, Ni, Pb, Pd, Sb, Sn and Zn. Data are missing for the Ni-Sb and Pd-Sb systems, and data for Bi-Ni are currently being validated. P-containing systems are currently under review. The datasets have been taken from the literature in most cases, although new datasets are being generated through the experimental and assessment programmes of COST 531, for example, for the Bi-Pd system.[13] In all cases, it was important to ensure that the phase names and the modelling were consistent where the same phase occurred in different systems. This is particularly important in the cases where there may be mixing between binary phases occurring in more than one system. For example, the dataset for the Ag-In was accepted initially from the work of Moser et al.[14] As can be seen in the calculated phase diagram (Figure 1), the Ag2In phase is modelled as a stoichiometric phase. As there is little evidence regarding the stoichiometry range of this phase,[15] this is a reasonable assumption. However, in studies involving the Ag-Cu-In system, it was discovered that this phase formed a continuous series of solutions with the Cu2In phase (CUIN_GAMMA in Table 1) in the Cu-In system. Therefore, it was necessary to remodel the Ag2In phase in the same way as the Cu2In phase in order to allow mixing of the Cu and Ag. The calculated phase diagram from the current dataset is shown in Figure 2. In the modelling of this phase (Table 1) it can be seen that Sn has also been introduced into the model, as this phase is actually □-brass.

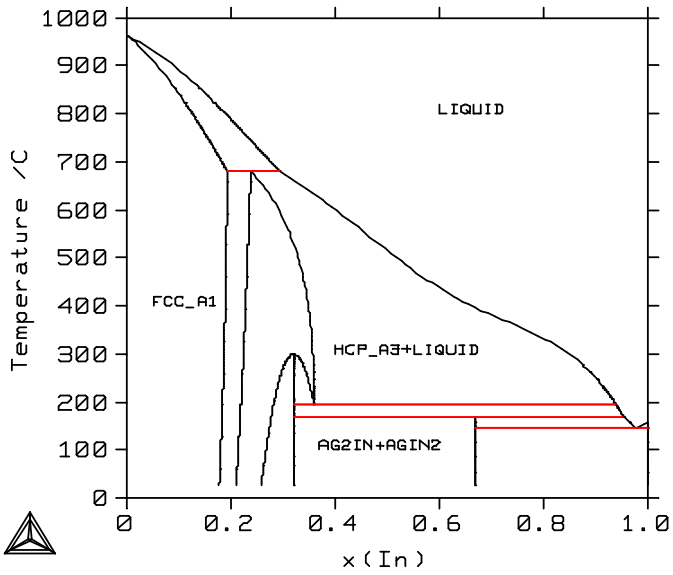


Figure 1. Calculated Ag-In phase diagram from (14) (Calculated using Thermo-Calc)

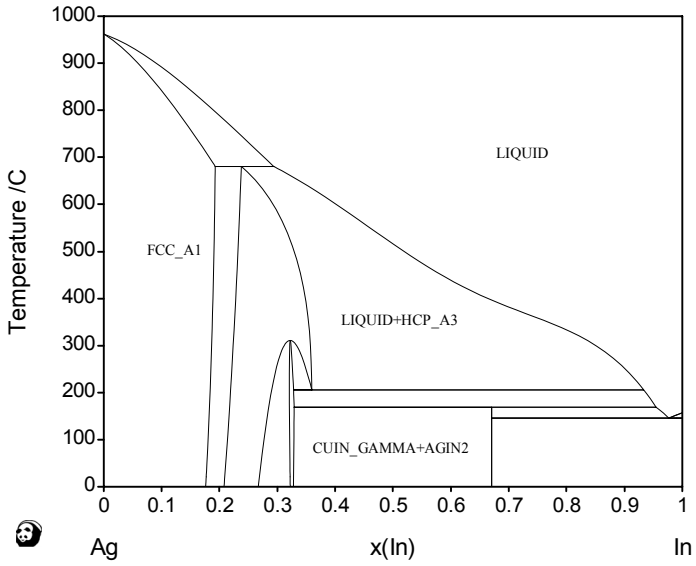
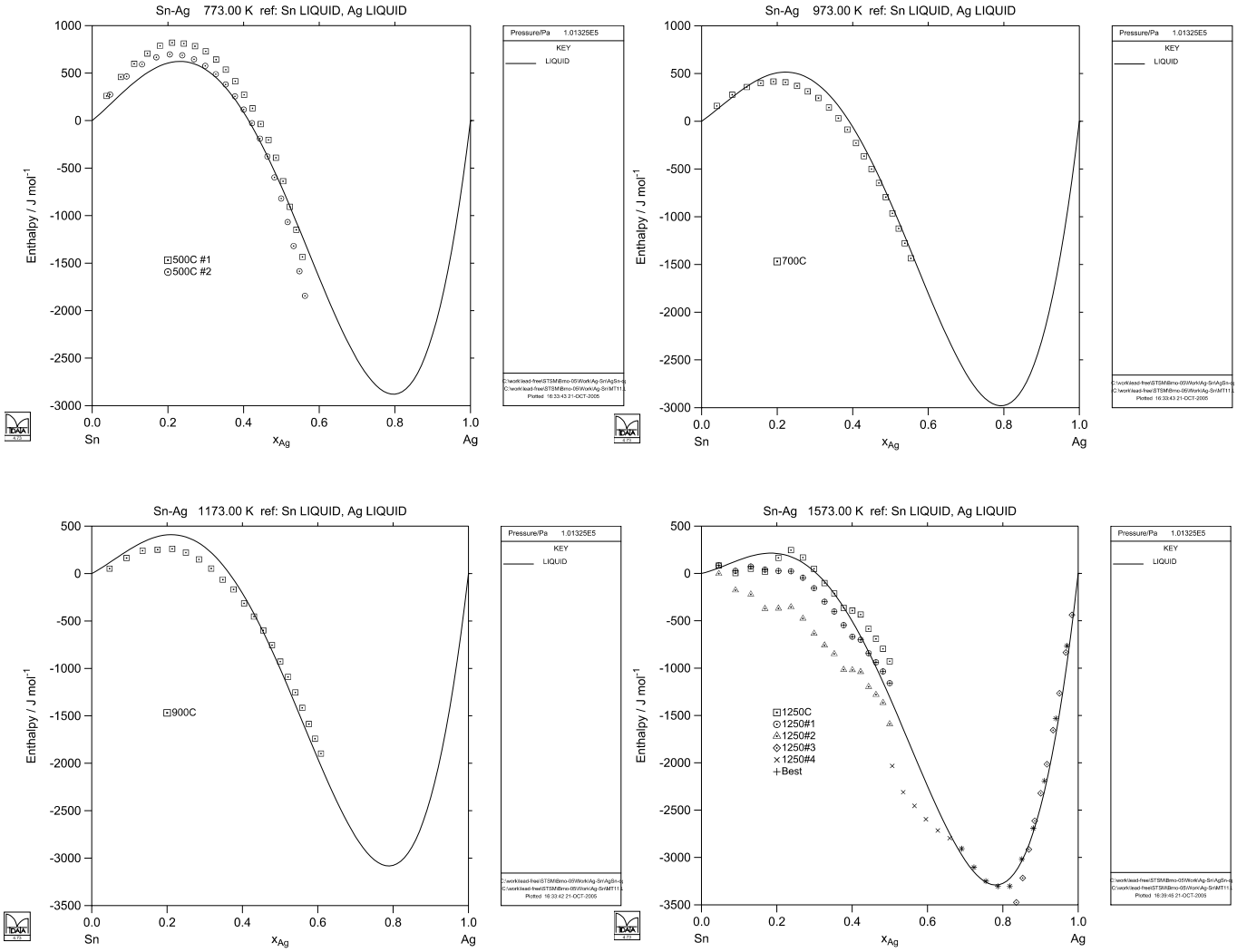


Figure 2. Calculated Ag-In phase diagram from the COST 531 database v2.0 (Calculated Using Pandat)

In Figure 2, the Ag2In phase now appears as CUIN_GAMMA and showing a small range of homogeneity.

Remodelling of published assessed binary systems was necessary following new experimental work that was undertaken as part of the COST 531 programme. For example, an assessment of the Ag-Sn system exists in the literature[16] and this was used in the early versions of the database. However, following experimental work

carried out under COST531, it was discovered that the enthalpy of mixing of the liquid phase has a temperature dependence.[17] As the thermodynamic description for Ag-Sn taken from Chang-Seok Oh et al.[16] doesn't reflect this, it was necessary to reoptimise the parameters for the liquid phase. Figures 3-6 show the assessed enthalpy curves calculated from the description in the COST531 database for temperatures of 500, 700, 900 and 1250°C, together with the new experimental data.



Figures 3-6. Enthalpies of mixing for Ag-Sn liquid calculated using the COST531 database, compared with experimental data, calculated using MTDATA.

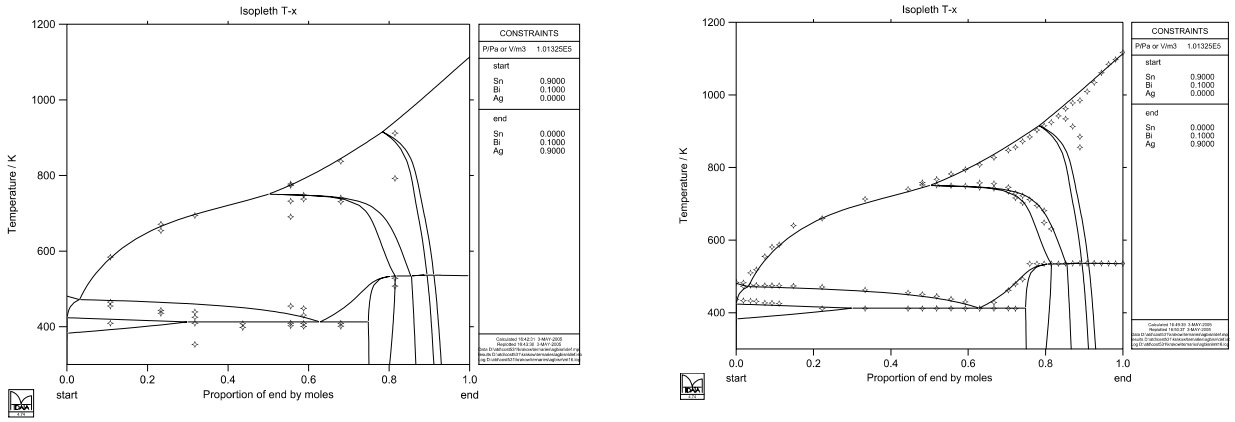
TERNARY SYSTEMS

A number of ternary assessments already exist in the literature, but before they can be included into the database, they have to be validated with the current set of binary descriptions. Often, the assessments in the literature have been made using different descriptions for the constituent binaries from those held in the COST531 database. Changing the binary descriptions can have a profound effect on the ternary system, so it is important that the fit of the calculated phase boundaries and thermodynamic properties to the experimental information remains as good as in the original work.

Often, reoptimisation is required. In extreme cases, a ternary assessment must be disregarded completely. On the other hand, this comparison with experimental data can result in a reselection of the binary system. The Au-In-Sn system is currently being assessed as part of the COST action. It was found that the accepted Au-In binary system[18] was in disagreement with the ternary information at the Au-rich end of the diagram. However, a more recent assessment was available and incorporated into the database[19] as it is in better agreement with the ternary data.
So far, there are 10 assessed ternary systems in the database, all of which are consistent with the binaries. These are listed in Table 2. A further 8 are either in the process of being validated, or are being assessed as part of the action.

Table 2. Ternary systems.

Included in the database	Being validated/assessed
Ag-Bi-Sn	Ag-Sn-Zn
Ag-Cu-Pb	Ag-Pb-Sb
Ag-Cu-Ni	Ag-Cu-Sn (following new experimental studies)
Ag-Cu-Sn	Ag-Cu-In
Ag-Ni-Sn	Au-In-Sn
Au-In-Sn	Cu-Ni-Sn (following remodelling of Ni-Sn)
Bi-In-Sn	Ag-In-Pd
Cu-In-Sn	In-Pd-Sn
In-Sn-Zn	Bi-Sn-Zn



Figures 7, 8. Calculated isopleths of the Ag-Bi-Sn system at 10 mol%Bi, together with experimental data. (Calculated using MTDATA)

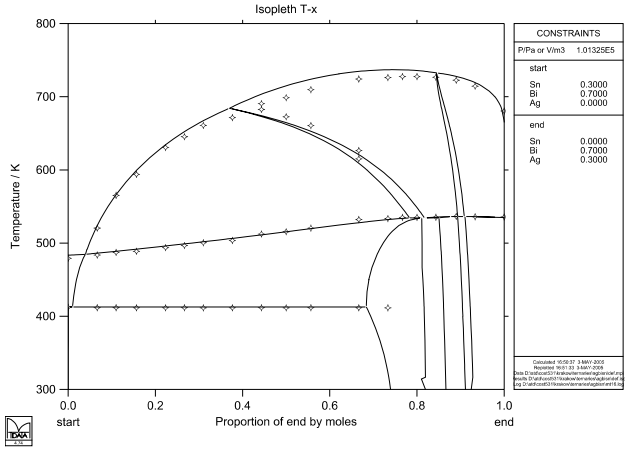
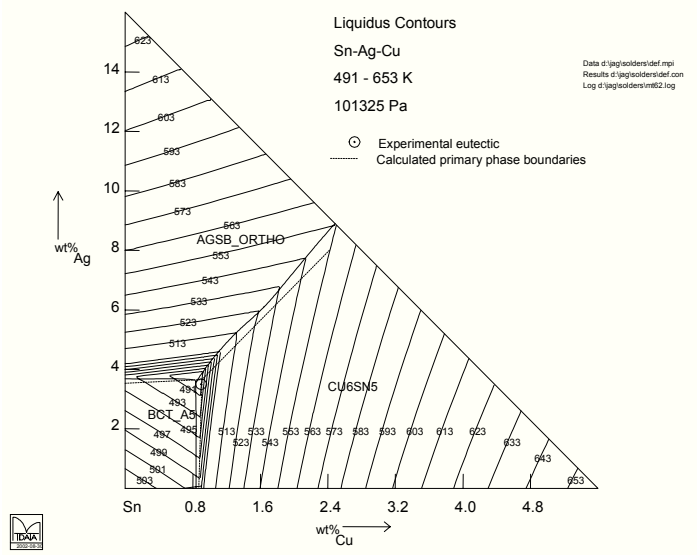
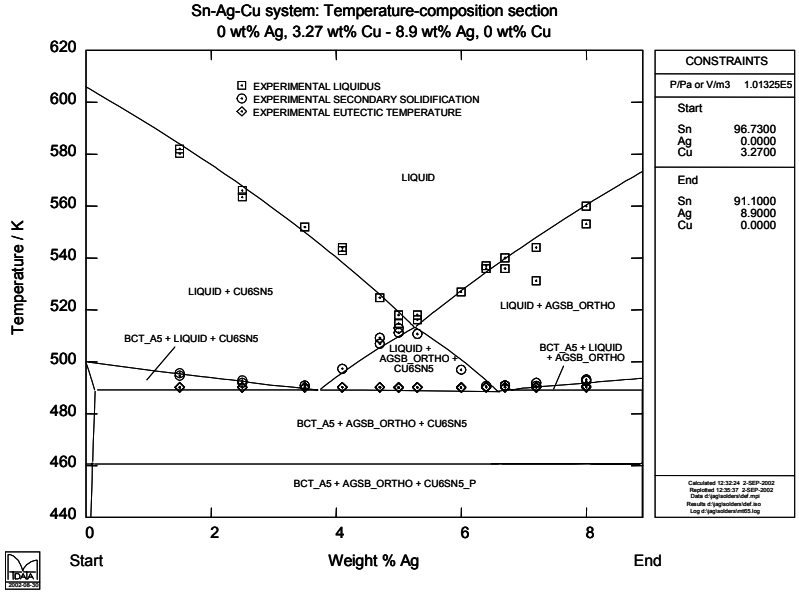


Figure 9. Calculated isopleth of the Ag-Bi-Sn system at 70 mol%Bi, together with experimental data. (Calculated using MTDATA)



Figures 10, 11. Calculated phase equilibria in the Ag-Cu-Sn system, together with experimental data. (Calculated using MTDATA).



Figures 7-9 show calculated isopleths for the Ag-Bi-Sn system using assessed data from the database, together with experimental data. Figures 7 & 8 are for the 10

mol%Bi isopleth, whereas Figure 9 is for 70 mol%Bi. In each case, a reasonable fit to the experimental data has been achieved. Figures 10 & 11 show calculations for the Ag-Cu-Sn system. Figure 10 is the calculated liquidus surface in the region of the ternary eutectic plotted on orthogonal axes. The experimentally determined eutectic composition is also plotted and can be seen to be in very good agreement with the calculation. Figure 11 shows an isopleth through the Ag-Cu-Sn system from Sn-3.27 wt%Cu to Sn-8.9 wt%Sn. Good agreement with the experimental data is achieved.

CONCLUSIONS

A self-consistent thermodynamic database for lead-free solder materials and electronic component substrates is under construction. So far, it contains assessed data for 52 binary systems and 10 ternary systems covering the elements Ag, Au, Bi, Cu, In, Ni, Sb, Sn, Pb, Pd and Zn. The database is being updated continuously following experimental programmes that are underway as part of the European COST action 531 on lead-free solders. The database will be invaluable in the design of new lead-free solder alloys and in gaining understanding how they interact with substrate materials. The database has been tested with MTDATA, Thermo-Calc and Pandat software.

Acknowledgements
This work was conducted under COST action 531 on Lead-free solders. The work was funded under “EPSRC Platform Grant (GR/R95798)”, “Measurement for Materials Processing Programme 2005-2008 project D4” and “by the Ministry of Education of the Czech Republic under contracts No.531.001 and 531.002, and by the Academy of Sciences of the Czech Republic under contract AV0Z20410507. The authors would also like to thank friends and colleagues working within COST531.

REFERENCES

(**1**) Schmid-Fetzer, R., Andersson, D., Chevalier, P. Y., Eleno, L., Fabrichnaya, O., Kattner, U.R., Sundman, B., Wang, C., Watson, A., Zabdyr & L., Zinkevich, M. “Assessment techniques, database design and software facilities for thermodynamics and diffusion: Group Report from the Ringberg Workshop on Thermodynamic Modeling and First Principles Calculations”, to be published in Calphad, 2006
(2) Special issue of Calphad journal 26(2), 2002, pp141-312
(3) Kattner, U.R. & Handwerker, C.A., “Calculation of Phase Equilibria in Candidate Solder Alloys”, Z. für Metallkde, 92(7), 2001, pp740-746
(4) Ohnuma, I., Miyashita, M., Anzai, K., Liu, X.J., Ohtani, H., Kainuma, R. & Ishida, K. “Phase Equilibria and the Related Properties of Sn-Ag-Cu Based Pb-free Solder Alloys” J. Electron. Mater., 29 (10), (2000), 1137 - 1144
(5) NPL solders database, The National Physical Laboratory, Teddington, UK. (*http://www.npl.co.uk/mtdata/databases.html*)
(6) Vrestal, J., Kroupa, A., Zemanova, A., & Vizdal, J., “Thermodynamic database on Lead free Solders,” Joint internal report, Masaryk University/Institute of Physics of Materials, Brno, Czech Republic, 2002
(7) Davies, R.H., Dinsdale, A.T., Gisby, J.A., Robinson, J.A.J., and Martin, S.M., “MTDATA - thermodynamic and phase equilibrium software from the national physical laboratory” Calphad 26(2), (2002), pp229-271

(8) Andersson, J.-O., Helander, T., Höglund, L., Pingfang Shi and Sundman, B., “Thermo-Calc & DICTRA, computational tools for materials science” Calphad, 26(2), (2002), pp273-312
(9) Chen, S.-L., Daniel, S., Zhang, F., Chang, Y.A., Yan, X.-Y., Xie, F.-Y., Schmid-Fetzer, R. and Oates, W.A., “The PANDAT software package and its applications”, Calphad, 26(2), (2002), pp175-188
(10) Dinsdale, A.T., “SGTE Data for Pure Elements”, Calphad, 15, (1991), pp317-425
(11) Redlich,O.& Kister, A.T., “Algebraic Representation of Thermodynamic Properties and Classification of Solutions”, Ind. & Eng. Chem., 40(2), (1948), p345
(12) Andersson, J.-O., Fernandez Guillermet, A., Hillert, M., Jansson, B. & Sundman, B., “A Compound Energy Model of Ordering in a Phase with Sites of Different Coordination Numbers”, Acta Metall., 34(3), (1986) pp437-445
(13) Vřešťál, J., Pinkas, J., Watson, A., Scott, A., Houserová, J & Kroupa, A., “Assessment of the Thermodynamic Properties and Phase Diagram of the Bi-Pd System”, Calphad, 30(1), (2006), pp14-17
(14) Moser, Z., Gasior, W., Pstrus, J., Zakulski, W., Ohnuma, I., Liu, X.J., Inohana, Y., Ishida, K., “Studies of the Ag-In phase diagram and surface tension measurements” J. Electron. Mater. 30(9), (2001), pp1120-1128
(15) “Binary Alloy Phase Diagrams” 2nd edition, 1990, Ed. Massalski, T.B., ASM International
(16) Chang-Seok Oh, Jae-Hyeok Shim, Byeong-Joo Lee and Dong Nyung Lee, “A thermodynamic study on the Ag-Sb-Sn system”, J. Alloys and Compounds, 238(1-2), (1996), pp155-166
(17) Leuf, C., Flandorfer, H. & Ipser, H., Unpublished work.
(18) Ansara, I. & Nabot, J-P., “A thermodynamic assessment of the Au-In system”, Thermochimica Acta, 129(1), (1988), pp89-97
(19) Liu, H. S., Cui, Y., Ishida, K. and Z. P. Jin, “Thermodynamic reassessment of the Au-In binary system”, Calphad, 27(1), (2003), pp27-37