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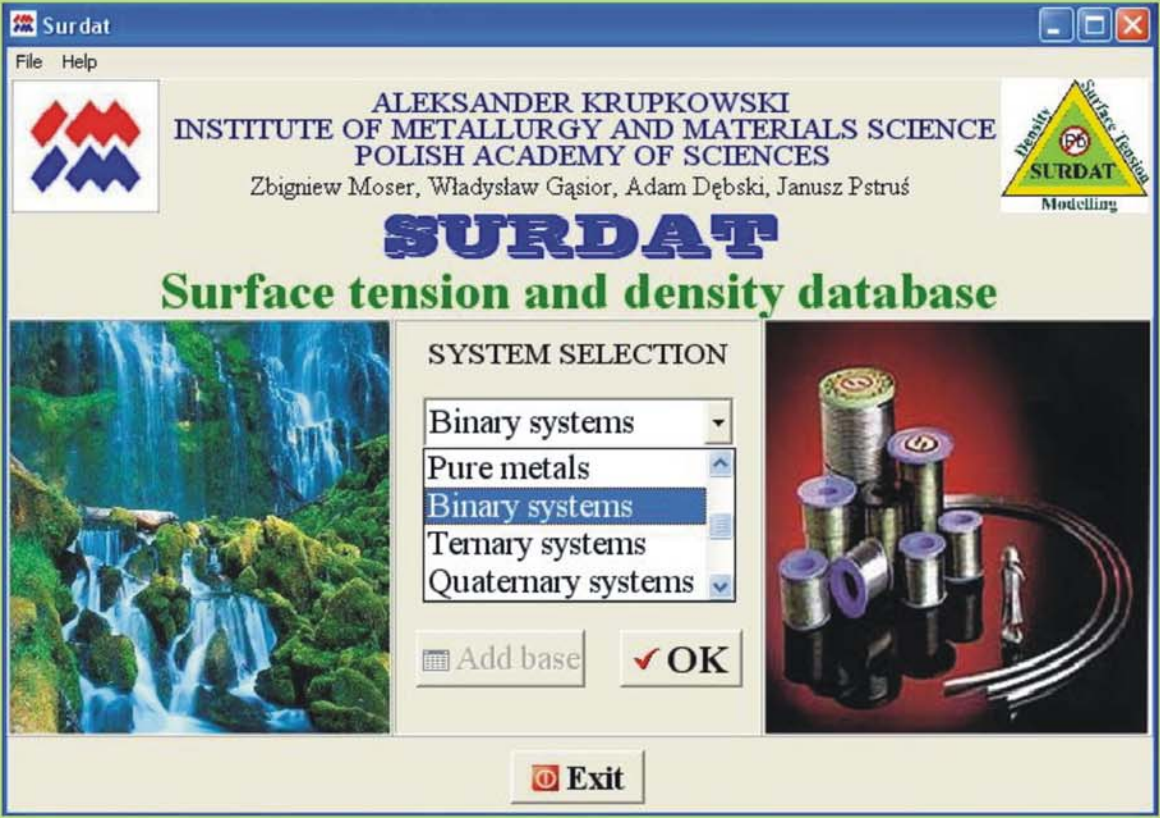
DATABASE OF LEAD - FREE SOLDERING MATERIALS



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SURDAT

Surface tension and density database

SYSTEM SELECTION

Binary systems

SURFACE TENSION, DENSITY AND MOLAR VOLUME

Institute of Metallurgy and Materials Science
Polish Academy of Sciences
Kraków 2007

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Outlook

Abstract

The European Union's RoHS (Restriction of Hazardous Substances in Electrical and Electronic Equipment) Directive will ban lead (Pb) from all new electronic consumer products sold in Europe from June 2006 on. Therefore, the pursuit of a Pb-free solder has become an important issue for the electronic material research and has led to the extensive studies and development work. In this respect, within the wettability research, the SURDAT database has been constructed.

The SURDAT electronic database has been created on the basis of the collected experimental materials and the modeling of the physical properties, in the aspect of thermodynamics, as a way of searching for substitute materials for the traditional tin-lead solders, commonly used since the Roman times. It was possible because of the systematic experimental work on surface tension, density and molar volume in Institute of Metallurgy and Materials Science, Polish Academy of Sciences in 1998, and its starting point were the studies of the Sn-Pb solders as the point of reference for the new lead-free materials. This subject area has been developed within two international networks: Associated Phase Diagram and Thermodynamics Committee and ELFNET, in the COST 531 programme, the national team CODATA, as well as in cooperation with Tohoku University in Japan and national industry institutions.

The material presented in the SURDAT database includes the results for pure metals, binary and multicomponent alloys, and, what is important, for solders based on two eutectics: Sn-Ag and Sn-Ag-Cu, commonly accepted as substitute materials for solders based on the Sn-Pb eutectic. The database consists of the descriptive part which introduces the user into the review of publications, the applied experimental methods and the modeling of surface

tension by means of the Butler method. The introductory part provides a description of the installation process of the programme, as well as examples concerning pure metals and alloys based on the Sn-Ag and Sn-Ag-Cu eutectics, the knowledge of which enables a self-sufficient use of the electronic database of the collected wide range of materials. What is extremely important, SURDAT will become available free of charge by being implemented into the ELFNET website and it is Poland's contribution to the international research, on the way of searching for substitute materials for the traditional Sn-Pb solders. The literature references make it possible to have an easy access to such problems as the modeling of surface tension by the Butler method, phase equilibrium studies for selected systems, solidification simulations and the meniscographic methods applied as the criteria for wettability in industrial practice.

Several industrial and trading consortia have conducted extensive investigations into suitable lead-free replacement for electronic components and assemblies. Although here is no single replacement for Sn-Pb solder, tin based solders with alloys such as Ag, Cu and Bi are used for production purposes.

1. Introduction

In the extensive studies undertaken all over the world in the last decade to replace traditional Sn-Pb solders by Pb-free materials, various properties of the candidate alloy systems have been considered. These include physical, chemical, mechanical and electrical properties, as well as cost and manufacturability. Among these, the physical properties, such as surface tension, interfacial tension and contact angles, are important because of their direct correlation with the wetting of the substrate by the solder.
The systematic studies of the surface tension and density of pure metals, binary and multi-component systems, including modeling of physical properties, initiated at the Institute of Metallurgy and Materials Science in Kraków, Poland, in 1998, were used to create the SURDAT database, which is an important step in the search for Pb-free soldering materials. These studies were started by surface tension, density [2001Gas2] and viscosity [2001Gas1] measurements of traditional Sn-Pb solders usually used for the purpose of comparison with new Pb-free soldering materials.

In the development of the SURDAT database for low melting alloys, the first years were devoted to collecting the surface tension and density results, mainly from experimental studies undertaken at the Institute of Metallurgy and Materials Science in Kraków, Poland, using the maximum bubble pressure method and the dilatometric technique. The possible substitutes of Pb in Sn-Pb solders with Bi, Cu, Sb, In and Ag, were examined, for which the literature data are scarce. Next, in the recent years, it was generally agreed those two eutectics: Sn-Ag and Sn-Ag-Cu should be the starting point for further research as the replacement of traditional Sn-Pb solders. Thus, the main stress has been laid on investigating the multi-component alloys. Sn-Ag (m.p.221 ºC) and Sn-Ag-Cu (m.p.217-219 ºC).

Both have their melting points higher than that of the Sn-Pb eutectic (m.p.183 ˚C), and therefore both will require higher soldering temperatures for industrial applications. To approach the melting point, (eutectic temperature) 183 ºC of Sn–Pb and its surface tension of about 470 mN/m, various additions of additional components to both eutectics Sn–Ag and Sn–Ag – Cu should be tested.

2. Theory of wetting

The driving force for formation of an interface between two materials is the decrease in Gibbs energy that occurs when intimate contact is established between the two material surfaces, as system strives towards a minimum total energy. The physics of wetting is governed by the Young-Dupré relation combining wettability σ_{SV} or σ_{SF} with the tendency to form an intermetallic compound denoted by σ_{SL}, the surface tension - by σ_{LV}, or the interfacial tension - by σ_{LF} and the contact angle - by ϕ. L indicates the liquid solder, S - the solid substrate, usually Cu, V - protective gas, and F - the flux. This is illustrated by the two schemes: (Eq.1, Fig.1a and Eq.2, Fig.1b).

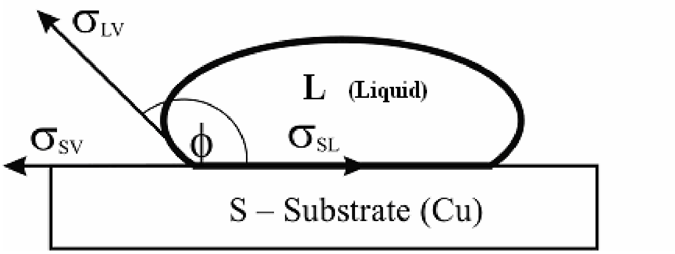


Fig. 1a. Drop of a solder resting on the solid substrate in the air (gas protective) atmosphere

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cdot \cos \phi \qquad (1)$$

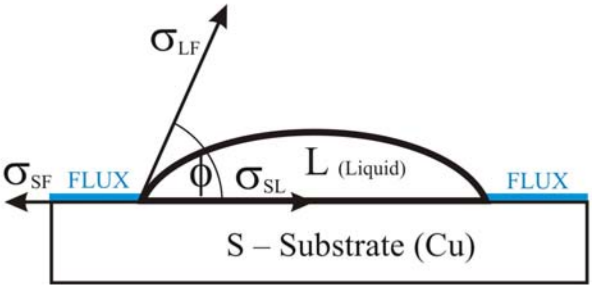


Fig. 1b. Drop of a solder resting on the solid substrate in the presence of flux

$$\sigma_{SF} = \sigma_{SL} + \sigma_{LF} \cdot \cos \phi \qquad (2)$$

Thus, the surface tension σ_{LV} measured under a protective atmosphere determines only one term in the Young-Dupré relation. The use of the sessile drop method [1988Iid] can be useful for the determination of contact angles and hence determining the difference (σ_{SV} - σ_{SL}).

In the first case, described by Eq. 1, σ_{SV} is the substrate-vapor (Cu-gas) surface tension and σ_{SL} is the substrate-liquid (Cu-solder) interfacial tension, and the sign of the difference will determine whether there will be a tendency for wetting or for beading. In the surface tension measurements, for instance by means of the maximum bubble pressure method, a decrease of surface tension (predicting the effect of the modifying elements on the solder properties) only shows an improvement of wettability, as does the decrease of contact angle in the sessile drop method.

The values of contact angle indicate also the wettability and for:

$0^o < \phi < 30^o$ - very good wetting,

$30^o < \phi < 40^o$ - good wetting,

$40^o < \phi < 55^o$ - acceptable,

$55^o < \phi < 70^o$- poor wetting, and

$\phi > 70^o$ - very poor wetting.

The second case, described by Eq. 2, is proper for meniscographic measurements of interfacial tension σ_{LF} using a flux and for calculating contact angles (from wetting force and the previously determined interfacial tension or directly from the sessile drop method). Similarly to the first case, we can only determine the difference (σ_{SF} - σ_{SL}) and thus evaluate the improvement of wettability. In both schemes of the Young-Dupré relation, the same term σ_{SL} corresponds to the reaction on the interface Cu / solder (a chemical reaction forming one or more intermetallic compounds, can occur). The rapid formation of an intermetallic phases on this interface contribute to lower σ_{SL} and the driving force at the substrate/solder interface reflects the wettability of liquid solder to the substrate [1998Lee]. Generally speaking, the values of interfacial tension are lower than those of the surface tension because the fluxes decrease the surface energy. The same is true for the contact angle measured with the use of a flux, in comparison with the results undertaken without flux by the sessile drop measurements [2006Mos1].

In view of the limitation of the use of Young - Dupré relation, searching for a generalized measure of wettability and its dependence on composition seems necessary.

3. Structure of the SURDAT database

The SURDAT database contains data of surface tension and density in an extensive range of temperatures and concentrations. Surface tension may be presented in various configurations, thus making easy the comparison with traditional Sn-Pb solders, while density is used for molar volume calculations (needed for surface tension modeling by the Butler method) and as a necessary parameter in the sessile drop and meniscographic method.

The possibilities of the SURDAT database:

a) Experimental temperature dependences of the surface tension and density for all investigated systems and compositions elaborated by linear equations.

b) Isotherms can be calculated from linear equations for the investigated compositions and are fitted by polynomials.

c) Isotherms of experimental data can be plotted at four different temperatures within 0 K – 2000 K.

d) It is possible to make a comparison of experimental data from various listed references.

e) For binary systems, surface tension can be modeled by the Butler method and can be compared (temperature dependences or isotherms) with values from various authors. For the multicomponent systems this option is currently available only for Ag-Cu-Sn ternary system for $X_{Sn}>0.6$ mole fraction.

f) It is possible to plot isotherms or temperature dependences of the surface tension, density and molar volume from previous publications.

g) For the chosen pure components, SURDAT stores the following information: atomic weight, melting point, boiling point, crystal structure, atomic, and covalent radius.

h) For binary systems and for Ag-Cu-Sn the application of Butler's method will be shown for modeling of the surface tension.

The SURDAT database, available in an electronic form, will be implemented on the ELFNET website and it includes surface tension, density and, partly, modeling of surface tension by the Butler method. The development of the SURDAT database within COST 531, ELFNET and modifications of these programs is possible with the inclusion of the updated new data of surface tension and density.

It should also be pointed out that, as for now, the properties of the new Pb-free alloys are far from those of the traditional Sn-Pb solders, considering the melting temperature, wettability, manufacturability and the reasonability of costs.

4. Experimental methods

Experimental techniques used for measuring surface tension, density and contact angles in protective atmosphere, interfacial tension and contact angles using flux in air, surface tension in air, wetting time and wetting force in air will be briefly discussed. These experimental techniques provide values with an accuracy of 2-3%. In the proceeding stages of the development of the SURDAT database they can be compared with similar data from another technique.

4.1. Maximum bubble pressure method

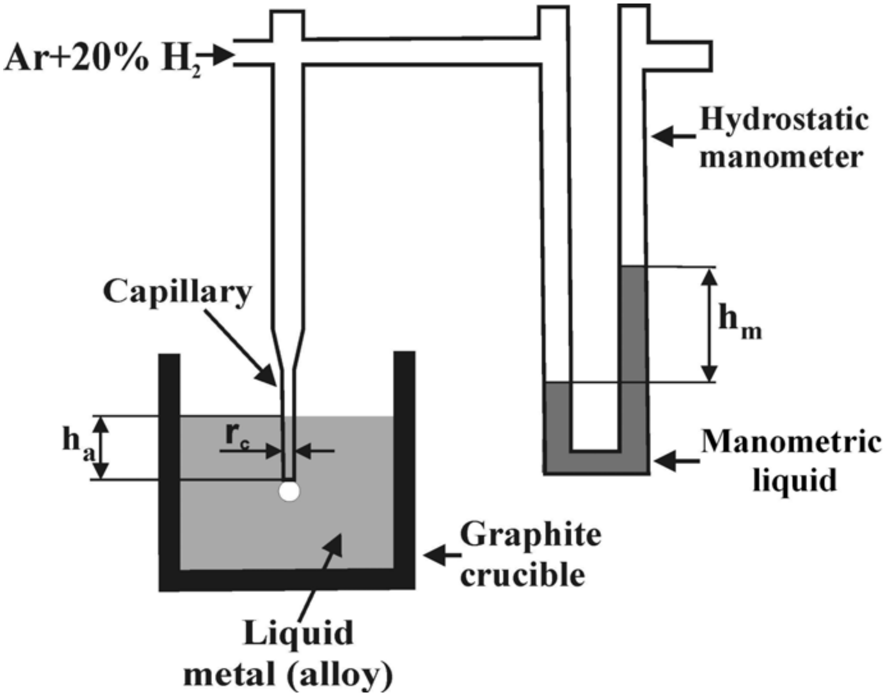


Fig. 2. Experimental arrangement for the surface tension measurements by the maximum bubble pressure method

The maximum bubble pressure method was used in the surface tension measurements. The method is based on the known capillarity equation:

$$\sigma = \frac{1}{2} r \Delta p \qquad [\mathrm{N/m}] \tag{3}$$

describing the relation between the surface tension σ, the radius of the capillary r and the pressure Δp necessary to form and to detach the gas bubble from the end of the capillary. The Δp is, in fact, the pressure difference between the gas pressure and the hydrostatic pressure of the liquid alloy and it is given by the following equation:

$$\Delta p = p_g - p_a \qquad [\mathrm{N/m^2}] \tag{4}$$

$$\Delta p = g(\rho_m h_m - \rho_a h_a) \qquad [\mathrm{N/m^2}] \tag{5}$$

where: p_g - the gas pressure, p_a - the hydrostatic pressure, g - the acceleration of gravity, ρ_a and ρ_m - the density of the investigated liquid alloy and manometric liquid, h_a - the immersion depth of the capillary and h_m - the height of the manometric liquid. The scheme for measuring the surface tension is shown in Fig.2. The surface tension calculated from Eq.3 presents the approximate value; thus, the exact values of surface tensions were calculated using the procedure proposed by Sugden [1922Sug].

4.2. Dilatometric method

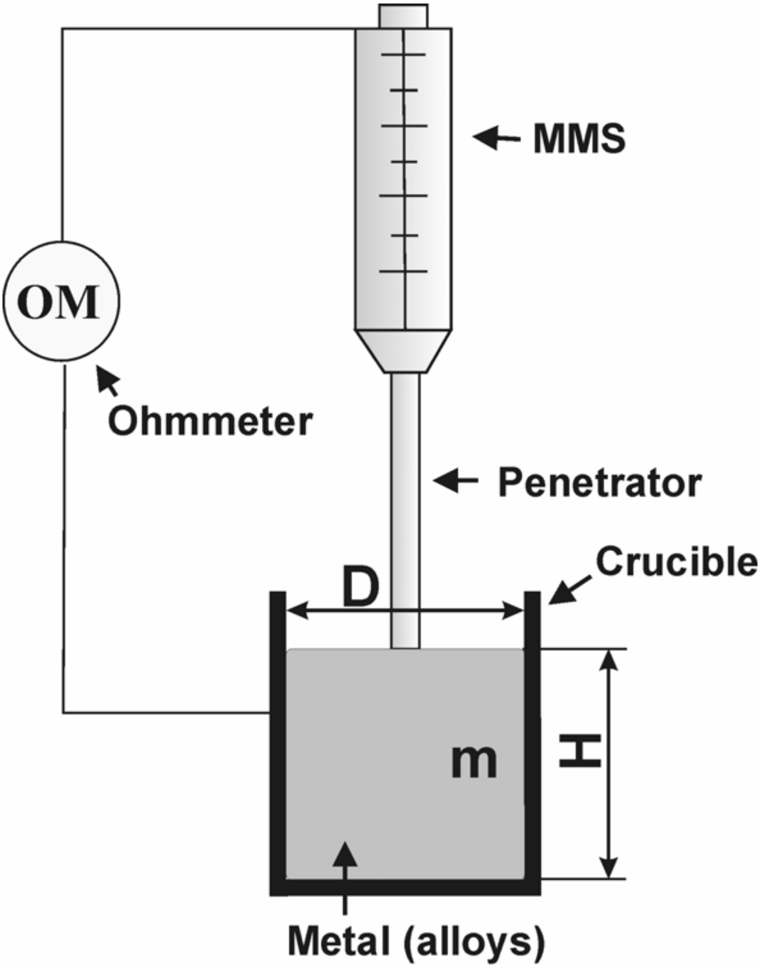


Fig. 3. Experimental set - up for density measurements by the dilatometric method. MMS denotes the screw micrometer

The densities were measured by the dilatometric method (shown schematically in Fig. 3) based on the measurement of the height of the constant weight of the alloy in the crucible of the diameter D. The density is calculated from the following equation:

$$\rho = \frac{m}{V} \tag{6}$$

$$V = \frac{\pi D^2 H}{4} \tag{7}$$

In equation (6) and (7) ρ is the density, m - the weight of alloy, V - the volume of the alloy, D - the crucible diameter and H - the height of the alloy in the crucible. The correction on the thermal expansion of the crucible was made at each measured temperature.

4.3. Meniscographic method

For the purpose of extension of the SURDAT database, two kinds of wetting balances (meniscographs) were used to observe the dynamic process of wetting by measuring the force that acts between the immersing specimen and molten solder in air. One meniscograph measures wetting force and wetting time on Cu wetted samples using a chosen flux. The second by means of non-wetted samples and the method proposed by Miyazaki el al. [1997Miy] is used for measurements of interfacial tension between solder and flux and separately the surface tension between solder and air. In Fig. 4 graphical determination of wetting time and wetting force is shown.

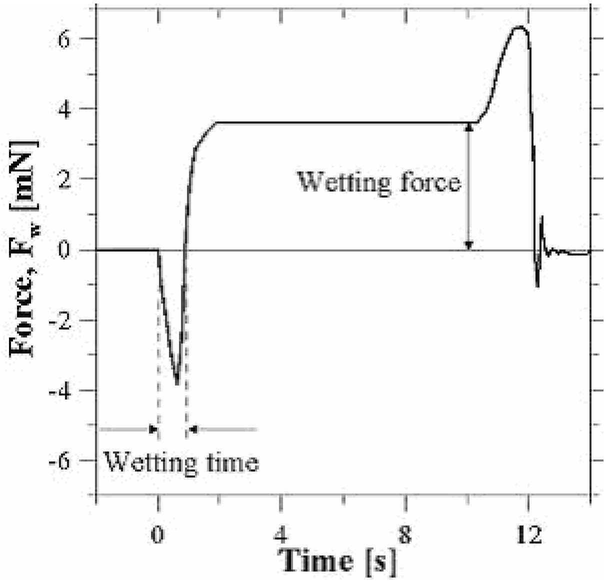


Fig. 4. The measurement of wetting force and wetting time by meniscographic method

In the Miyazaki method, a non-wetting teflon specimen was immersed into a molten solder bath at a fixed speed, and the interfacial tension σ_{LF} or surface tension σ_{LV} [N/m] were calculated by analyzing the measured force (F_r) [N/m] – immersion depth relationships:

$$F_r = \sigma_{LF} L \cos \phi - \rho V g \tag{8}$$

$$F_r = \sigma_{LV} L \cos \phi - \rho V g \tag{9}$$

In Eqs. 8 and 9 L [m] denotes circumference of the immersed teflon sample, ρ is the density of the solder in kg/m^3 (data from measurements in protective atmosphere), V [m^3] is the immersion volume of specimen, g [m/s^2] is the standard gravity, and ϕ is the contact angle. More detailed discussions of the procedures can be found in [2006Mos1] and [2006Ohn].

Using wetting force and interfacial tension contact angles in air using flux were calculated, while the contact angles in protective atmosphere without flux were obtained by sessile drop method.

4.4. Sessile drop method

Sessile drop measurements were made with a vertical furnace fitted with a macro-converter which allowed a motion-picture camera to take pictures of the solder drop resting on a Cu substrate under a protective Ar-H_2 atmosphere (see Fig.1). The camera was switched on prior to the melting of the drop and the temperature was raised to the desired value of measurement. The contact angles were determined with this apparatus by the evaluation of the pictures with a special programme designed for that purpose. More detailed discussions of the procedures can be found in [1988Iid].

5. Surface Tension Modeling from Thermodynamic Properties

The modeling of physical properties, such as surface tension, viscosity and molar volume, with the use of the thermodynamic properties of components of liquid solutions, has been more and more commonly used in recent years.

At the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences, in Kraków, Poland, the extensive studies were undertaken for more than 40 years on metallic alloys to confirm mutual correlations between thermodynamic properties, physical properties, structure of liquid alloys and the character of the phase diagram. Two examples from our previous studies of Li-Sn [1986Mos] and Mg-Sn [1999Mos] systems clearly indicate that such correlations exist and are visible at the range of existence of intermetallic compound Mg_2Sn in the Mg-Sn system, and in the case of Li-Sn where the most stable intermetallic phases are present. At this range the extreme values of electrical resistivity, surface tension, viscosity, integral enthalpy and integral excess entropies are observed. In recent years, research was directed on wettability of Pb-free soldering materials and on passing from basic research to application.

In the case of surface tension modeling, the Butler equation [1932But] is one of the earliest relations between the surface tension and the molar surface areas, as well as the partial excess Gibbs energies of components in the liquid phase. In its implementation, Butler made an assumption that the mono-atomic surface layer is a separate phase and that its molar surface possesses the properties of ideal solution, which results in the equality of the partial molar surfaces and the molar surfaces of the pure components of the solution. The relation derived by Butler for binary Ag-Sn solutions has the following form:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\mathbf{Ag}} + \frac{\mathbf{RT}}{\mathbf{A}_{\mathbf{Ag}}}\mathbf{ln}\frac{\mathbf{X}^{\mathbf{S}}_{\mathbf{Ag}}}{\mathbf{X}^{\mathbf{B}}_{\mathbf{Ag}}} + \frac{\mathbf{1}}{\mathbf{A}_{\mathbf{Ag}}}(\mathbf{G}^{\mathbf{E,S}}_{\mathbf{Ag}} - \mathbf{G}^{\mathbf{E,B}}_{\mathbf{Ag}})$$

$$= \boldsymbol{\sigma}_{\mathbf{Sn}} + \frac{\mathbf{RT}}{\mathbf{A}_{\mathbf{Sn}}}\mathbf{ln}\frac{\mathbf{X}^{\mathbf{S}}_{\mathbf{Sn}}}{\mathbf{X}^{\mathbf{B}}_{\mathbf{Sn}}} + \frac{\mathbf{1}}{\mathbf{A}_{\mathbf{Sn}}}(\mathbf{G}^{\mathbf{E,S}}_{\mathbf{Sn}} - \mathbf{G}^{\mathbf{E,B}}_{\mathbf{Sn}}) \qquad (10)$$

X_{Ag} and X_{Sn} are the mole fractions in the surface and the bulk phase, $G^{E,S}$ and $G^{E,B}$ [J/mol] are the partial excess Gibbs energies of component in the surface and bulk phase. A is the molar surface area in a monolayer of pure liquid Ag and Sn in (m^2) calculated from Eq. (11), R gas constant [$J \cdot mol^{-1} \cdot K^{-1}$], σ, $\sigma_{Ag,}$ and σ_{Sn} are the surface tension [mN/m].

Although in his paper, Butler [1932But] does not give any information how to calculate the molar surface of the components, in the following years the molar volume of the liquid components and the assumption of the closely-packed atomic structure in the surface layer were used for that purpose, and it was calculated using the following equation:

$$\mathbf{A} = \mathbf{L}\mathbf{V}^{2/3}\mathbf{N}^{1/3} \qquad (11)$$

In equation (11) **V** denotes the molar volume of the component [m^3], **N** – the Avogadro number and **L** – the geometrical parameter, which equals 1.091 for the close packing of the atoms.

The knowledge of the relation describing the excess Gibbs free energy of the surface phase, necessary in the calculation, is as follows:

$$\mathbf{G}^{\mathbf{E,S}}_{\mathbf{i}}(\mathbf{T},\mathbf{X}^{\mathbf{S}}_{\mathbf{i}}) = \boldsymbol{\beta}\mathbf{G}^{\mathbf{E,B}}_{\mathbf{i}}(\mathbf{T},\mathbf{X}^{\mathbf{S}}_{\mathbf{i}}) \qquad [\mathrm{J/mol}] \qquad (12)$$

where: β is the ratio of the coordination number of the atoms in the surface layer to that of the volume layer Z^S/Z^B, which, according to the proposal of Tanaka et al. [1996Tan], is assumed as equal β = 0.83 for metals. It is, however, necessary to mention that in the literature, one can encounter some papers in which the calculations were made for different values of β.

The common use of the Butler relation is due to the lack of appropriate models for the molar surface of the surface phase and thus its constituent partial values. Certain new approach, both to the correlation between the excess Gibbs energy of the bulk phase (equation 12) and the molar surface of the surface layer, has been recently presented in the dissertation by Gąsior [2006Gas]. After a thorough analysis of the influence of the mentioned quantities on the agreement of the Butler model (Eqs. 10, 11, 12) and the experimental values of the surface tension, measured by the maximum bubble pressure method, the author proposed new relations for calculating the molar surface of the surface phase, as well as the β parameter, on the basis of the composition of the solution (alloy), and temperature.

It was found, that the Butler method is suitable for thermodynamic modeling of the surface tension. However, the curvilinear temperature dependence of surface tension in this model, probably is connected with the assumed constant parameters, which should be temperature dependent. This was analyzed in a paper on Ag-Bi liquid alloys [2003Gas1].

6. Utilization of the data in Pb-free alloy design

The main aim of the current investigation program undertaken in co-operation with Tohoku University, within the COST 531 Program and industrial institutes: Institute of Non – Ferrous Metals Gliwice, Poland and, the following Tele and Radio Research Institute from Warszawa, Poland is to measure the effects of alloying additions on Pb-free solders. This is done by combining the surface tension and density data with interfacial tension and contact angle to find the links between this basic data and the industrial applications of Pb-free solders and to suggest a generalized measure of wettability on composition. It seems that in basic measurements in protective atmosphere, surface tension and contact angles indicate the wettability. In search for a dependence of wettability, the extensive experimental studies are needed to draw final conclusions. To resolve these problems we have examined the data for Sn-Ag [2001Mos1], Sn-Ag-Cu [2002Mos, 2004Gas1], Sn-Ag-Cu-Bi [2006Mos1, 2006Ohn], Sn-Ag-Cu-Sb [2004Gas3, 2006Mos2] and Sn-Ag-Cu-Bi-Sb [2005Mos1] solder alloys. Next, the results of the surface tension obtained in a protective atmosphere at 250 ºC were combined with the meniscographic studies in air. Finally, the data of the wetting force, wetting time, interfacial tensions and the contact angles were determined also in the case when flux was used. In these extensive studies it was concluded that also interfacial tension and contact angles are the two most important parameters used as a dependence of wettability. Our observations make it clear that the suggestions concerning the role of wetting time and wetting force in a recent paper by Lopez et al. [2005Lop] are correct as for the fact that wetting force is not a generalized dependence of solderability because it cannot account for the significant effect of the solder/flux interfacial tension on the wetting and spreading phenomenon. On the other hand, wetting time is more representative of wetting kinetics than wettability. Due to this, the wetting time and wetting force together with contact angles are often used in practice for comparison of various solders and they do not exhibit a general dependence on composition as does the interfacial tension in combination with contact angles.

Fig.5 presents examples of the surface tensions of the Sn-Ag and Sn-Ag-Cu liquid alloys, measured in air or in a protective atmosphere, as well as the interfacial tension of the Sn-Ag-Cu solders, measured in air with the use of flux, in comparison with σ data for the traditional Sn-Pb eutectic alloy. The data for the interfacial tension is lower due to the use of flux, but the tendency in both cases is similar. The same is true for contact angles calculated from meniscographic studies when compared with the sessile drop method without flux (Table 1), reported in a recent paper [2006Mos1].

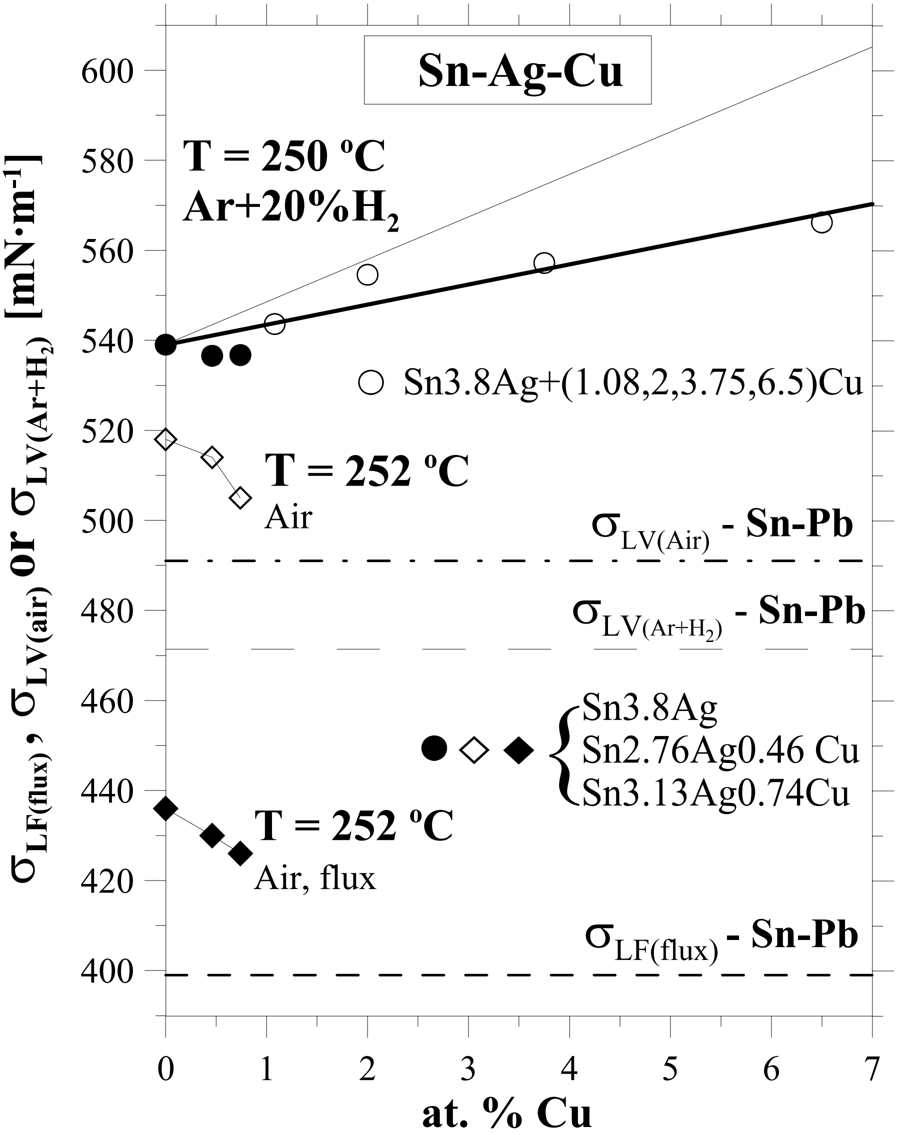


Fig. 5. The surface tensions (σ) of the binary eutectic Sn-Ag and the ternary Sn-Ag-Cu liquid alloys obtained by the maximum pressure method (○, ● - measured in argon with hydrogen) together with σ data from the meniscographic technique (◇- measured in air), as well as interfacial tensions (◆- measured in air with flux), compared with σ of the $(Sn\text{-}Pb)_{eut}$ liquid alloys (indicated by various dotted lines) as an illustration of the distance from the investigated Pb-free alloys [2006Mos1]

Table 1. Calculated contact angles from meniscographic studies together with experimental values from sessile drop measurements [2006Mos1]

Type of alloy	**Alloy % at.**	**Contact angle**	
		Sessile drop method	**Meniscographic method**
Binary eutectic	Sn3.8Ag	58º	47º
Ternary alloy	(Sn3.8Ag) + 0.46Cu	56º	45º
Ternary alloy	Sn3.8Ag) + 0.74Cu	61º	46º

On the other hand, the continued studies of the effect of Bi [2006Mos1, 2006Ohn] and Sb [2006Mos2] additions to Sn-Ag-Cu alloys close to eutectic, decrease the surface tension and bring the melting point closer to the traditional Sn-Pb solders, but due to the lifting-off failure and other unacceptable properties, have revealed that, we are very limited in the extent of additions, and the practical limit is 1 mass percent. In the parallel studies on Sn-In, Sn-Ag-In [2002Liu] and Sn-Ag-Cu-In it was documented that due to the nearly the same surface tension values of pure Sn and In, no change of surface tension is observed when adding In to Sn-based alloys and the positive influence of In on wettability is connected with the lowering of the contact angles [2006Mos3].

7. Distribution and further plans

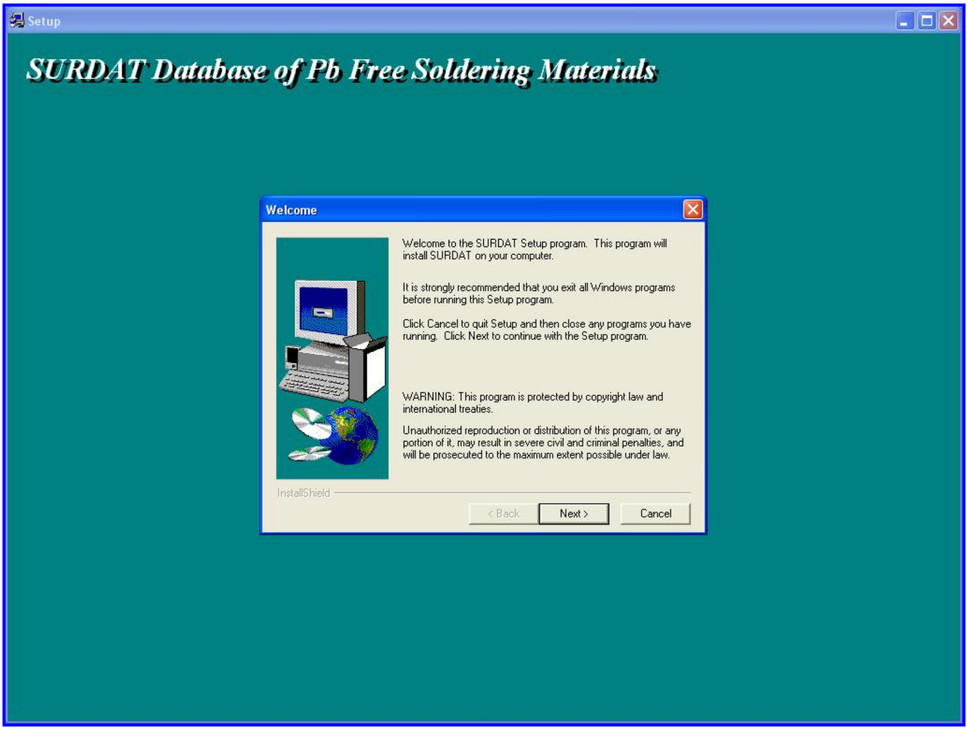
The updated version of the SURDAT database, available in an electronic form, will be implemented on the ELFNET website and it includes surface tension, density and, partly, modeling of surface tension by Butler's method. Due to the interest in SAC (Sn-Ag-Cu alloys close to eutectic composition), the results of the surface tension, interfacial tension (solder/flux), wetting time, wetting force and the calculated contact angles from the meniscographic method for Ag-Sn, Sn-Ag-Cu, Sn-Ag-Cu-Bi and Sn-Ag-Cu-Bi-Sb alloys and for Cu substrate will also be added in the future. In the case of the latter, also the electrical and mechanical properties have been examined [2004Kis, 2005Kis]. The development of the SURDAT database within COST 531, ELFNET and modifications of these programs is possible with the inclusion of the updated new data on surface tension and density. The extension of COST 531 as a new program, similarly to ELFNET 2, seems probable, in view of the interest in other low-melting solders, such as those based on the Sn-Zn eutectic, and the high-melting alloys of the Cu and Ag base, with Ti and Li additions, partly supporting the flux action.

8. Instructions for users

This section presents the issues connected with the programme. It describes the process of its installation, the first run, as well as the programme windows and the principles of its application.

8.1. Program installation

SURDAT is a program which requires a process of installation. In order to install it, you have to open the installation file SETUP.EXE., after which the window presented in Fig. 8.1 will appear.



Welcome to the SURDAT Setup program. This program will install SURDAT on your computer.

It is strongly recommended that you exit all Windows programs before running this Setup program.

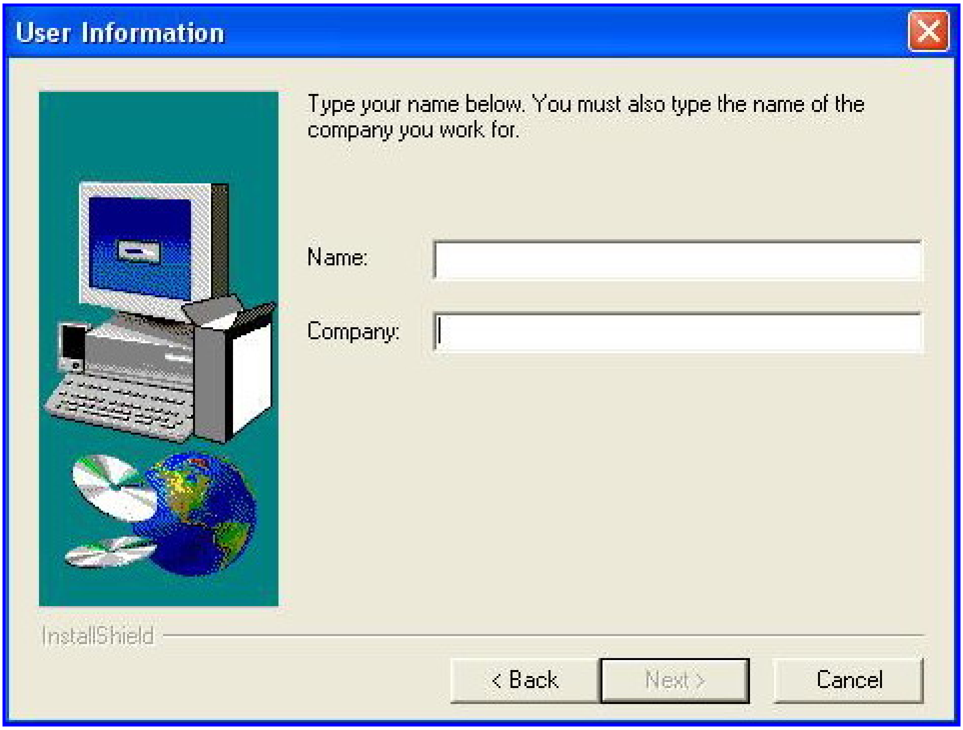
Click Cancel to quit Setup and then close any programs you have running. Click Next to continue with the Setup program.

WARNING: This program is protected by copyright law and international treaties.

Unauthorized reproduction or distribution of this program, or any portion of it, may result in severe civil and criminal penalties, and will be prosecuted to the maximum extent possible under law.

Fig. 8.1. The first window of the installation file

By pressing the „Next” button, you proceed to the next window of the installation file with the user information (The „Name” and „Company” fields will be optionally filled in by the program).



User Information

Type your name below. You must also type the name of the company you work for.

Fig. 8.2. The second window of the installation file

Pressing the „Next” button opens the next window of the installation file. The installation window presented in Fig. 8.3 shows us the destination directory for the installation of the programme.


Choose Destination Location

Setup will install SURDAT in the following directory.

To install to this directory, click Next.

To install to a different directory, click Browse and select another directory.

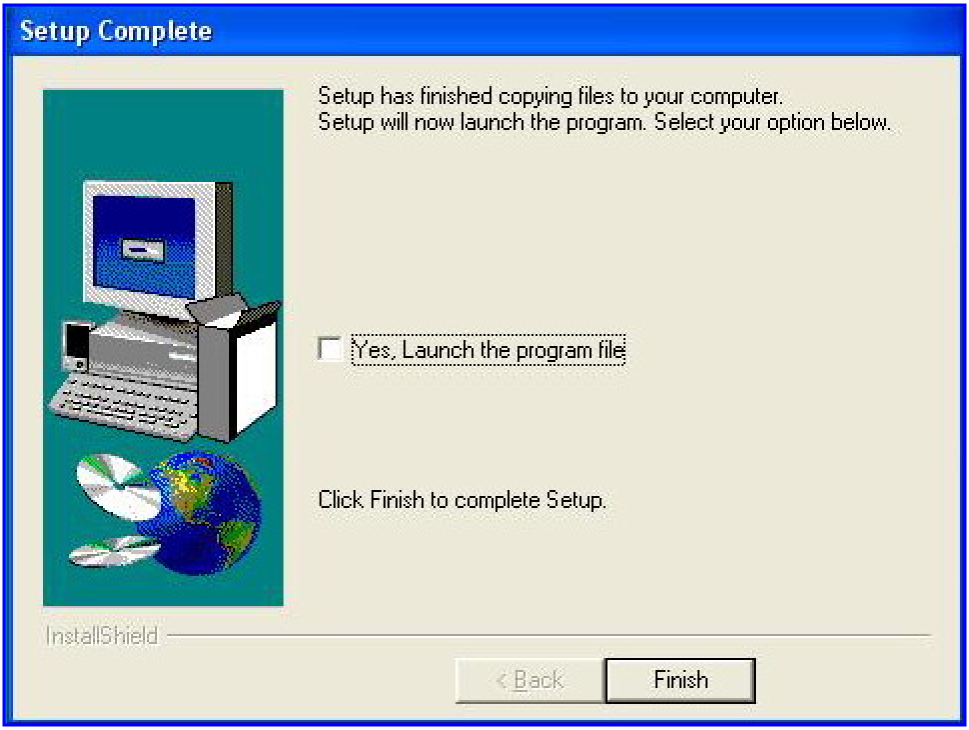
You can choose not to install SURDAT by clicking Cancel to exit Setup.

Destination Directory

C:\Program Files\IMIM PAN\SURDAT

Fig. 8.3. The third window of the installation file

You can change the destination directory for the installation by pressing the „Browse…” button and giving the selected location at which to install the programme. On pressing „Next”, the installation programme will proceed to the last installation window (Fig. 8.4). By pressing the „Finish” button, you complete installation.



Setup Complete

Setup has finished copying files to your computer.
Setup will now launch the program. Select your option below.

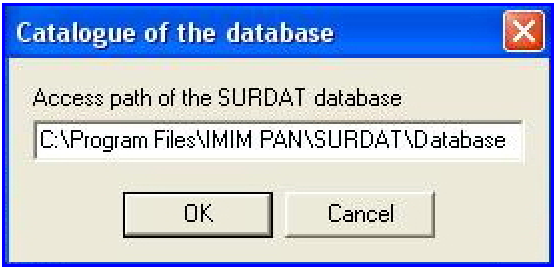
☐ Yes, Launch the program file

Click Finish to complete Setup.

Fig. 8.4. The finishing window of the installation

8.2. First Run

You run the programme by opening the SURDAT.exe file. After the first start of the programme, it will ask for the footpath of the access to the database presented in Fig. 8.5.



Catalogue of the database

Access path of the SURDAT database: C:\Program Files\IMIM PAN\SURDAT\Database

Fig. 8.5. Access path of the SURDAT database

If you do not wish to change the directory of the installation, enter:

C:\Program Files\IMIM PAN\SURDAT\Database

and press „OK”. If you do wish to change the directory, you must give the correct location of the database. After pressing „OK”, you start the programme.

With subsequent runs of the programme, you will not have to repeat this step, in order to start the programme.

9. Database Presentation

In the present version of the SURDAT data for 10 pure metals, 11 binary -, 4 ternary - and 2 quaternary systems are available as listed in Table 2. The literature references for the systems from Table 2 are available on each level of the databases (after pressing the “References” button in the lower window of the programme). Most data are connected with the binary eutectic Sn-Ag or various amounts of a third metal added to this eutectic. The higher order systems are composed on the basis of the ternary eutectic Sn-Ag-Cu, with Bi and Sb additions. It is in agreement with the studies undertaken all over the world, recommending alloys on the tin base with additions of Ag and Cu as substitutes for the traditional Sn-Pb solders.

Table 2. The investigated liquid metals and alloys

Metals	Binary Alloys	Multicomponent Alloys
Pb Sn In Ag Bi Sb Cu Zn Al Au	Pb – Sn Ag – Sn Ag – In Bi – Sn In – Sn Ag – Bi Sb – Sn Sn – Zn Ag – Sb Cu – Sn Cu – Sb	$(Sn\text{-}Ag)_{eut}+In$ $(Sn\text{-}Ag)_{eut}+Bi$ $(Sn\text{-}Ag)_{eut}+Cu$ $(Sn\text{-}Ag)_{eut}+Sb$ $(Sn\text{-}Ag)_{eut}+Cu+Sb$ $(Sn\text{-}Ag)_{eut}+Cu+Bi$

Fig. 9.1 Shows the functional scheme of the SURDAT database.

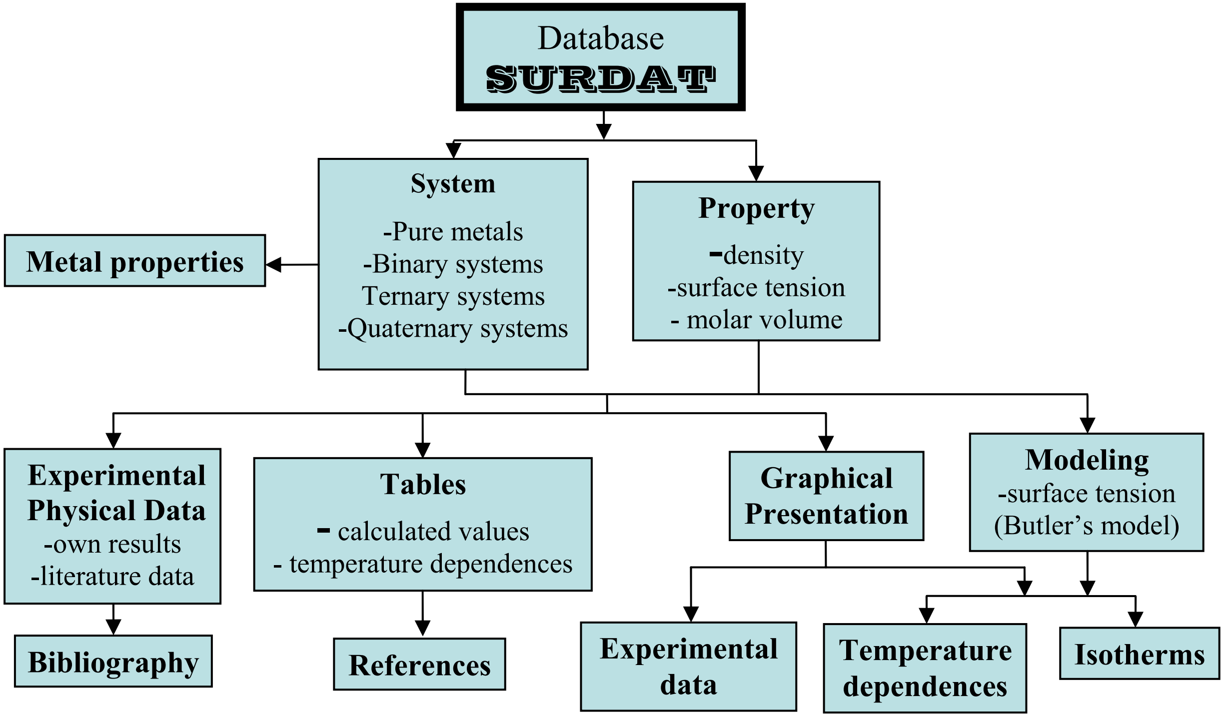
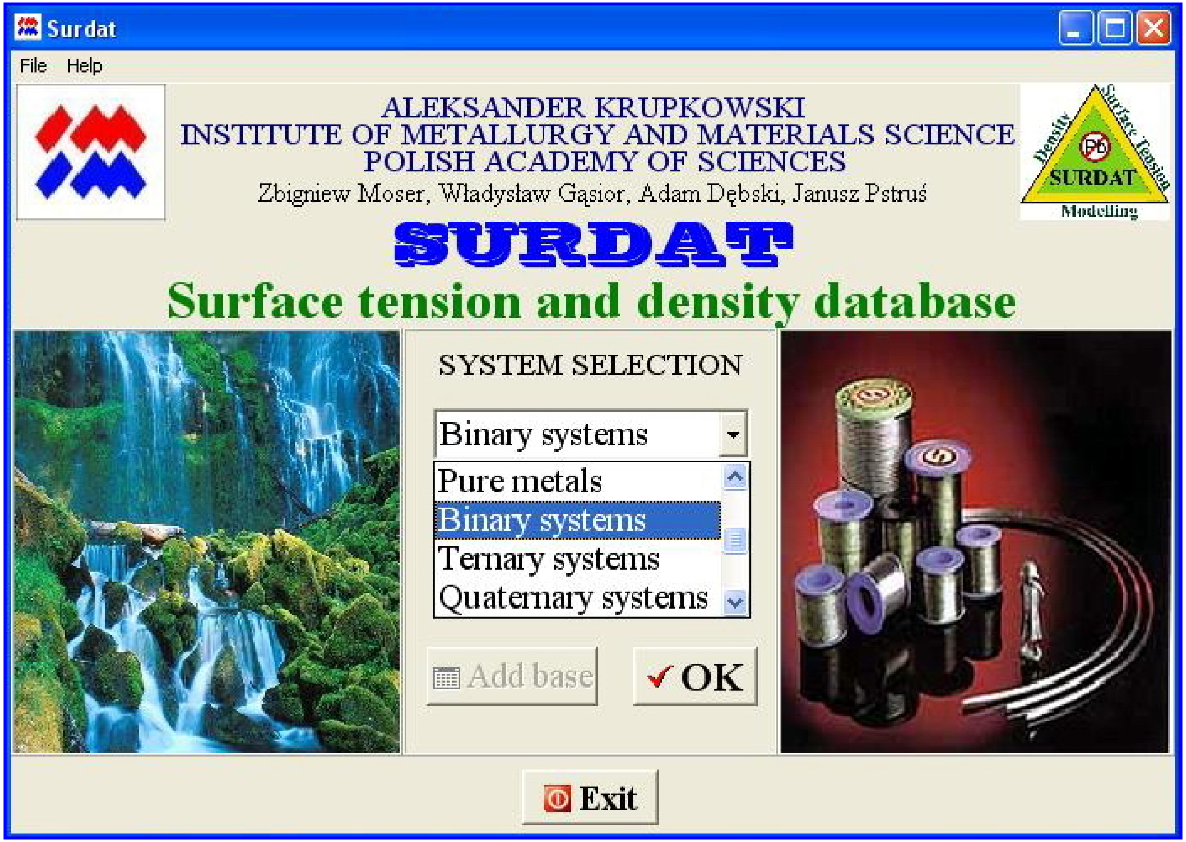


Fig.9.1. Operation scheme of the SURDAT database

The capabilities of the SURDAT database will be presented by using the data on Ag and Ag–Sn and Ag-Cu-Sn systems.

After the opening of the SURDAT computer database, the first window appearing on the screen (Fig. 9.2.) gives essential basic information with the window for the selection of the system. In order to proceed to the other options of the database, you should select the appropriate system in the „SYSTEM SELECTION” section.

By selecting the „Pure metals” option and pressing the „OK” button, you proceed to the next window of the programme (Fig. 9.3.), where you have a possibility to select both the metal and the system (if you did not select the „Pure metals” option in the previous window), as well as the physical properties („SELECT PROPERTIES”).



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SURDAT

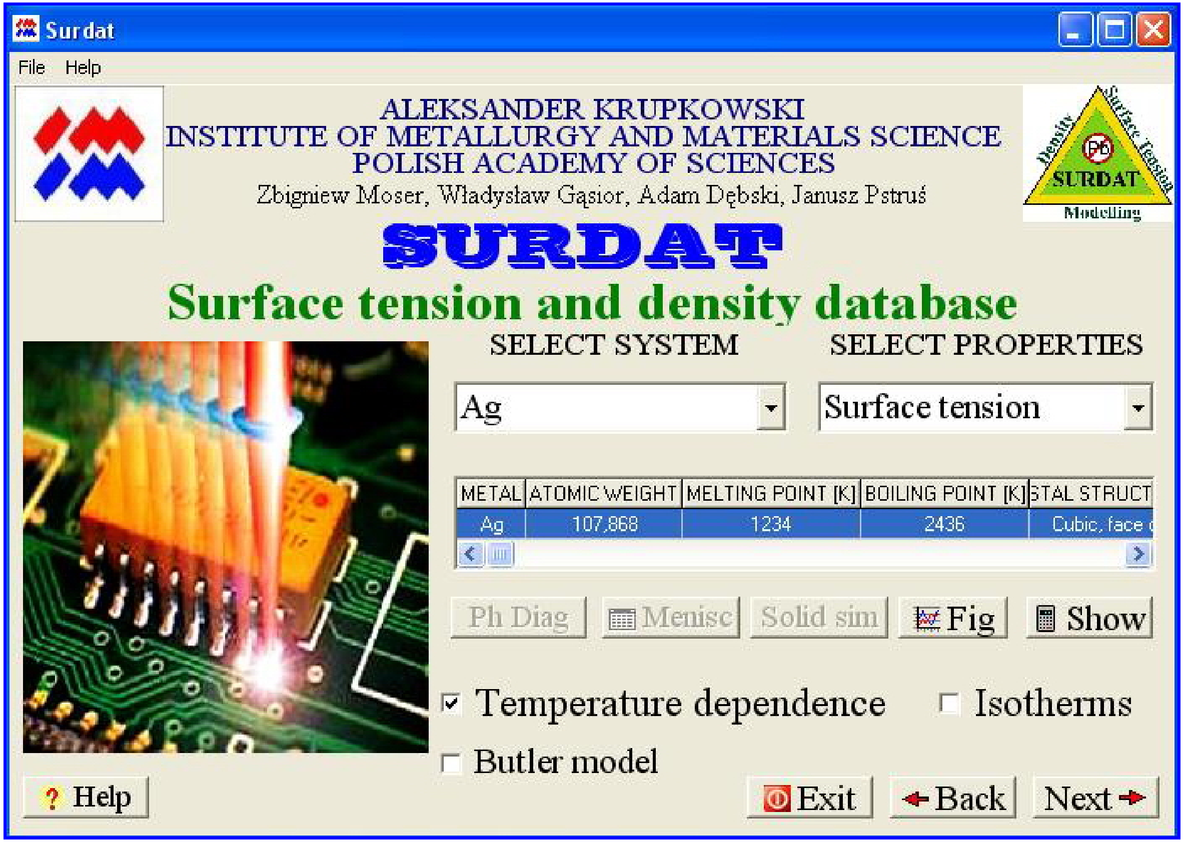
Surface tension and density database

SYSTEM SELECTION

Binary systems

Fig. 9.2. The first window of the SURDAT database. Selection of the system type

If you choose „Ag” in the „SELECT SYSTEM” section and click the „SHOW” button, the programme will give you the selected data for Ag from the periodic table, such as: ATOMIC WEIGHT, MELTING POINT, BOILING POINT, CRYSTAL STRUCTURE (at room temperature), as well as COVALENT RADIUS and ATOMIC RADIUS (both not visible in Fig. 9.3).



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SURDAT

Surface tension and density database

SELECT SYSTEM: Ag

SELECT PROPERTIES: Surface tension

METAL	ATOMIC WEIGHT	MELTING POINT [K]	BOILING POINT [K]	STAL STRUCT
Ag	107,868	1234	2436	Cubic, face

☑ Temperature dependence ☐ Isotherms

☐ Butler model

Fig. 9.3. The second step in SURDAT, which enables the selection of the suitable system and the property which will be observed

The „Fig" option makes it possible to browse the temperature and isotherms determined and presented in publications. For pure metals, only the temperature dependences are available. If you select the property „Surface tension" in the „SELECT PROPERTIES" window, and additionally „temperature dependence", the programme will show a diagram of the surface tension dependence on temperature, measured by various authors (Fig. 9.4). Further, by pressing the „References" button, you open the window with the list of publications used as sources of the data. (Fig. 9.5).

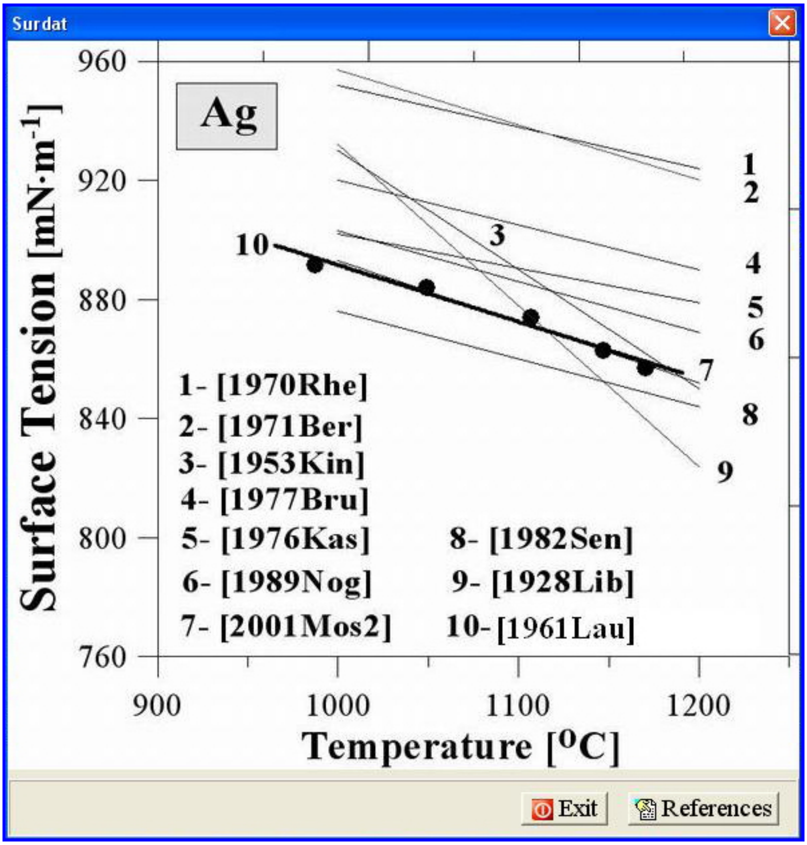
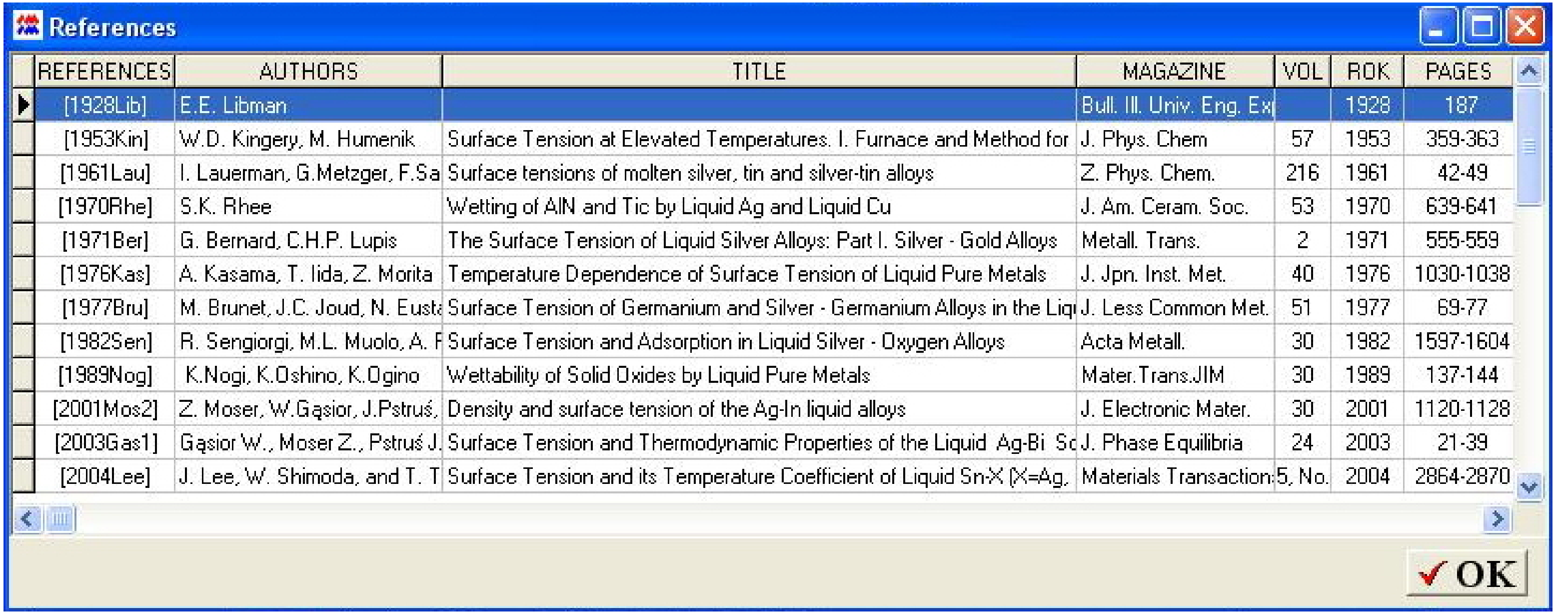


Fig. 9.4. Comparison of the temperature dependence of surface tension of the liquid silver available in the literature with experimental points from [2001Mos2]



REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	ROK	PAGES
[1928Lib]	E.E. Libman		Bull. Ill. Univ. Eng. Ex		1928	187
[1953Kin]	W.D. Kingery, M. Humenik	Surface Tension at Elevated Temperatures. I. Furnace and Method for	J. Phys. Chem	57	1953	359-363
[1961Lau]	I. Lauerman, G.Metzger, F.Sa	Surface tensions of molten silver, tin and silver-tin alloys	Z. Phys. Chem.	216	1961	42-49
[1970Rhe]	S.K. Rhee	Wetting of AlN and Tic by Liquid Ag and Liquid Cu	J. Am. Ceram. Soc.	53	1970	639-641
[1971Ber]	G. Bernard, C.H.P. Lupis	The Surface Tension of Liquid Silver Alloys: Part I. Silver - Gold Alloys	Metall. Trans.	2	1971	555-559
[1976Kas]	A. Kasama, T. Iida, Z. Morita	Temperature Dependence of Surface Tension of Liquid Pure Metals	J. Jpn. Inst. Met.	40	1976	1030-1038
[1977Bru]	M. Brunet, J.C. Joud, N. Eust	Surface Tension of Germanium and Silver - Germanium Alloys in the Liq	J. Less Common Met.	51	1977	69-77
[1982Sen]	R. Sengiorgi, M.L. Muolo, A.	Surface Tension and Adsorption in Liquid Silver - Oxygen Alloys	Acta Metall.	30	1982	1597-1604
[1989Nog]	K.Nogi, K.Oshino, K.Ogino	Wettability of Solid Oxides by Liquid Pure Metals	Mater.Trans.JIM	30	1989	137-144
[2001Mos2]	Z. Moser, W.Gąsior, J.Pstruś,	Density and surface tension of the Ag-In liquid alloys	J. Electronic Mater.	30	2001	1120-1128
[2003Gas1]	Gąsior W., Moser Z., Pstruś J.	Surface Tension and Thermodynamic Properties of the Liquid Ag-Bi Sc	J. Phase Equilibria	24	2003	21-39
[2004Lee]	J. Lee, W. Shimoda, and T. T	Surface Tension and its Temperature Coefficient of Liquid Sn-X (X=Ag,	Materials Transaction	5, No.	2004	2864-2870

Fig. 9.5. The references for the surface tension of Ag

After selecting the „Binary system” option (Fig. 9.2) and next the „Ag-Sn” system and the „Density” option, by choosing the „Fig” option, the user can see the temperature („Temperature dependence”, Fig. 9.6) and the isotherms („Isotherms”) of density created on the basis of the experimental data (Fig. 9.7).

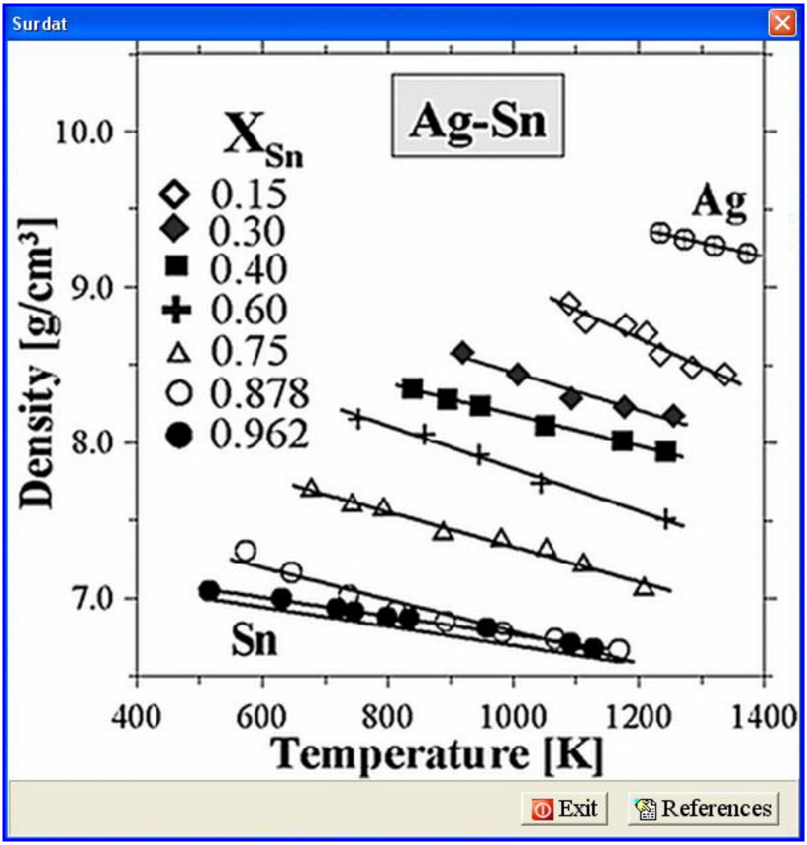


Fig. 9.6. The temperature dependence of the density of Ag-Sn liquid alloys

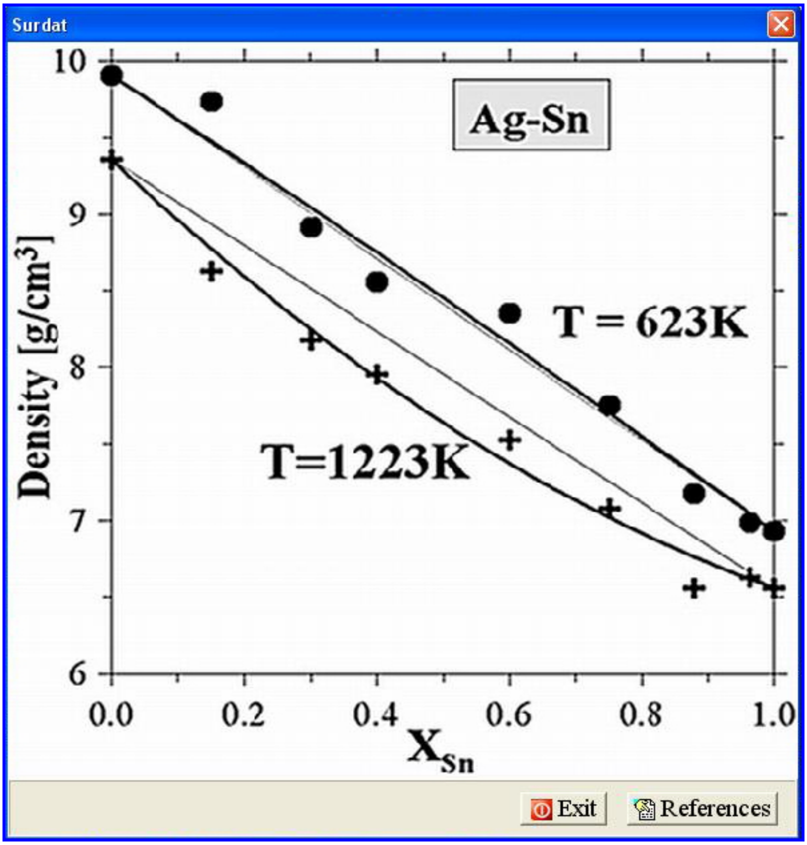


Fig. 9.7. The isotherms of the density of Ag-Sn liquid alloys

If you choose the „Surface tension” option in the „SELECT PROPERTIES” window, you will have the possibility of browsing the temperature dependence (Fig. 9.8) and the isotherms of the surface tension (Fig. 9.9). In the „Butler model” option, the programme will show the temperature and the isotherms of the surface tension, presented in Figs. 9.10 and 9.11, respectively.

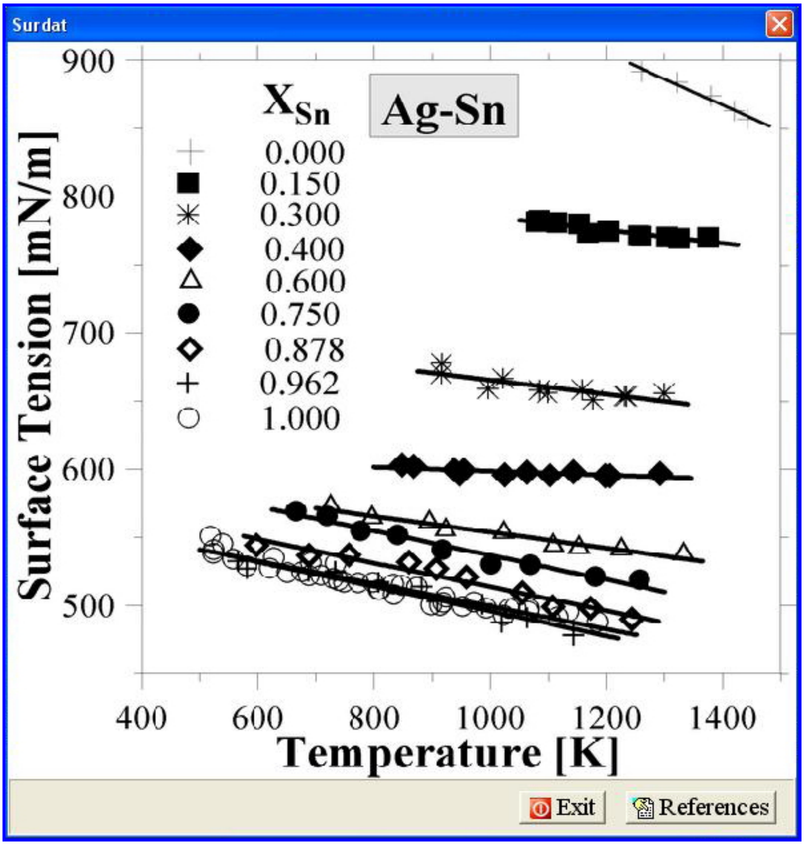


Fig. 9.8. The temperature dependence of the surface tension of Ag-Sn liquid alloys

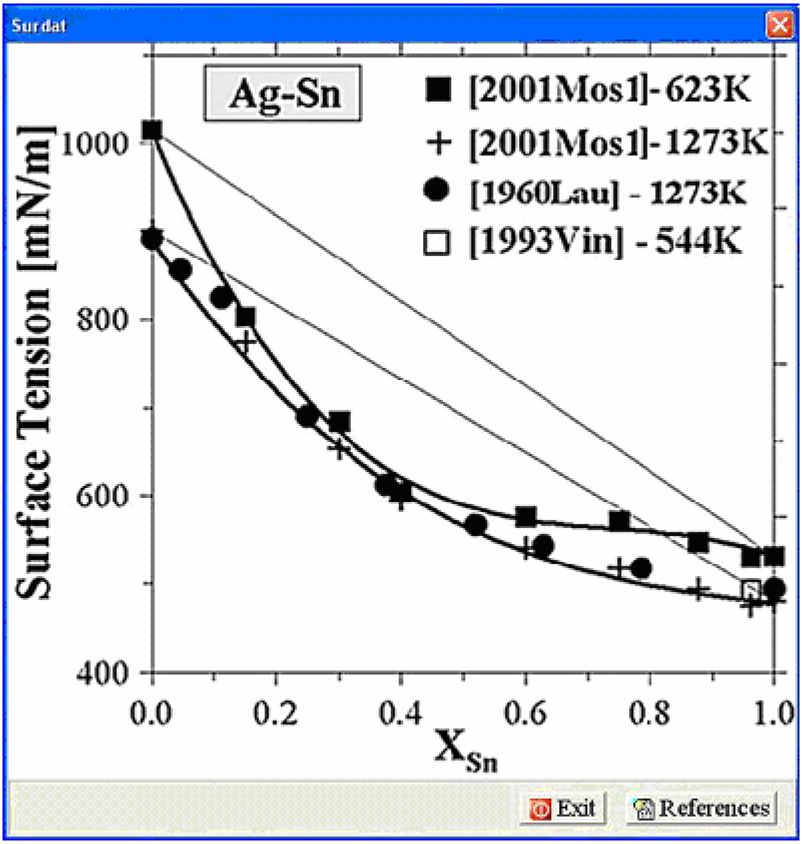


Fig. 9.9. The isotherms of the surface tension of Ag-Sn liquid alloys

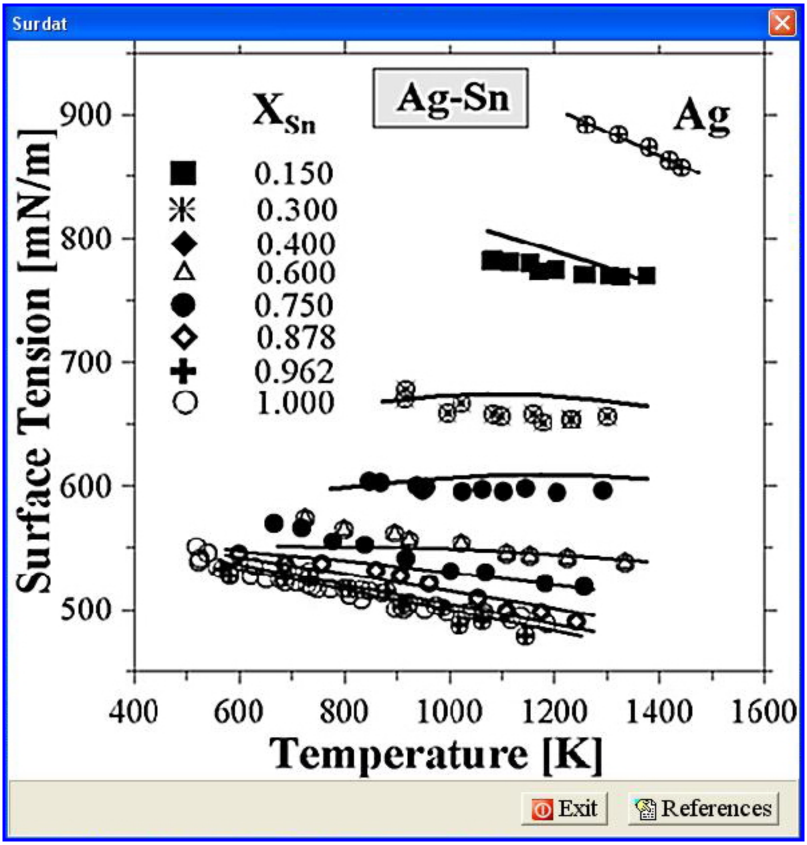


Fig. 9.10. The temperature dependence of the surface tension of Ag-Sn, calculated from the Butler model, and the experimental data (symbols)

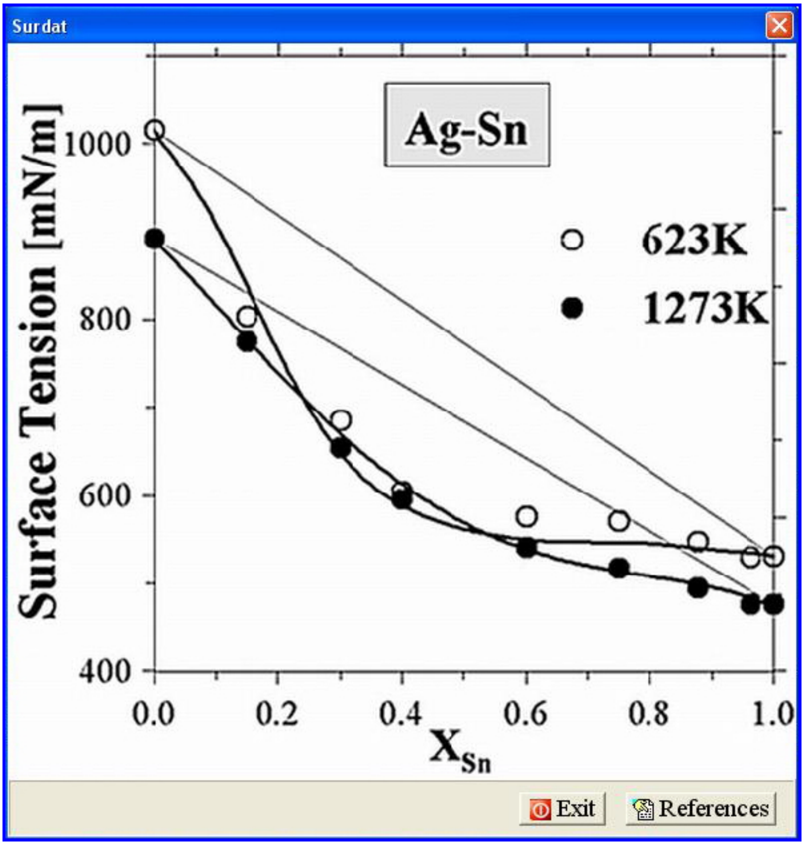


Fig. 9.11. The isotherms of the Ag-Sn, calculated from the Butler model, and experimental data (symbols) at 623 K and 1273 K

For the molar volume, only the „Isotherms" option is available in the database (Fig. 9.12).

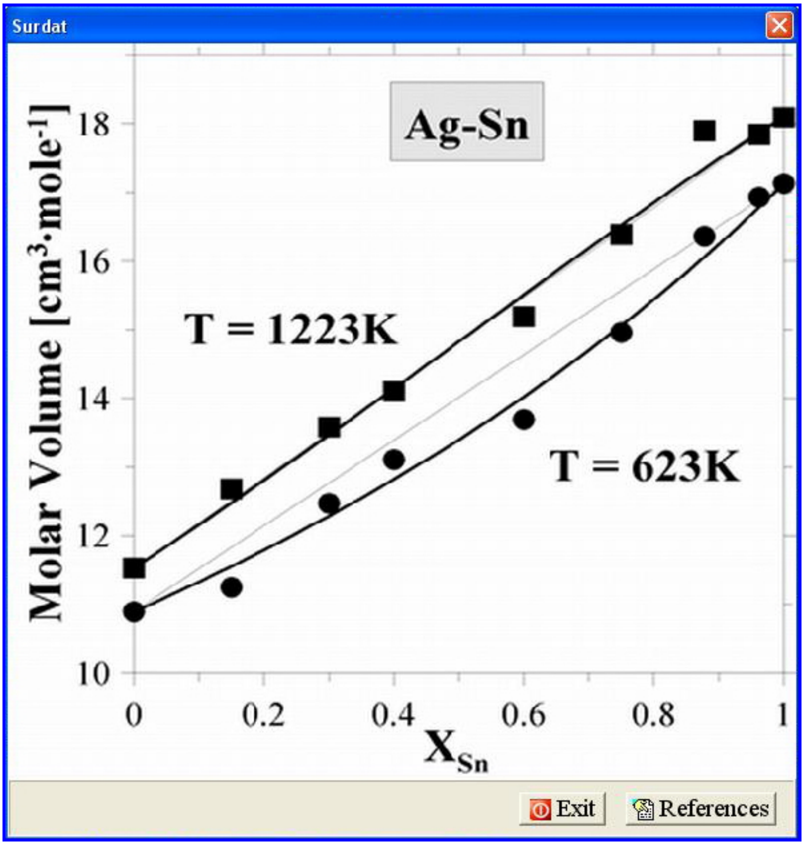
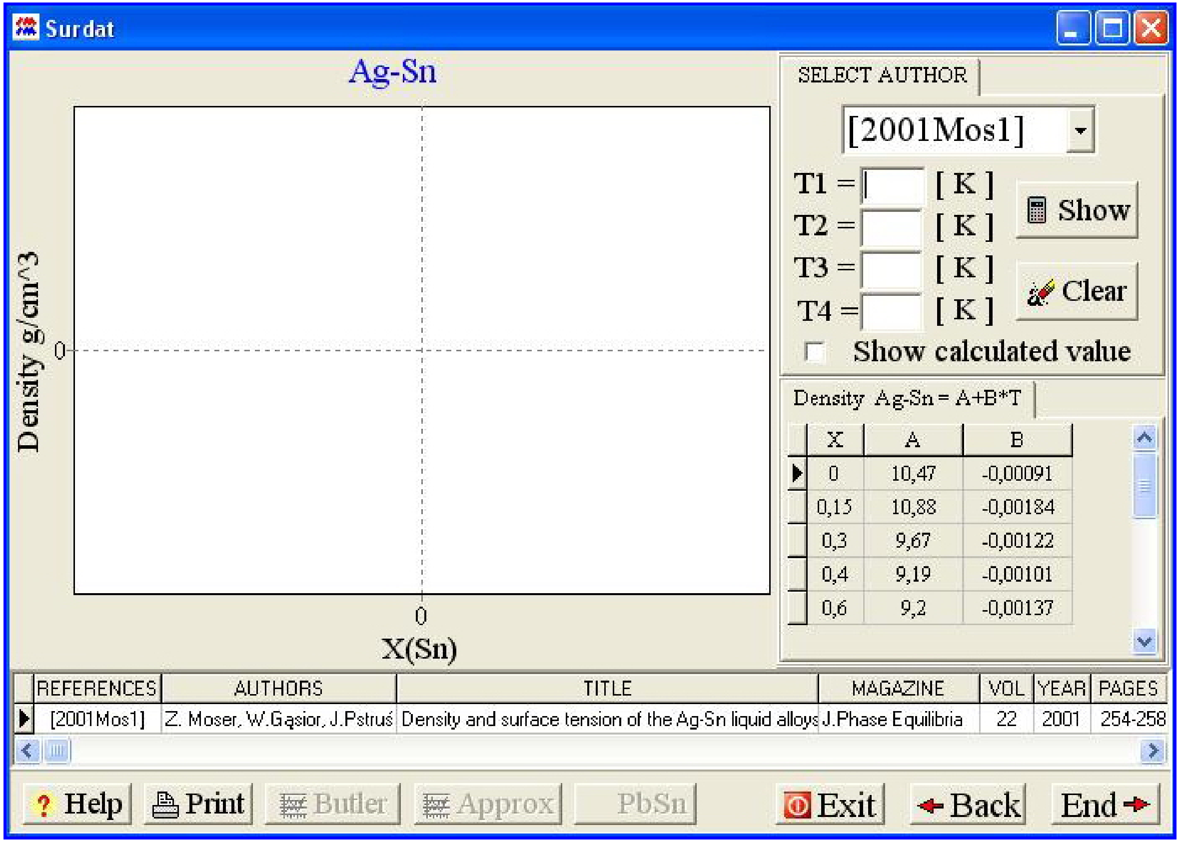


Fig. 9.12. The isotherms of the molar volume of Ag-Sn liquid alloys

Browsing the physical properties in the „Fig" option is arranged in the same way for all the systems available in the database. Using the example of the Ag–Sn and Ag-Sn-Cu systems, other functions of the SURDAT database will be presented, including the surface tension modeling with the use of the Butler relation. Entering the binary systems begins in the start window (Fig. 9.2), with the selection of the „Binary systems" option, as well as in the scrollable windows for the system and physical property selection (Fig. 9.3). After choosing the „Ag-Sn" system and the „Density" as well as the type of presentation of „Isotherms", click the „Next" button, which opens the window, where you are able to model, process and analyze the data collected by various authors. When you select an author („SELECT

AUTHOR”) (Fig. 9.13) and click „Show”, the programme will show the density equation of the given author, in the bottom right-hand corner of the window, and the source-publication of the data, in the lower window. If you select „Show calculated value” option and insert the temperature (maximum 4 values), the programme will calculate the density and present it graphically on the diagram (Fig. 9.14).



SELECT AUTHOR: [2001Mos1]

☐ Show calculated value

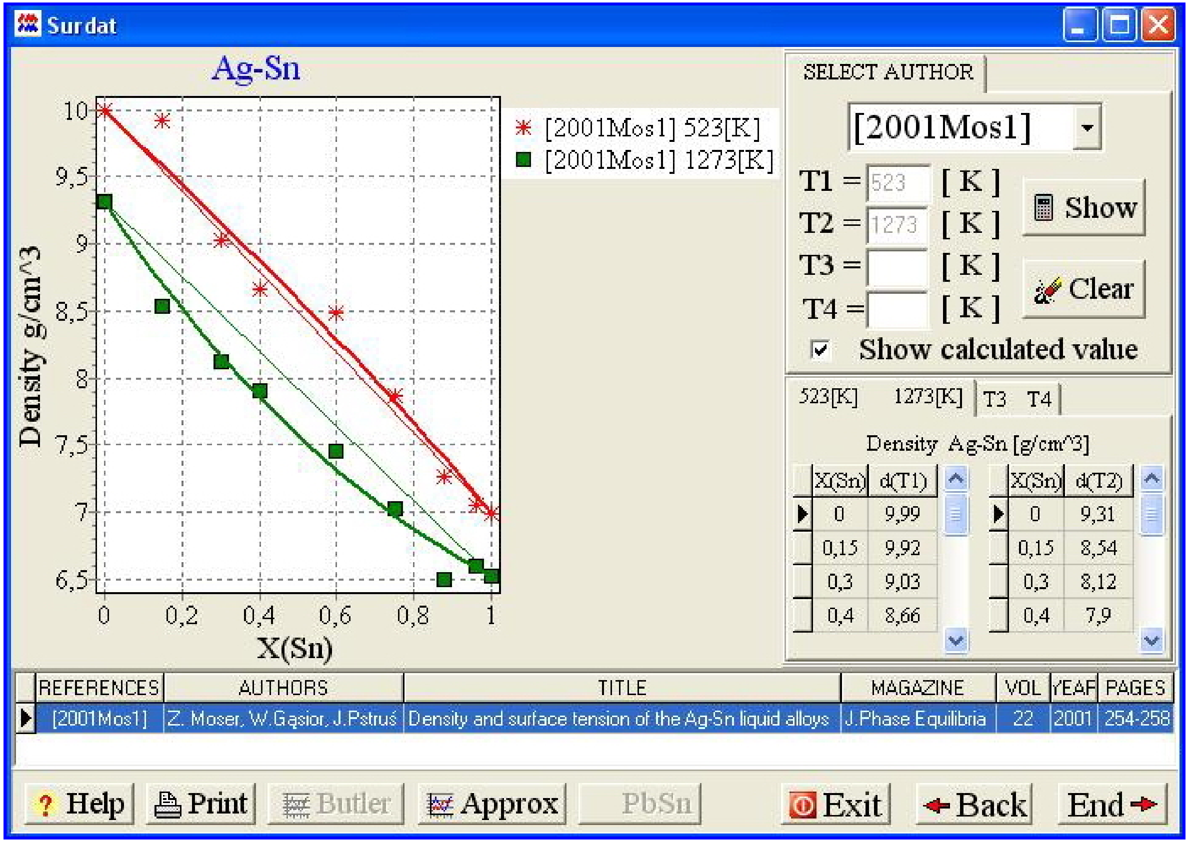
Density Ag-Sn = A+B*T

X	A	B
0	10,47	-0,00091
0,15	10,88	-0,00184
0,3	9,67	-0,00122
0,4	9,19	-0,00101
0,6	9,2	-0,00137

REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAR	PAGES
[2001Mos1]	Z. Moser, W.Gąsior, J.Pstruś	Density and surface tension of the Ag-Sn liquid alloys	J.Phase Equilibria	22	2001	254-258

Fig. 9.13. The density relations of a selected author for the Sn-Ag system

The calculated values of density for the respective concentrations at a given temperature are shown in the tables in the bottom right-hand corner of the window. This option makes it possible to observe the temperature dependences of the analyzed system and, if other authors' data is available, compare the former with the latter, once again starting with the selection of the author („SELECT AUTHOR”). By choosing „Approx”, you have a possibility to fit the experimental points by a polynomial. In the lower part, you will see „References”. Clicking the „Clear” button clears the diagram and erases the figures.



SELECT AUTHOR

[2001Mos1]

T1 = 523 [K]

T2 = 1273 [K]

T3 = [K]

T4 = [K]

☑ Show calculated value

523[K] 1273[K] T3 T4

Density Ag-Sn [g/cm^3]

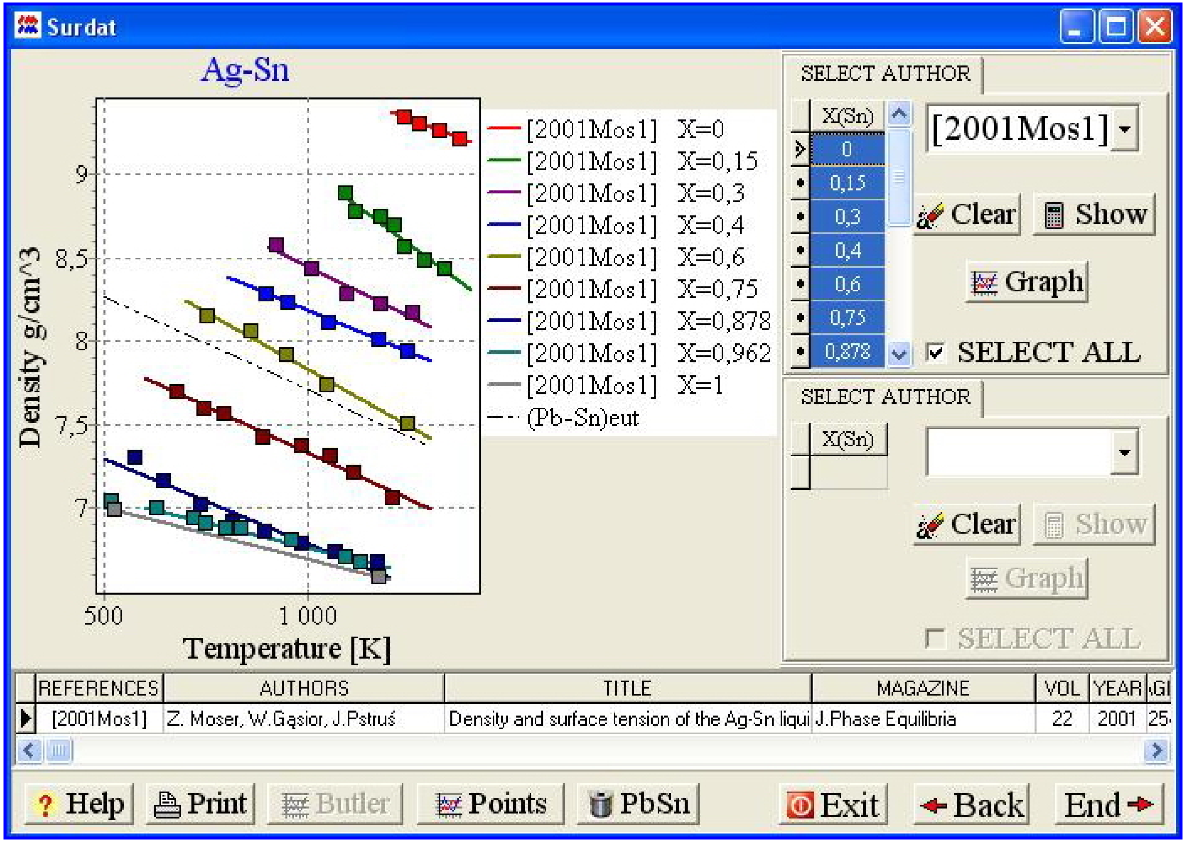
X(Sn)	d(T1)
0	9,99
0,15	9,92
0,3	9,03
0,4	8,66

X(Sn)	d(T2)
0	9,31
0,15	8,54
0,3	8,12
0,4	7,9

REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAF	PAGES
[2001Mos1]	Z. Moser, W.Gąsior, J.Pstruś	Density and surface tension of the Ag-Sn liquid alloys	J.Phase Equilibria	22	2001	254-258

Fig. 9.14. The isotherms of the density of the Ag-Sn liquid alloys for 523 K and 1273 K

When you select „Temperature dependence” and the author in the previous window (Fig. 9.3) and then press the „Show” button, the programme will show you the available concentrations. You can choose all of them by selecting „SELECT ALL” or just those which interest you. When you press „Points”, the programme will show the experimental points for the given concentrations (Fig. 9.15) (originating from the author seen in the upper window). On clicking the „Graph” button, you can adjust the linear regression of the experimental points. You have the possibility to print the diagram, after clicking „Print”. If you wish to compare the density of a given system with the density of the traditional tin-lead solders, press the „PbSn” button.



REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAR	GI
[2001Mos1]	Z. Moser, W.Gąsior, J.Pstruś	Density and surface tension of the Ag-Sn liqui	J.Phase Equilibria	22	2001	25

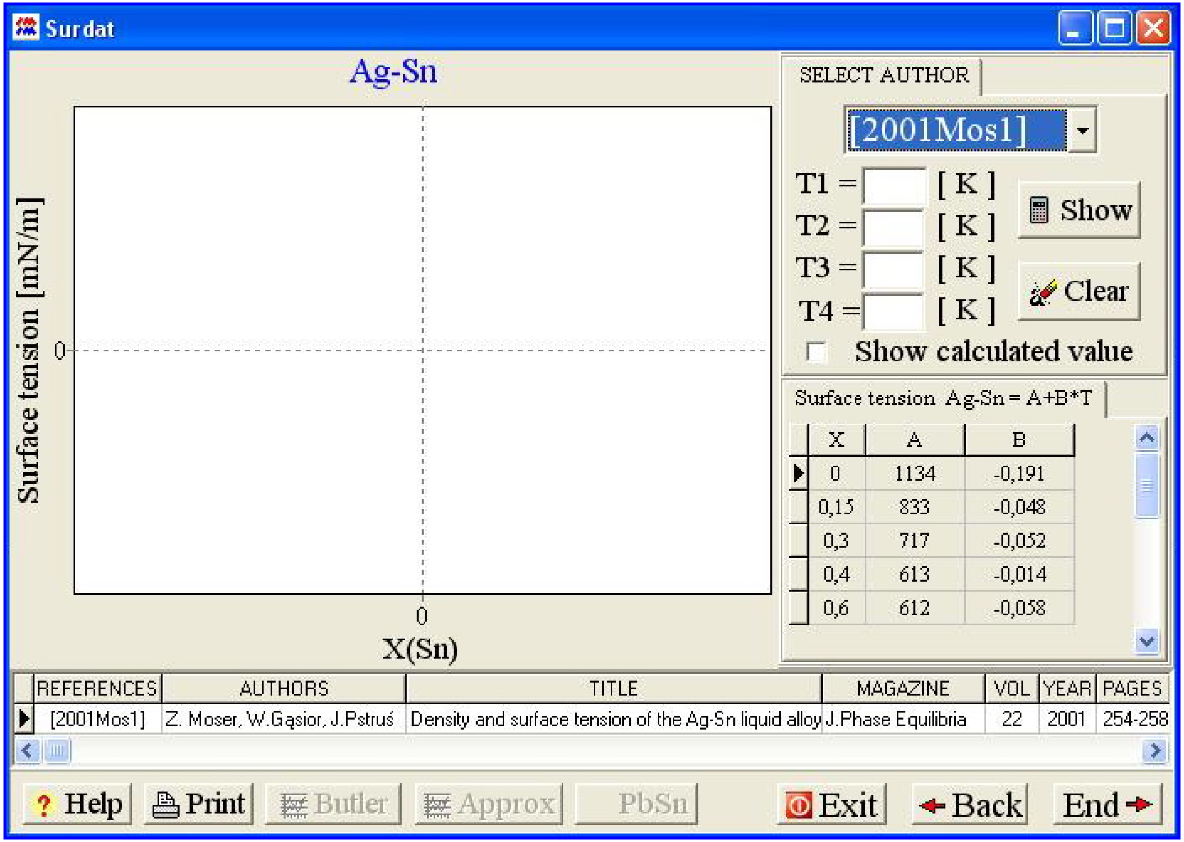
Fig. 9.15. The temperature dependence of the density of Ag-Sn liquid alloys and $(Sn\text{-}Pb)_{eut}$

By going backwards (Fig. 9.3) and selecting surface tension, similar to density, you can:

a) see the parameters A and B of the linear equations $\sigma = A+BT$ describing the temperature dependence of the surface tension for the different concentrations ($X_{(Sn)}$) (Fig. 9.16),

b) calculate the isotherms at a chosen temperature and

c) compare the isotherms with the data of another author (Fig. 9.17).



SELECT AUTHOR: [2001Mos1]

T1 = [K]
T2 = [K]
T3 = [K]
T4 = [K]

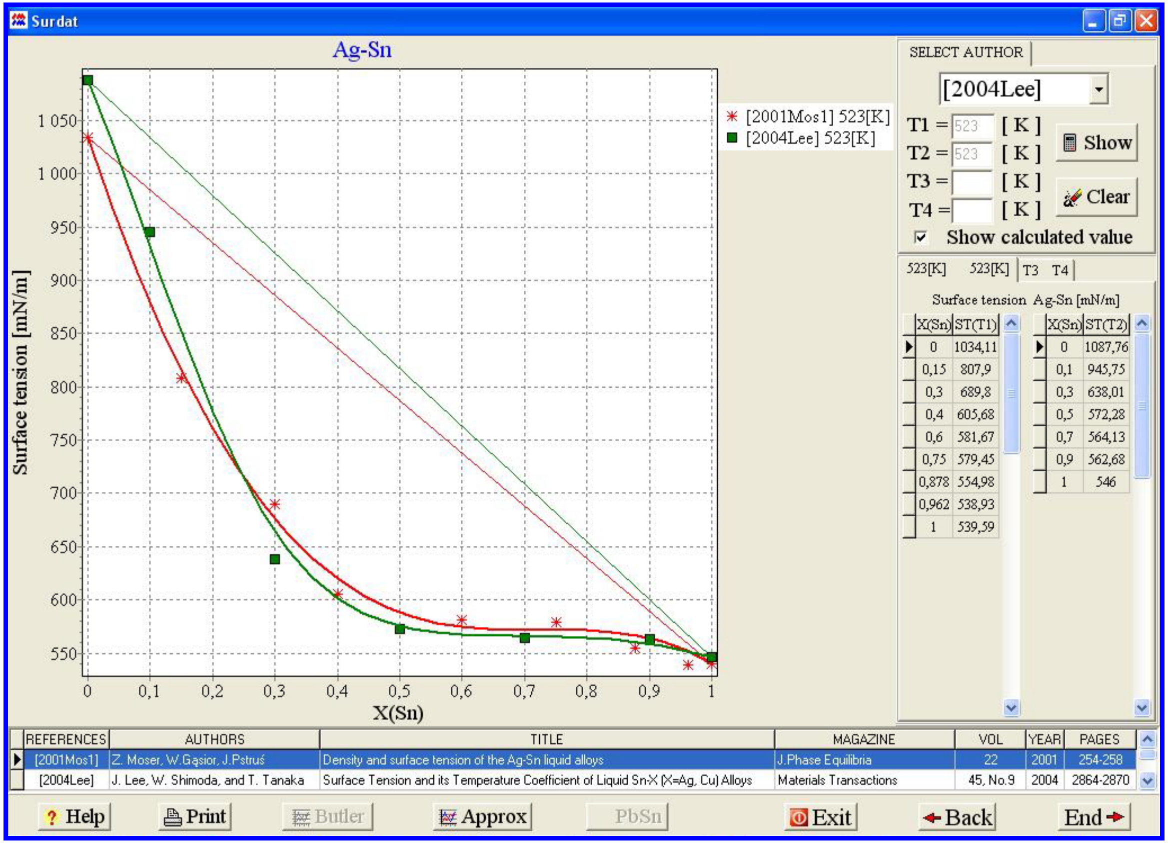
☐ Show calculated value

Surface tension Ag-Sn = A+B*T

X	A	B
0	1134	-0,191
0,15	833	-0,048
0,3	717	-0,052
0,4	613	-0,014
0,6	612	-0,058

REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAR	PAGES
[2001Mos1]	Z. Moser, W.Gąsior, J.Pstruś	Density and surface tension of the Ag-Sn liquid alloy	J.Phase Equilibria	22	2001	254-258

Fig. 9.16. The surface tension relation by a given author for the Ag-Sn system



T1 = 523 [K]
T2 = 523 [K]
T3 = [K]
T4 = [K]

☑ Show calculated value

523[K] 523[K] | T3 T4

Surface tension Ag-Sn [mN/m]

X(Sn)	ST(T1)
0	1034,11
0,15	807,9
0,3	689,8
0,4	605,68
0,6	581,67
0,75	579,45
0,878	554,98
0,962	538,93
1	539,59

X(Sn)	ST(T2)
0	1087,76
0,1	945,75
0,3	638,01
0,5	572,28
0,7	564,13
0,9	562,68
1	546

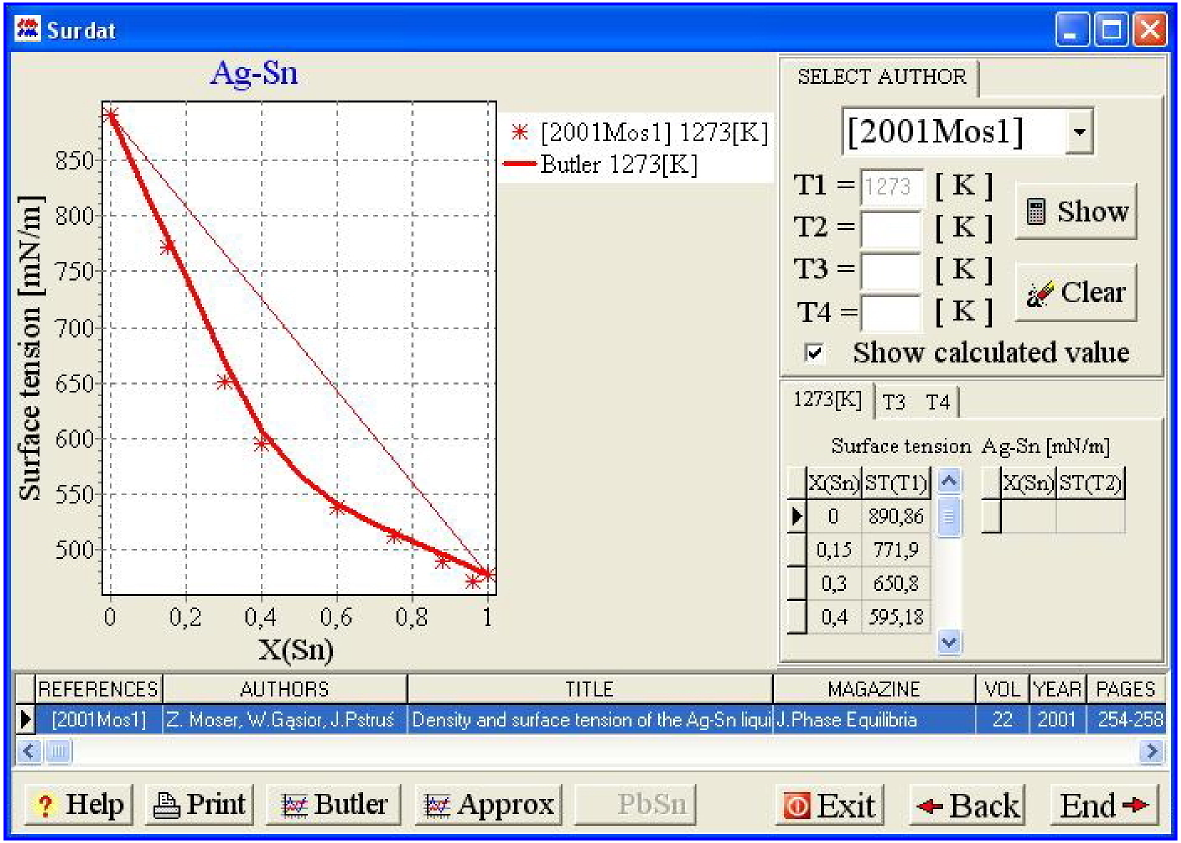
REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAR	PAGES
[2001Mos1]	Z. Moser, W.Gąsior, J.Pstruś	Density and surface tension of the Ag-Sn liquid alloys	J.Phase Equilibria	22	2001	254-258
[2004Lee]	J. Lee, W. Shimoda, and T. Tanaka	Surface Tension and its Temperature Coefficient of Liquid Sn-X (X=Ag, Cu) Alloys	Materials Transactions	45, No.9	2004	2864-2870

Fig. 9.17. The isotherms of the surface tension of Sn-Ag of different authors, calculated at a chosen temperature, (523K lines) compared with the experimental data

In the previous stages of modeling of Pb-free solders reported in the literature, the Butler method [1932But] was used for calculations of the surface tension. The SURDAT database makes it also possible to compare experimental data for surface tension with that coming from the Butler modeling for all tested binary systems and in addition for Sn-Ag-Cu.

The comparison between the data from experiments and the modeling shows a reasonable agreement. Thus in the further studies the necessary experiments can be limited due to the possibility of modeling. To proceed this way, we need the relation among surface tension and temperature with concentration. In the SURDAT database for two systems, Ag-Sn and Sn-Ag-Cu, using Butler's modeling the surface tension was calculated at various temperatures and concentrations similar to other binary systems documented in Annex.

By choosing the „Butler model" option in the window shown in Fig 9.3, the user can calculate the surface tension from the Butler relation by means of the „Butler" button and verify its agreement with the data obtained from the experiment (Fig. 9.18). Selecting „Temperature dependence" and the authors of the paper makes it possible to see the temperature relation diagram (Fig. 9.19). If other authors' experimental data are available, there is a possibility of displaying and comparing them on the same diagram. If you wish to compare the surface tension of a given system with that of the traditional tin-lead solders, press „PbSn". By clicking on the diagram with the left mouse-button, you will enlarge the diagram to the full-screen size (Fig. 9.20). When you click again, the window returns to its previous size. Selecting the „Butler" option enables you to calculate the temperature dependences from the Butler model for all the concentrations available from a given author (the „SELECT ALL" option) and to compare them with the experimental data (Fig. 9.21), or for a particular concentration (Fig. 9.22).



T1 = 1273 [K]
T2 = [K]
T3 = [K]
T4 = [K]

☑ Show calculated value

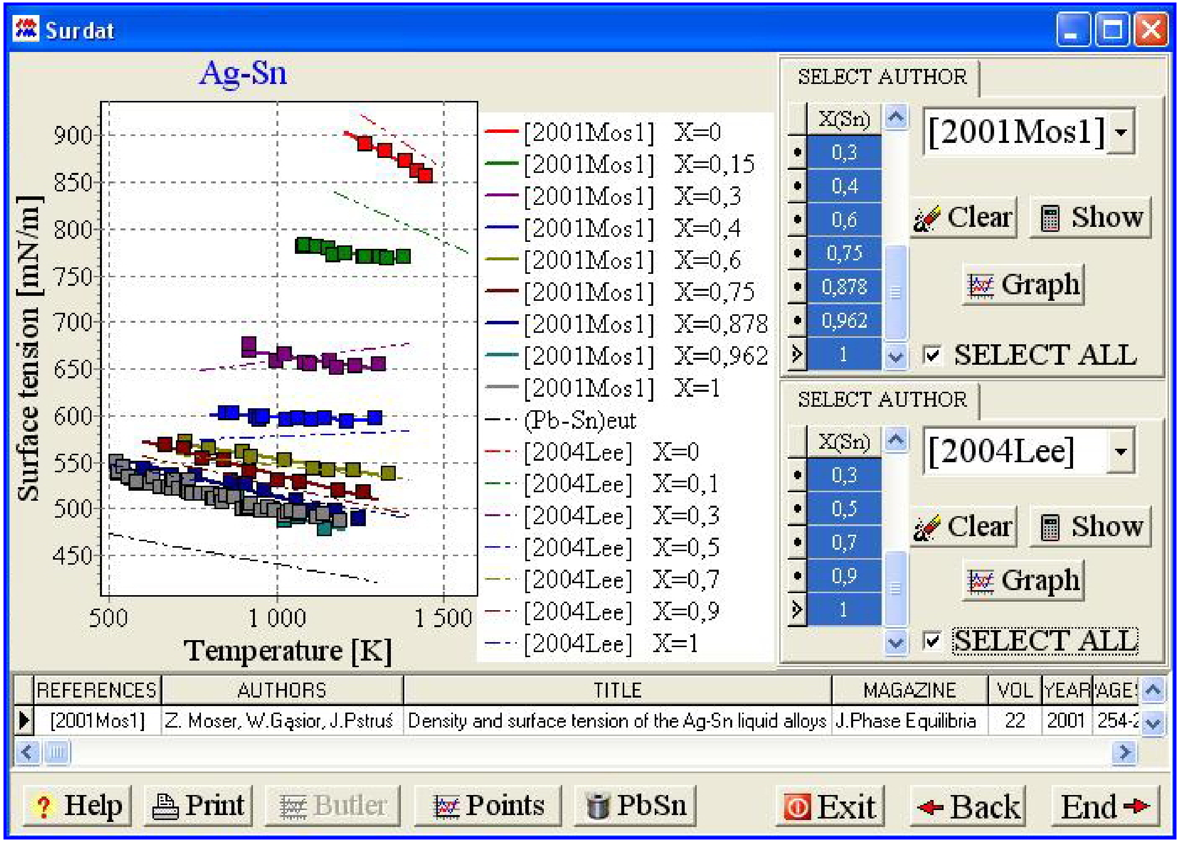
Surface tension Ag-Sn [mN/m]

X(Sn)	ST(T1)
0	890,86
0,15	771,9
0,3	650,8
0,4	595,18

X(Sn)	ST(T2)

REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAR	PAGES
[2001Mos1]	Z. Moser, W.Gąsior, J.Pstruś	Density and surface tension of the Ag-Sn liqui	J.Phase Equilibria	22	2001	254-258

Fig. 9.18. The isotherms of Ag-Sn calculated from the Butler model and the experimental data (symbols) at 1273 K



REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAR	AGE
[2001Mos1]	Z. Moser, W.Gąsior, J.Pstruś	Density and surface tension of the Ag-Sn liquid alloys	J.Phase Equilibria	22	2001	254-2

Fig. 9.19. The temperature dependence of the surface tension of Sn-Ag liquid alloys, together with the references for two authors and $(Sn\text{-}Pb)_{eut}$

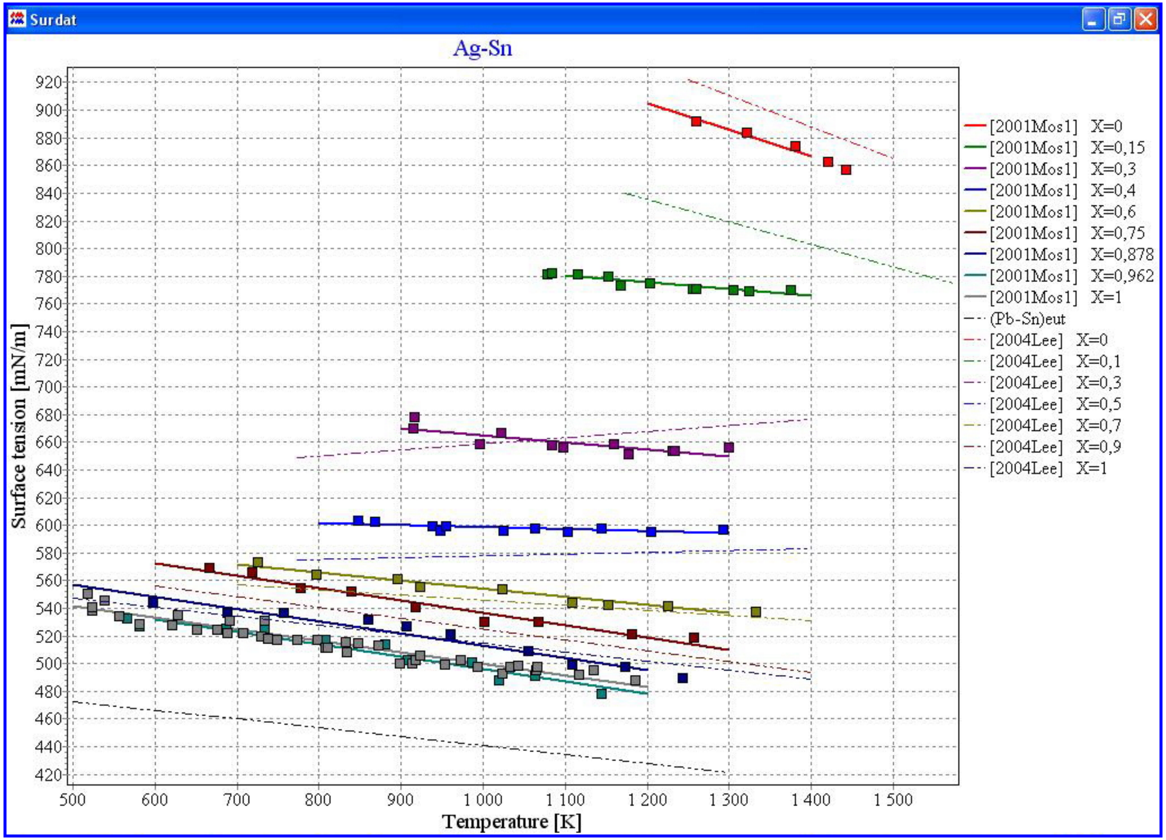
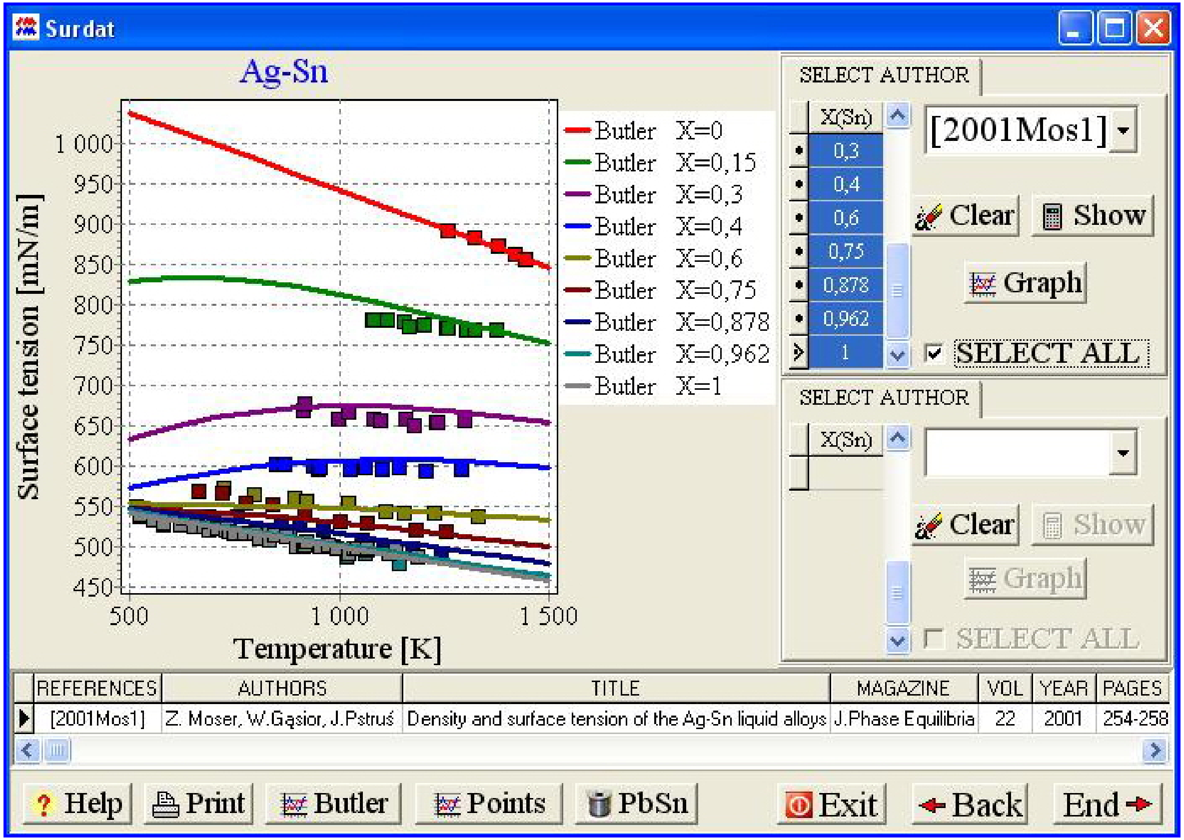
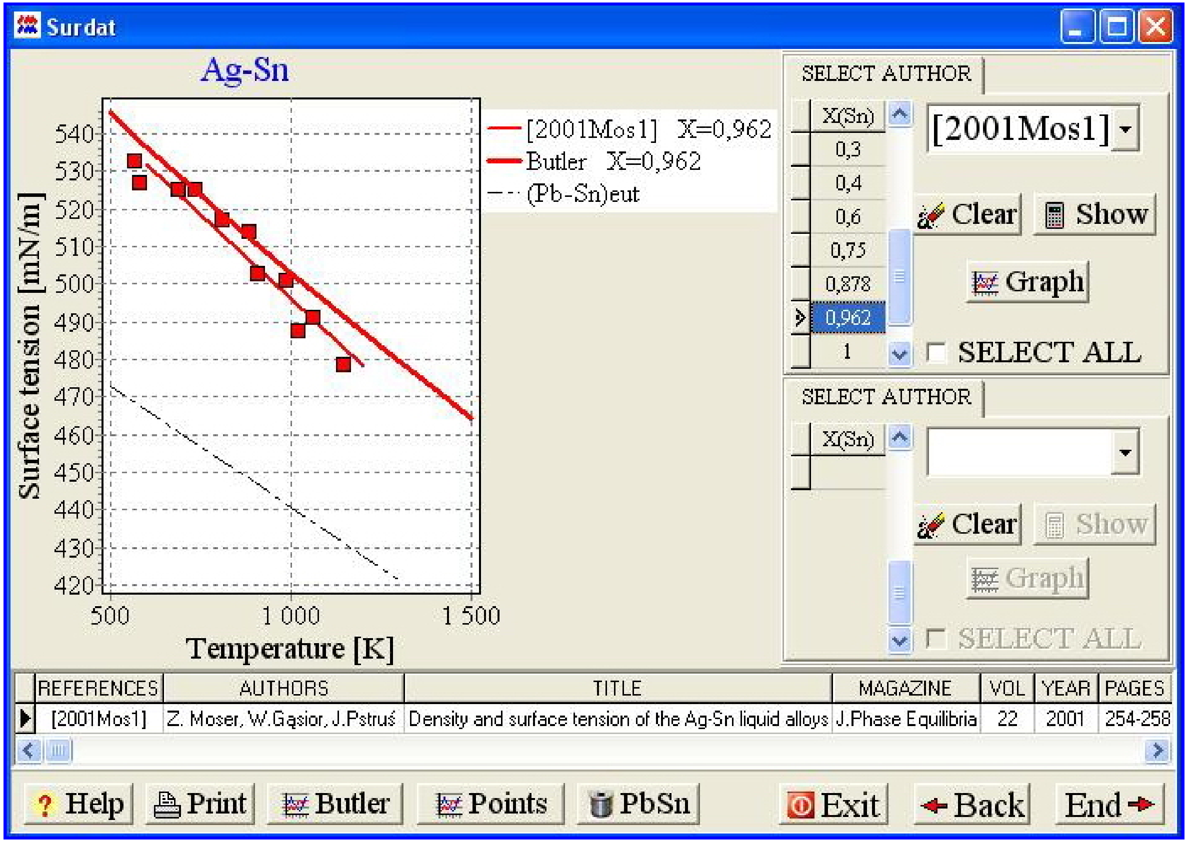


Fig. 9.20. The temperature dependence of the surface tension of Sn-Ag liquid alloys, together with the results of the two authors and for $(Sn\text{-}Pb)_{eut}$



REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAR	PAGES
[2001Mos1]	Z. Moser, W.Gąsior, J.Pstruś	Density and surface tension of the Ag-Sn liquid alloys	J.Phase Equilibria	22	2001	254-258

Fig. 9.21. The temperature dependence of the surface tension of Ag-Sn calculated from the Butler model and the experimental data (symbols)



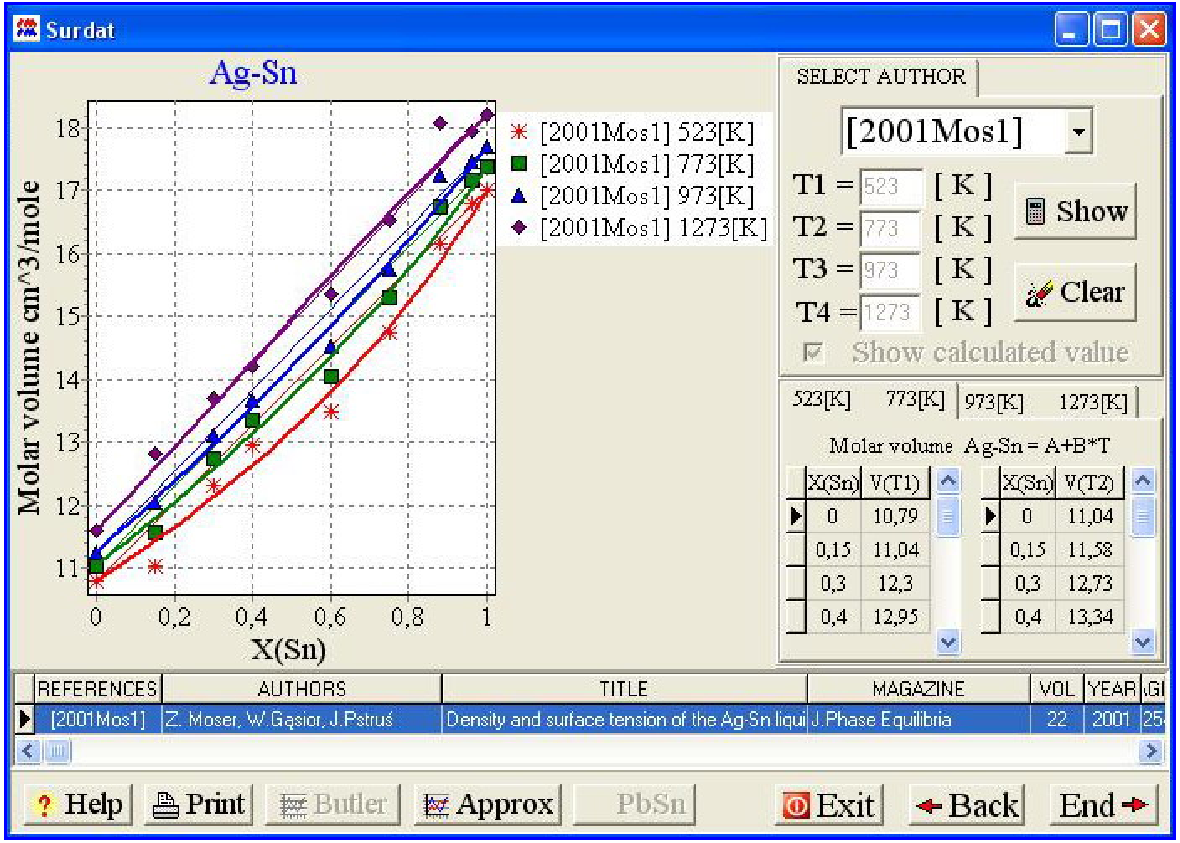
REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAR	PAGES
[2001Mos1]	Z. Moser, W.Gąsior, J.Pstruś	Density and surface tension of the Ag-Sn liquid alloys	J.Phase Equilibria	22	2001	254-258

Fig. 9.22. The temperature dependence of the surface tension of $(Ag\text{-}Sn)_{eut}$ calculated from the Butler model and the experimental data (symbols) for $(Pb\text{-}Sn)_{eut}$ (dashed line)

Besides the surface tension and density, the SURDAT database gives a possibility to determine and see the relations of the molar volume of the solutions as the function of concentration, by choosing the „Molar volume” and „Isotherms” options in the property selection window (Fig. 9.3). There is a possibility of calculation and graphical representation of as many as four isotherms (Fig. 9.23).

For the ternary Ag-Cu-Sn system, the surface tension calculated from the Butler model as the function of concentration for two chosen temperatures and compared with the results by a chosen author (Fig. 9.24) (data calculated from the worked out linear equations).

Fig 9.25 shows the temperature dependences of the surface tension for two chosen Cu concentrations, calculated form the Butler relation, and compared with the experimental points from a chosen author.



SELECT AUTHOR

[2001Mos1]

T1 = 523 [K]
T2 = 773 [K]
T3 = 973 [K]
T4 = 1273 [K]

☑ Show calculated value

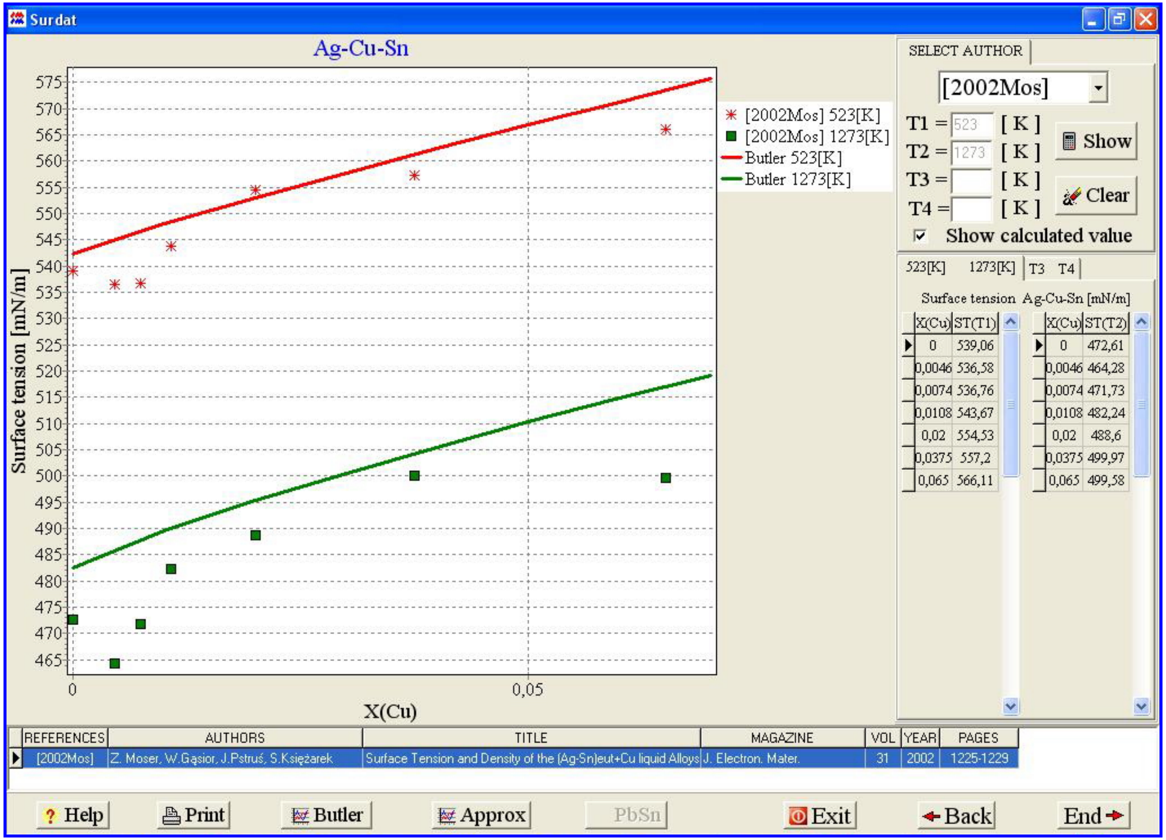
Molar volume Ag-Sn = A+B*T

X(Sn)	V(T1)
0	10,79
0,15	11,04
0,3	12,3
0,4	12,95

X(Sn)	V(T2)
0	11,04
0,15	11,58
0,3	12,73
0,4	13,34

REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAR	GI
[2001Mos1]	Z. Moser, W.Gąsior, J.Pstruś	Density and surface tension of the Ag-Sn liqui	J.Phase Equilibria	22	2001	25

Fig. 9.23. The isotherms of the molar volume of Sn-Ag, calculated at 4 temperatures (523 K, 773 K, 973 K and 1273 K) compared with the experimental data



SELECT AUTHOR: [2002Mos]

T1 = 523 [K]
T2 = 1273 [K]
T3 = [K]
T4 = [K]
☑ Show calculated value

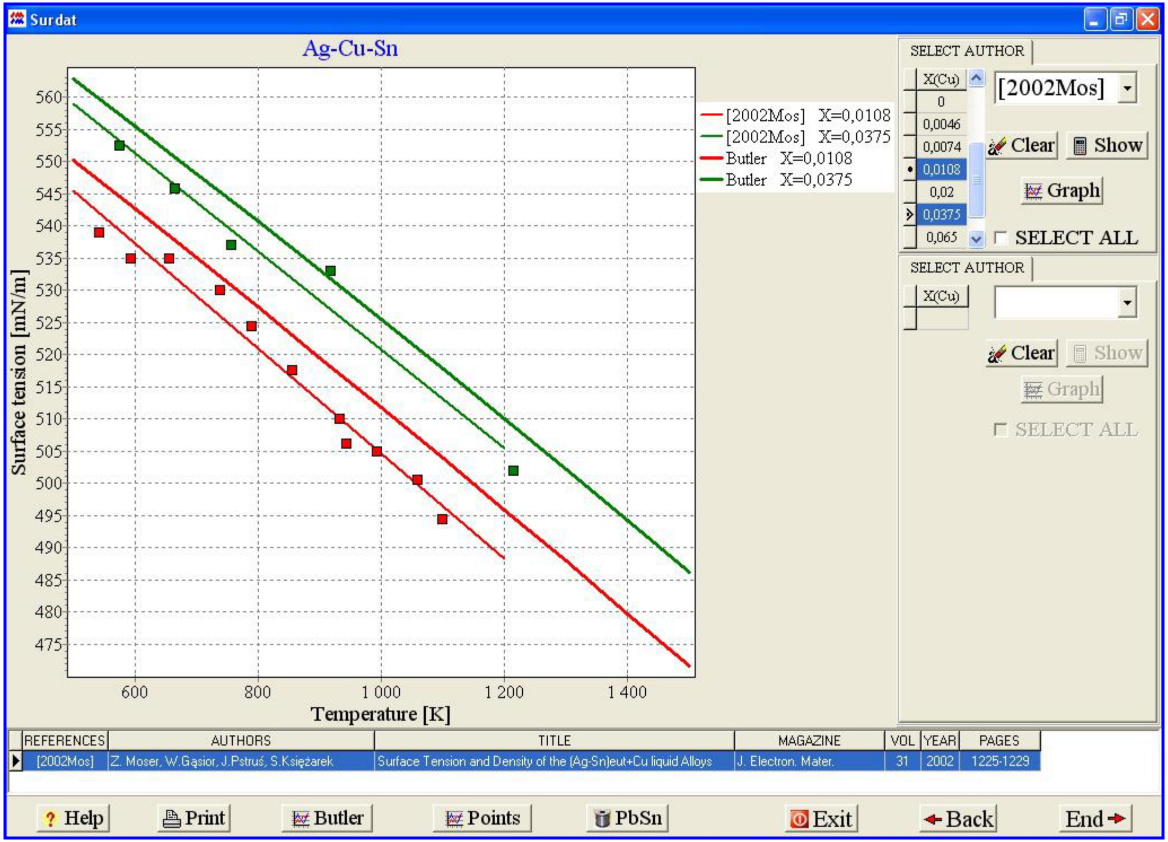
Surface tension Ag-Cu-Sn [mN/m]

X(Cu)	ST(T1)
0	539,06
0,0046	536,58
0,0074	536,76
0,0108	543,67
0,02	554,53
0,0375	557,2
0,065	566,11

X(Cu)	ST(T2)
0	472,61
0,0046	464,28
0,0074	471,73
0,0108	482,24
0,02	488,6
0,0375	499,97
0,065	499,58

REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAR	PAGES
[2002Mos]	Z. Moser, W.Gąsior, J.Pstruś, S.Księżarek	Surface Tension and Density of the (Ag-Sn)eut+Cu liquid Alloys	J. Electron. Mater.	31	2002	1225-1229

Fig. 9.24. The isotherms of Ag-Cu-Sn calculated from the Butler model and the experimental data (symbols) at 523 K and 1273 K



REFERENCES	AUTHORS	TITLE	MAGAZINE	VOL	YEAR	PAGES
[2002Mos]	Z. Moser, W.Gąsior, J.Pstruś, S.Księżarek	Surface Tension and Density of the (Ag-Sn)eut+Cu liquid Alloys	J. Electron. Mater.	31	2002	1225-1229

Fig. 9.25. The temperature dependence of the surface tension of Ag-Cu-Sn calculated from the Butler model and the experimental data (symbols)

The SURDAT database makes available brief characterizations of the experimental methods. If you select „Experimental methods” from the „File” menu, you will find descriptions of four experimental methods (Fig. 9.26):

1. Maximum bubble pressure method,
2. Dilatometric method,
3. Meniscographic method,
4. Sessile drop method.

For example, in the „Maximum bubble pressure method” option, the programme will display the window shown in Fig. 9.27.

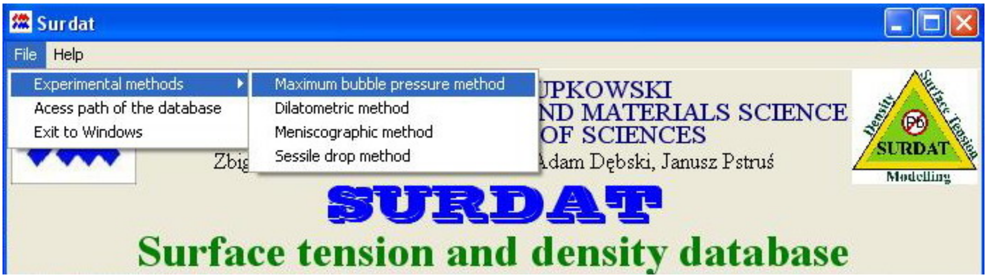
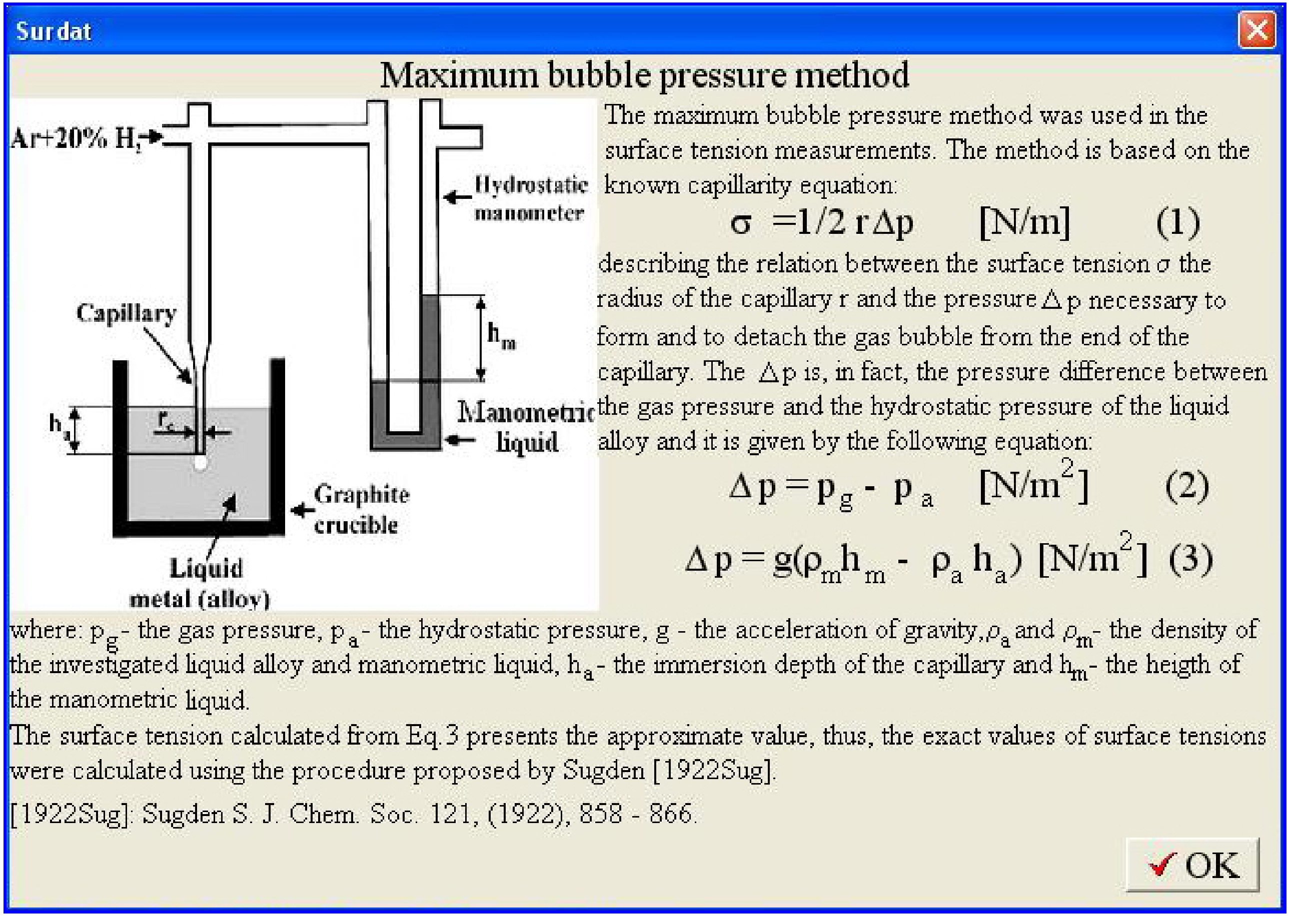


Fig. 9.26. The menu in SURDAT



Maximum bubble pressure method

The maximum bubble pressure method was used in the surface tension measurements. The method is based on the known capillarity equation:

$$\sigma = 1/2\, r \Delta p \quad [N/m] \qquad (1)$$

describing the relation between the surface tension σ the radius of the capillary r and the pressure Δp necessary to form and to detach the gas bubble from the end of the capillary. The Δp is, in fact, the pressure difference between the gas pressure and the hydrostatic pressure of the liquid alloy and it is given by the following equation:

$$\Delta p = p_g - p_a \quad [N/m^2] \qquad (2)$$

$$\Delta p = g(\rho_m h_m - \rho_a h_a) \quad [N/m^2] \qquad (3)$$

where: p_g - the gas pressure, p_a - the hydrostatic pressure, g - the acceleration of gravity, ρ_a and ρ_m - the density of the investigated liquid alloy and manometric liquid, h_a - the immersion depth of the capillary and h_m - the heigth of the manometric liquid.

The surface tension calculated from Eq.3 presents the approximate value, thus, the exact values of surface tensions were calculated using the procedure proposed by Sugden [1922Sug].

[1922Sug]: Sugden S. J. Chem. Soc. 121, (1922), 858 - 866.

Fig. 9.27. The description of the experimental methods in SURDAT. „Maximum bubble pressure method"

10. References

Note: The references in blue are directly used in the SURDAT database.

[2006Gas] Gąsior W., *Modeling of the Thermodynamic Properties from the Surface Tension Measurements* (in Polish), Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Kraków 2006.

[2006Mos1] Moser Z., Gąsior W., Bukat K., Pstruś J., Kisiel R., Ohnuma I., Ishida K., *Pb – free Solders: Part I. Wettability Testing of Sn-Ag-Cu Alloys with Bi Additions,* J. Phase Equilib. Diffus., **27**, (2006), 133-139.

[2006Mos2] Moser Z., Gąsior W., Pstruś J., Ohnuma I., Ishida K., *Influence of Sb additions on surface tension and density. Experiment vs. Modeling.* Z. Metallkd., **97**, (2006), 365-370.

[2006Mos3] Moser Z., Gąsior W., Pstruś J., *Influence of In additions on surface tension and density of In-Sn, Sn-Ag-In and Sn-Ag-Cu-In liquid solders. Experiment vs. modeling*, COST Action 531, Lead – free Solder Materials, Mid-Term Meeting, February 23 & 24, (2006), 29.

[2006Ohn] Ohnuma I., Ishida K., Moser Z., Gąsior W., Bukat K., Pstruś J., Kisiel R., Sitek J., Pb – *free solders. Application of ADAMIS data base in modeling of Sn – Ag – Cu alloys with Bi additions. Part II.* J. Phase Equilib. Diffus. **27**, (2006), 245-254

[2005Kis] Kisiel R., Gąsior W., Moser Z., Pstruś J., Bukat K., Sitek J., *Electrical and Mechanical Studies of the Sn-Ag-Cu-Bi and Sn-Ag-Cu-Bi-Sb Lead Free Soldering Materials*, Archs. Metall. and Mater., **50**, (2005), 1065-1071.

[2005Lop] Lopez E.P., Vianco P.T., and Rejent J.A., *Solderability testing of Sn-Ag-XCu Pb-Free Solders on Copper and Au-Ni Plated Kovar Substrates*, J. Electron. Mater., **34**, (2005), 299-310.

[2005Mos1] Moser Z., Gąsior W., Ishida K., Ohnuma I., Liu X.J., Bukat K. et al, *Experimental Wettability Studies Combined With the Related Properties from Data Base for Tin Based Alloys With Silver, Copper, Bismuth and Antimony Additions.* TMS, 134th Annual Meeting & Exhibition, Book of Final Program, San Francisco, USA, February 13 - 17, 2005.

[2005Mos2] Moser Z., Gąsior W., Pstruś J., *Influence of Sb additions on surface tension and density of Sn-Sb, Sn-Ag-Sb and Sn-Ag-Cu-Sb alloys. Experiment vs. modeling,* Calphad XXXIV May 22-27, 2005 Maastricht, The Netherlands, Programme and Abstracts, 64.

[2004Gas1] Gąsior W., Moser Z., Pstruś J., Bukat K., Kisiel R., Sitek J., *(Sn-Ag)$_{eut}$ + Cu Soldering Materials, Part 1: Wettability Studies,* J. Phase Equilib. Diffus., **24** (2004), 115-121.

[2004Gas2] Gąsior W., Moser Z., Pstruś J., Ishida K., Ohnuma I., *Surface Tension and Density Measurements of Sn-Ag-Sb Liquid Alloys and Phase Diagram Calculations of the Sn-Ag-Sb Ternary System*, Mater. Trans., **45**, (2004), 652-660.

[2004Gas3] Gąsior W., Moser Z., Pstruś J., *SnAgCu+Sb Measurements of the Surface Tension and Density of Tin Based Sn-Ag-Cu-Sb Liquid Alloys,* Archs. Metall. and Mater., **49**, (2004), 155-167.

[2004Kis] Kisiel R., Gąsior W., Moser Z., Pstruś J., Bukat K., Sitek J., *(Sn-Ag)$_{eut}$ + Cu Soldering Materials, Part II: Electrical and Mechanical Studies*, J. Phase Equilib. Diffus., **24** (2004), 122-124.

[2004Lee] Lee J., Shimoda W., and Tanaka T., *Surface Tension and its Temperature Coefficient of Liquid Sn-X (X=Ag, Cu) Alloys*, Mater. Trans., **45**, (2004), 2864-2870.

[2004Mos] Moser Z., Gąsior W., Pstruś J., Ishida K., Ohnuma I., Bukat K., Sitek J., Kisiel R., *Experimental Wettability Studies Combined with the Related Properties from Data Base for Lead – free Soldering Materials,* CALPHAD XXXIII, May 30 - June 4, 2004, Kraków, Poland, Program of Abstracts, , 81.

[2004Pst] Pstruś J, Moser Z., Gąsior W., *Surface Tension and Density Measurements of Liquid Zn-Sn and Zn-In Alloys*, TOFA 2004, Discussion Meeting on thermodynamics of Alloys, Book of Abstracts, Program, Vienna, Austria, September 12-17.

[2003Gas1] Gąsior W., Moser Z., Pstruś J., Krzyżak B., Fitzner K., *Surface Tension and Thermodynamic Properties of the Liquid Ag-Bi Solutions*, J. Phase Equilib., **24**, (2003), 40-49.

[2003Gas2] Gąsior W., Moser Z., Pstruś J., *Density and Surface Tension of Sb-Sn Liquid Alloys. Experiment vs. Modeling*, J. Phase Equilib., **24**, (2003), 504-510.

[2002Liu] Liu X.J., Inohana Y., Ohnuma I., Kainuma R., Ishida K., Moser Z., Gąsior W., Pstruś J., *Experimental Determination and Thermodynamic Calculation of the Phase Equilibria and Surface tension of the Ag-Sn-In System*, J. Electron. Mater., **31**, (2002), 1139-1151.

[2002Mos] Moser Z., Gąsior W., Pstruś J., Księżarek S., *Surface Tension and Density of the (Ag-Sn)$_{eut}$+Cu liquid Alloys*, J. Electron. Mater., **31**, (2002), 1225-1229.

[2001Gas1] Gąsior W., Moser Z., Pstruś J., Kucharski M., *Viscosity of the Pb-Sn Liquid Alloys*, Arch. of Metall., **46 (1),** (2001), 23-32.

[2001Gas2] Gąsior W., Moser Z., Pstruś J., *Surface Tension and Density of the Pb-Sn Liquid Alloys*, J.Phase Equilib., **22**, (2001), 20-25.

[2001Mos1] Moser Z., Gąsior W., Pstruś J., *Density and surface tension of the Ag-Sn liquid alloys*, J. Phase Equilib., **22**, (2001), 254-258.

[2001Mos2] Moser Z., Gąsior W., Pstruś J., Zakulski W., Ohnuma I., Liu X.J., Inohana Y., Ishida K., *Density and surface tension of the Ag-In liquid alloys*, J. Electron. Mater., **30**, (2001), 1120-1128.

[2001Mos3] Moser Z., Gąsior W., Pstruś J., *Surface tension measurements of the Sn-Bi and Sn-Bi-Ag liquid alloys*, J. Electron. Mater., **30**, (2001), 1104-1111.

[2000Moo] Moon K.-W., Boettinger W.J., Kattner U.R., Biancaniello F.S. and Hadwerker C.A., *Experimental and Thermodynamic Assessment of Sn-Ag-Cu Solder Alloys,* J. Electron. Mater., **29**, (2000), 1122-1136.

[1999Mos] Moser Z., Fitzner K., *The use experimental thermodynamic data in the phase equilibria verification*, Termochim. Acta, **332**, (1999), 1-19.

[1998Lee] Lee H. M. Yoon S. W. and Lee B – J: *Thermodynamic Prediction of Interface at Cu/Solder Joints*, J. Electron. Mater., **27**, (1998), 1161-1166.

[1997Miy] Miyazaki M., Mitutani M., Takemoto T & Matsunawa A., *Conditions for Measurement of Surface Tension of Solders with a Wetting Balance Tester*, Trans. of JWRI, **26(1)**, (1997) 81-84.

[1996Tan] Tanaka T., Hack K., Iida T., Hara S., *Applications of Thermodynamic Database to the Evaluation of Surface Tension of Molten Alloys, Salt Mixtures and Oxide Mixtures*, Z. Metallkde., **87**, (1996), 380-389.

[1993Vin] Vincent J.H., Richards B.P., *Part2: UK Progress and Preliminary Trials*, Circuit World, **19**, (1993), 32-38.

[1990Pas] Passerone A.P., Ricci F., Sangorgi R., *Influence of oxygen contamination on the surface tension of liquid tin*, J.Mater.Sci., **25**, (1990), 4266-4272.

[1989Nog] Nogi K., Oshino K., Ogino K., *Wettability of Solid Oxides by Liquid Pure Metals,* Mater. Trans. JIM, **30**, (1989), 137-145.

[1988Dar] Ownby, P.D. and Liu, J., *Surface Energy of Liquid Copper and Its Wetting Behavior on Sapphire Substrates*, J. Adhes Sci. Tech., **2 (4)**, (1988), 255-269.

[1988Iid] Iida T. and Guthrie R.I.L., *The Physical Properties of Liquid Metals*, Clarendon Press, Oxford, (1988).

[1986Mos] Moser Z., Gąsior W., Sommer F., Schwitzgebel G., Predel B., *Calorimetric and Emf Studies on Liquid Li-Sn Alloys*, Metall.Trans., **17 B**, (1986), 791-796.

[1985Som] Somol V., Berenek M., *Surface Tension Measurements of Liquid Pb- Sn Alloys (in Czech)*, Hutn.Listy, **4**, (1985), 278-280.

[1984Pam] Pamies A., Garcia-Cordovilla C., Louis E., *Measurements of Surface Tension of Liquid Aluminium by Means of the Maximum Bubble Pressure Method : the Effect of Surface Oxidation*, Scr. Metall., **18**, (1984), 869-872.

[1984Som] V. Somol, M. Beranek, Sb.Vysk.Sk.Chem.-Technol.Praze Anorg.Chem. Technol., **B30**, (1984), 199-205.

[1983Bra] Brandes E.A., Smithells Metals Reference Book, Sixth Edition (Editor E.A. Brandes BSc, ARCS, CEng, FIM In association with Fulmer Research Institute Ltd), (1983).

[1982Sen] Sengiorgi R., Muolo M.L., Passerone A., *Surface Tension and Adsorption in Liquid Silver – Oxygen Alloys*, Acta Metall., **30**, (1982), 1597-1604.

[1979Lep] Lepinskikh B.M., Doc. VINITI, USSR, **4/5**, (1979), 1813-1879.

[1979Zad] Zadumkin S.N., Ibrachimov Ch.I. and Ozniew D.T., *Surface tension and density measurements overcooled Sn, In, Bi, and Pb (in Russian)*, Izv.VUZ, Cvet. Metall., **22**, (1979), 82-85.

[1977Bru] Brunet M., Joud J.C., Eustathopoulos N., Desre P., *Surface Tension of Germanium and Silver – Germanium Alloys in the Liquid State*, J. Less Common Met., **51**, (1977), 69-77.

[1977Kuc] Kucharski M., *Density and Surface Tension of Sn-Cd Alloys*, Arch. Hut., **22**, (1977), 181-194.

[1977Lan] Lang G., Laty P., Joud J.C. and Desre P., *Measurement of the surface tension of some fluid metals with different methods (in German)*, Z. Metallkd., **68**, (1977), 113-115.

[1977Par] Paramonov V.A., Karamyshev E.P., Ukhov V.F., *Colloq. on physics and chemistry of surface melts*, In Fiz. khim. poverkh. rasp, Tbilisi, Metsniyerba, (1977), 155.

[1976Kas] Kasama A., Iida T., Morita Z., *Temperature Dependence of Surface Tension of Liquid Pure Metals*, J. Japan Inst. Metals, **40**, (1976), 1030-1038.

[1975Abd] Abdel-Azis A.K., Kirshak H.R., *Surface Tension of Molten Tin and an Estimate of its Critical Temperature*, Z. Metallkde., **66**, (1975), 183-184.

[1974Lan] Lang G., *The Influence of Alloying Elements to The Surface Tension of Liquid Super Purity Aluminum*, Aluminium, **50**, (1974), 731-734.

[1972Ada] Adachi A., Morita Z., Kita Y., Kasama A., *Surface Tension of Liquid Lead – Tin Alloys Measured by the Maximum Bubble – Pressure Method*, Technol.Rep.Osaka Univ., **22**, (1972), 1027-1052.

[1972Yat] Yatsenko S.P., Kononenko W.I., Schukman A.L., *Experimental studies of the temperature dependence of the surface tension and density of tin, indium, aluminium and gallium*, Teplofiz. Vys. Temp., **10**, (1972), 55-66.

[1971Ber] Bernard G., Lupis C.H.P., *The Surface Tension of Liquid Silver Alloys: Part I. Silver – Gold Alloys*, Metall. Trans., **2**, (1971), 555-559.

[1971Lan] Lang G., *The Surface Tension of Mercury and Liquid Lead, Tin, and Bismuth*, J.Inst.Metals., **104**, (1971), 300-308.

[1971Whi] White D.W.G., *The Surface Tension of Pb, Sn, and Pb – Sn Alloys*, Metall.Trans., **2**, (1971), 3067-3071.

[1970Rhe] Rhee S.K., *Wetting of A1N and TiC by Liquid Ag and Liquid Cu*, J. Am. Ceram. Soc., **53**, (1970), 639-641.

[1968Thr] Thresh H.R., Crawley A.F., White D.W.G., *The Densities of Liquid Tin, and Tin – Lead Alloys*, Trans. TMS-AIME, **242**, (1968), 819-822.

[1964Lau] Lauerman I., Sauerwald F., *Measurements of the surface tension of melted metals X. Surface tension measurements of molten metals copper, silver, antimony, copper-tin, copper-antimony and silver-antimony (in German)*, Z. Metallkd., **55 (10)**, (1964), 605-612.

[1964Laz] Lazarev V.B., *Experimental Studies of the Surface Tension of Liquid In-Sb Alloys*, Russ.J.Phys. Chem., **38**, (1964), 325-330.

[1961Lau] Lauerman I., Metzger G., Sauerwald F., *Surface tensions of molten silver, tin and silver-tin alloys(in German)*, Z. für Phys. Chem., **216**, (1961), 42-49.

[1959Pok] Pokrowski N.L., *Investigations of the surface – active films of the liquid metallic surface (in Russian)*, P.S.Dok.Akad.Nauk SSSR, **128**, (1959), 1228-1231.

[1957Hoa] Hoar T.P., Melford D.A., *The Surface Tension of Binary Liquid Mixtures: Lead + Tin and Lead + Ind Alloys,* Trans. Faraday Soc., **53**, (1957), 315-326.

[1956Mel] Melford D.A., Hoar T.P., *Determination of the Surface Tension of Molten Lead, Tin, and Indium by an Improved Capillary Method*, J. Inst. of Metals, **85**, (1956), 197-205.

[1956Tay] Taylor J.W., *The Surface Tension of Liquid – Metal Solutions,* Acta Metall., **4**, (1956), 460-468.

[1953Kin] Kingery W.D., Humenik M., *Surface Tension at Elevated Temperatures. I. Furnace and Method for use of the Sessile Drop Method; Surface Tension of Silicon, Iron and Nickel*, J. Phys. Chem., **57**, (1953), 359-363.

[1949Pel] Pelzer E., Berg – und Hüttenmännische. Monatshefte, *Surface tensions of liquid metals and alloys II (in German)*, **94**, (1949), 10-17.

[1945Gug] Guggenheim E.A., *Statistical Thermodynamics of the Surface of Regular Solutions*, Trans. Faraday Soc., **41**, (1945), 150-156.

[1934Bir] Bircumshaw L.L., Phil. Mag, **17**, (1934), 181-192.

[1932But] Butler J.A. V., *The Thermodynamics of the Surfaces of Solutions*, Proceedings of the Royal Society of London series A, **CXXXV**, (1932) 348-375.

[1929Kra] Krause W., Sauerwald F., Micalke M., *Density measurements at high temperature. About the density of liquid gold and liquid gold-copper and silver- copper alloys (in German)*, **181**, Z. Anorg. Chem., (1929), 347-352.

[1928Lib] Libman E.E., Bull. Ill. Univ. Eng. Exp. Sta., **187**, (1928),

[1927Dra] Drath G. and Sauerwald F., *Surface tensions of molten metals and alloys II (in German)*, Z. anorg. u. allg. Chem., **162**, (1927), 301-320.

[1922Sug] Sugden, S. *Determination of surface tension from the maximum pressure in bubbles*, J. Am. Chem. Soc., **121**, (1922), 858-866.

[1921Hog] Hognes T.R., *The Surface Tension and Density of Liquid Mercury, Cadmium, Zinc, Lead, Tin and Bismuth*, J. Am. Chem. Soc., **43**, (1921), 1621-1628.

[1869Dup]: Dupré A.,*Theorie Mechanique de la Chaleur*, Paris, (1869), 207.

[1805You]: Young T., Phil.Trans.Roy.Soc. London 95, (1805), 65; reprinted with additions in Works of Dr. Young (Peacock, ed.) London, **1**, (1855), 418.

11. Annex 1

The Annex compiles the temperature-concentration relations of the surface tension calculated by the Butler method with the standard deviations, for all the examined binary systems. There is a possibility to calculate the surface tension by means of the Butler method for other systems, unavailable in the SURDAT database. In order to receive further information, please contact the authors of this paper.

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The calculated by the Butler relation (Eq. 10), in the extensive temperature range and in the entire range of concentrations, the surface tension σ_{AB} of the binary alloys was worked out using the following equation:

$$\begin{aligned}\boldsymbol{\sigma}_{\mathbf{AB}} &= \boldsymbol{\sigma}_{\mathbf{A}}\mathbf{X}_{\mathbf{A}} + \boldsymbol{\sigma}_{\mathbf{B}}\mathbf{X}_{\mathbf{B}} + \Delta\boldsymbol{\sigma}_{\mathbf{AB}} = \\ &\boldsymbol{\sigma}_{\mathbf{A}}\mathbf{X}_{\mathbf{A}} + \boldsymbol{\sigma}_{\mathbf{B}}\mathbf{X}_{\mathbf{B}} + \mathbf{X}_{\mathbf{A}}\mathbf{X}_{\mathbf{B}}\sum_{\mathbf{i=0}}^{\mathbf{n}}(\mathbf{a}_{\mathbf{i}} + \mathbf{b}_{\mathbf{i}}\mathbf{T} + \mathbf{c}_{\mathbf{i}}\mathbf{T}^{2})(\mathbf{X}_{\mathbf{A}} - \mathbf{X}_{\mathbf{B}})^{\mathbf{i}}\end{aligned} \tag{1A}$$

$\mathbf{X_A}$, $\mathbf{X_B}$, $\boldsymbol{\sigma_A}$ and $\boldsymbol{\sigma_B}$ are the concentrations and the surface tensions of components A and B, and $\mathbf{a_i}$, $\mathbf{b_i}$, and $\mathbf{c_i}$, are the parameters of the presented function describing the deviations of the calculated surface tension σ_{AB} from the linear changes $(\boldsymbol{\sigma_A}\mathbf{X_A}+\boldsymbol{\sigma_B}\mathbf{X_B})$.

In the calculations of the surface tension of binaries and in Ag-Cu-Sn system were used own data of surface tension of pure components from the following equations and References:

$\sigma_{Ag} = 1133.9541 - 0.1904719 \cdot T$ [2001Mos2] (2A)

$\sigma_{Bi} = 405 - 0.0492 \cdot T$ [2001Mos3] (3A)

$\sigma_{Cu} = 1475.6 - 0.1422 \cdot T$ [2005Mos2] (4A)

$\sigma_{In} = 593.8 - 0.09421 \cdot T$ [2001Mos2] (5A)

$\sigma_{Pb} = 497.5 - 0.1096 \cdot T$ [2001Gas2] (6A)

$\sigma_{Sb} = 419 - 0.0561 \cdot T$ [2004Gas2] (7A)

$\sigma_{Sn} = 582.826 - 0.083361 \cdot T$ [2001Gas2] (8A)

$\sigma_{Zn} = 892.5 - 0.1246 \cdot T$ [2004Pst] (9A)

The equations for the binary systems available in **SURDAT** are presented below.

Pb-Sn

$$\begin{aligned}
\sigma = {} & \sigma_{Pb} \cdot X_{Pb} + \sigma_{Sn} \cdot X_{Sn} + \\
& X_{Pb} \cdot X_{Sn} \cdot [(-190 + 0.13912 \cdot T - 0.0000471 \cdot T^2) + \\
& (-249.947 + 0.264891 \cdot T - 0.0000706023 \cdot T^2) \cdot (X_{Sn} - X_{Pb}) + \\
& (-303.3 + 0.59411 \cdot T - 0.0002891 \cdot T^2) \cdot (X_{Sn} - X_{Pb})^2 + \\
& (-183.5 + 0.49614 \cdot T - 0.0002890 \cdot T^2) \cdot (X_{Sn} - X_{Pb})^3] \qquad (10A)
\end{aligned}$$

Standard deviation = 0.4 mN/m

T = 573 K - 1273 K

Ag-Sn

$$\sigma = \sigma_{Ag}\bullet X_{Ag}+\sigma_{Sn}\bullet X_{Sn}+$$
$$X_{Ag}\bullet X_{Sn}\bullet[(-1350.7+0.93116\bullet T-0.0001902\bullet T^2) +$$
$$(1300.7-1.39459\bullet T+0.0004202\bullet T^2)\bullet(X_{Sn}-X_{Ag}) +$$
$$(-1063.5+1.91129\bullet T-0.0006179\bullet T^2)\bullet(X_{Sn}-X_{Ag})^2+$$
$$(1020 -1.6385\bullet T+0.0002337\bullet T^2)\bullet(X_{Sn}-X_{Ag})^3+$$
$$(1286.8+0.41782\bullet T-0.0011270\bullet T^2)\bullet(X_{Sn}-X_{Ag})^4+$$
$$(-3289.7-1.96031\bullet T+0.0039233\bullet T^2)\bullet(X_{Sn}-X_{Ag})^5+$$
$$(1252.7-1.1378\bullet T+0.0000723\bullet T^2)\bullet(X_{Sn}-X_{Ag})^6+$$
$$(-620.1+10.388\bullet T-0.0076522\bullet T^2)\bullet(X_{Sn}-X_{Ag})^7+$$
$$(996.9-7.41334\bullet T+0.0049454\bullet T^2)\bullet(X_{Sn}-X_{Ag})^8] \tag{11A}$$

Standard deviation = 1.4 mN/m

T = 523 K - 1473 K

Ag-In

$$\sigma = \sigma_{Ag}\bullet X_{Ag}+\sigma_{In}\bullet X_{In}+$$
$$X_{Ag}\bullet X_{In}\bullet[(-1183.8 + 0.93781\bullet T - 0.0002364\bullet T^2) +$$
$$(542.1 - 0.84518\bullet T + 0.0002442\bullet T^2)\bullet(X_{In}-X_{Ag}) +$$
$$(1175. - 0.60466\bullet T + 0.000199\bullet T^2)\bullet (X_{In}-X_{Ag})^2 +$$
$$(-1263.7+ 0.27965\bullet T + 0.0005825T^2)\bullet (X_{In}-X_{Ag})^3 +$$
$$(-301.6+ 0.20752\bullet T - 0.0007608\bullet T^2)\bullet (X_{In}-X_{Ag})^4 +$$
$$(1081+ 1.08580\bullet T - 0.0014129\bullet T^2)\bullet (X_{In}-X_{Ag})^5 +$$
$$(-976+ 0.00892\bullet T + 0.0010596\bullet T^2)\bullet (X_{In}-X_{Ag})^6] \tag{12A}$$

Standard deviation = 1.2 mN/m

T = 523 K - 1473 K

Bi – Sn

$$\begin{aligned}
&\sigma = \sigma_{Bi}\bullet X_{Bi}\bullet{+}\sigma_{Sn}\bullet X_{Sn}+\\
&X_{Bi}\bullet X_{Sn}\bullet[(-305.5+ 0.29948\bullet T - 0.0000947\bullet T^{2}) +\\
&(247.9- 0.29995\bullet T + 0.0001027\bullet T^{2})\bullet(X_{Sn}-X_{Bi}) +\\
&(-412.4 + 0.65851\bullet T - 0.0002686\bullet T^{2})\bullet (X_{Sn}-X_{Bi})^{2} +\\
&(425.5 - 0.73613\bullet T + 0.0003147\bullet T^{2})\bullet (X_{Sn}-X_{Bi})^{3}] \qquad (13A)
\end{aligned}$$

Standard deviation = 0.7 mN/m

T = 523 K - 1373 K

Cu – Sn

$$\begin{aligned}
&\sigma = \sigma_{Cu}\bullet X_{Cu}+\sigma_{Sn}\bullet X_{Sn}+\\
&X_{Cu}\bullet X_{Sn}\bullet[(-2027.9+ 0.80588\bullet T - 0.0001180\bullet T^{2}) +\\
&(1909.6-1.13676\bullet T + 0.0002308 \bullet T^{2}) \bullet (X_{Sn}-X_{Cu}) +\\
&(235.5 + 0.07635\bullet T - 0.00019\bullet T^{2}) \bullet (X_{Sn}-X_{Cu})^{2} +\\
&(107.1+ 0.23187\bullet T - 0.0003515\bullet T^{2}) \bullet (X_{Sn}-X_{Cu})^{3}+\\
&(-13295.8 + 10.6837\bullet T -0.0010440\ T^{2}) \bullet (X_{Sn}-X_{Cu})^{4}+\\
&(4166.4 - 11.0688\bullet T + 0.0051838\bullet T^{2}) \bullet (X_{Sn}-X_{Cu})^{5}+\\
&(34495- 19.2175\bullet T - 0.0024011\bullet T^{2}) \bullet (X_{Sn}-X_{Cu})^{6}+\\
&(-5852.8+ 13.0761\bullet T - 0.0053852\bullet T^{2}) \bullet (X_{Sn}-X_{Cu})^{7}+\\
&(-26551.9+ 10.5779\bullet T + 0.0040823\bullet T^{2}) \bullet (X_{Sn}-X_{Cu})^{8}] \qquad (14A)
\end{aligned}$$

Standard deviation = 1.8 mN/m

T = 523 K - 1473 K

Ag – Bi

$$\begin{aligned}
&\sigma = \sigma_{Ag}\bullet X_{Ag}+\sigma_{Bi}\bullet X_{Bi}+\\
&X_{Ag}\bullet X_{Bi}\bullet[(-1492.9+ 0.76147\bullet T - 0.0001216\bullet T^{2}) +\\
&(1738.4- 1.37566\bullet T + 0.000404\bullet T^{2}) \bullet (X_{Bi}-X_{Ag}) +\\
&(-1904.2+ 2.33459\bullet T - 0.0009596\bullet T^{2}) \bullet(X_{Bi}-X_{Ag})^{2} +\\
&(4419.2- 0.37469\bullet T - 0.0016177\bullet T^{2}) \bullet (X_{Bi}-X_{Ag})^{3} +\\
&(-5139.5- 4.24837\bullet T + 0.0051161\bullet T^{2}) \bullet(X_{Bi}-X_{Ag})^{4} +\\
&(-13848.8+ 4.43033\bullet T + 0.0033977\bullet T^{2}) \bullet (X_{Bi}-X_{Ag})^{5} +\\
&(16423.3+ 4.62766\bullet T - 0.010732\bullet T^{2}) \bullet (X_{Bi}-X_{Ag})^{6} +\\
&(25325.2- 17.8596\bullet T + 0.0009436\bullet T^{2}) \bullet (X_{Bi}-X_{Ag})^{7} +\\
&(-27660.6+ 12.8574\bullet T + 0.0035671\bullet T^{2}) \bullet (X_{Bi}-X_{Ag})^{8}] \qquad (15A)
\end{aligned}$$

Standard deviation = 2.6 mN/m

T = 523 K - 1473 K

Sb – Sn

$$\begin{aligned}
&\sigma = \sigma_{Sb}\bullet X_{Sb}+\sigma_{Sn}\bullet X_{Sn}+\\
&X_{Sb}\bullet X_{Sn}\bullet[(-118.7 + 0.1112\bullet T - 0.0000271\bullet T^{2}) +\\
&(-3 + 0.0291\bullet T - 0.0000175\bullet T^{2}) \bullet (X_{Sn}-X_{Sb}) +\\
&(-254.5 + 0.36484\bullet T - 0.000143\bullet T^{2}) \bullet(X_{Sn}-X_{Sb})^{2} +\\
&(-169.7+ 0.17951\bullet T - 0.0000439\bullet T^{2}) \bullet (X_{Sn}-X_{Sb})^{3}] \qquad (16A)
\end{aligned}$$

Standard deviation = 0.3 mN/m

T = 573 K - 1473 K

In – Sn

$$\begin{aligned}
&\sigma = \sigma_{In}\bullet X_{In}\bullet+\sigma_{Sn}\bullet X_{Sn}+\\
&X_{In}\bullet X_{Sn}\bullet [(1.9 + 0.00461\bullet T) + 3.8\bullet(X_{Sn}-X_{In})] \qquad (17A)
\end{aligned}$$

Standard deviation = 0.05 mN/m

T = 523 K - 1233 K

Sn – Zn

$$\sigma = \sigma_{Sn} \bullet X_{Sn} + \sigma_{Zn} \bullet X_{Zn} +$$

$$X_{Sn} \bullet X_{Zn} \bullet [(-727.8 + 0.59511 \bullet T - 0.0001511 \bullet T^2) +$$

$$(1440.8 - 2.48597 \bullet T + 0.0013053 \bullet T^2) \bullet (X_{Sn} - X_{Zn}) +$$

$$(-2792.2 + 6.49153 \bullet T - 0.0040674 \bullet T^2) \bullet (X_{Sn} - X_{Zn})^2 +$$

$$(-997.1 + 8.52386 \bullet T - 0.0078256 \bullet T^2) \bullet (X_{Sn} - X_{Zn})^3 +$$

$$(5103 - 24.0004 \bullet T + 0.0199273 \bullet T^2) \bullet (X_{Sn} - X_{Zn})^4 +$$

$$(1900.4 - 19.7816 \bullet T + 0.0194024 \bullet T^2) \bullet (X_{Sn} - X_{Zn})^5 +$$

$$(-4746.5 + 37.4526 \bullet T - 0.0354238 \bullet T^2) \bullet (X_{Sn} - X_{Zn})^6 +$$

$$(10193.7 - 6.03384 \bullet T - 0.0051557 \bullet T^2) \bullet (X_{Sn} - X_{Zn})^7 +$$

$$(-11698 + 3.61051 \bullet T + 0.0097675 \bullet T^2) \bullet (X_{Sn} - X_{Zn})^8] \qquad (18A)$$

Standard deviation = 2.1 mN/m

T = 523 K - 973 K

Ag – Sb

$$\sigma = \sigma_{Ag} \bullet X_{Ag} + \sigma_{Sb} \bullet X_{Sb} +$$

$$X_{Ag} \bullet X_{Sb} \bullet [(-1848.7 + 1.19478 \bullet T - 0.0002300 \bullet T^2) +$$

$$(1924.4 - 1.66853 \bullet T + 0.0004027 \bullet T^2) \bullet (X_{Sb} - X_{Ag}) +$$

$$(-1784.5 + 1.981 \bullet T - 0.0004095 \bullet T^2) \bullet (X_{Sb} - X_{Ag})^2 +$$

$$(2285 - 3.2914 \bullet T + 0.000814 \bullet T^2) \bullet (X_{Sb} - X_{Ag})^3 +$$

$$(1868.1 + 2.69826 \bullet T - 0.0025555 \bullet T^2) \bullet (X_{Sb} - X_{Ag})^4 +$$

$$(-5217.6 + 0.2239 \bullet T + 0.002635 \bullet T^2) \bullet (X_{Sb} - X_{Ag})^5 +$$

$$(1279 - 7.36562 \bullet T + 0.0041302 \bullet T^2) \bullet (X_{Sb} - X_{Ag})^6 +$$

$$(53 + 8.35367 \bullet T - 0.0057608 \bullet T^2) \bullet (X_{Sb} - X_{Ag})^7] \qquad (19A)$$

Standard deviation = 0.9 mN/m

T = 873 K - 1473 K

Cu – Sb

$$
\begin{aligned}
\sigma = {} & \sigma_{Cu} \bullet X_{Cu} + \sigma_{Sb} \bullet X_{Sb} + \\
& X_{Cu} \bullet X_{Sb} \bullet [(-2178.9 + 0.60831 \bullet T - 0.0000353 \bullet T^2) + \\
& (1764 - 0.46138 \bullet T - 0.0000289 \bullet T^2) \bullet (X_{Sb} - X_{Cu}) + \\
& (-2712.4 + 0.4.14396 \bullet T - 0.0019924 \bullet T^2) \bullet (X_{Sb} - X_{Cu})^2 + \\
& (8245.5 - 8.31152 \bullet T + 0.0025979 \bullet T^2) \bullet (X_{Sb} - X_{Cu})^3 + \\
& (722.6 - 18.6579 \bullet T + 0.0122689 \bullet T^2) \bullet (X_{Sb} - X_{Cu})^4 + \\
& (-24804.9 + 27.3240 \bullet T - 0.0088438 \bullet T^2) \bullet (X_{Sb} - X_{Cu})^5 + \\
& (4412.6 + 34.5203 \bullet T - 0.0252669 \bullet T^2) \bullet (X_{Sb} - X_{Cu})^6 + \\
& (33066.3 - 33.7612 \bullet T + 0.0102734 \bullet T^2) \bullet (X_{Sb} - X_{Cu})^7 + \\
& (-19160.3 - 8.44712 \bullet T + 0.0130687 \bullet T^2) \bullet (X_{Sb} - X_{Cu})^8] \qquad (20A)
\end{aligned}
$$

Standard deviation = 3.1 mN/m

T = 873 K - 1473 K

Ag – Cu – Sn

The calculated by the Butler model (Eq. 21A)

$$
\begin{aligned}
\boldsymbol{\sigma} &= \boldsymbol{\sigma}_{Ag} + \frac{RT}{A_{Ag}} \ln \frac{X^{S}_{Ag}}{X^{B}_{Ag}} + \left(\frac{G^{E,S}_{Ag} - G^{E,B}_{Ag}}{A_{Ag}} \right) \\
&= \boldsymbol{\sigma}_{Sn} + \frac{RT}{A_{Sn}} \ln \frac{X^{S}_{Sn}}{X^{B}_{Sn}} + \left(\frac{G^{E,S}_{Sn} - G^{E,B}_{Sn}}{A_{Sn}} \right) \\
&= \boldsymbol{\sigma}_{Cu} + \frac{RT}{A_{Cu}} \ln \frac{X^{S}_{Cu}}{X^{B}_{Cu}} + \left(\frac{G^{E,S}_{Cu} - G^{E,B}_{Cu}}{A_{Cu}} \right) \qquad (21A)
\end{aligned}
$$

the surface tension for the Sn – Ag – Cu alloys, for $X_{Sn} \geq 0.7$, was described by the following relation:

$$\sigma_{SnAgCu} = \sigma_{AgCu} \frac{X_{Cu}}{X_{Cu} + X_{Sn}} +$$

$$\sigma_{AgSn} \frac{X_{Sn}}{X_{Cu} + X_{Sn}} + \Delta\sigma_{CuSn}(1 - X_{Ag} - X_{Cu}) + \Delta\sigma_{SnAgCu} \qquad (22A)$$

X_{Ag}, X_{Cu} and X_{Sn} are the mole fraction in ternary alloys and the other symbols in Eq. 22A describe the following equations:

$$\sigma_{AgCu} = \sigma_{Ag} C_{Ag} + \sigma_{Cu} C_{Cu} + C_{Ag} C_{Cu} \sum_{i=0}^{n} (a_i + b_i T + c_i T^2)(C_{Ag} - C_{Cu})^i \qquad (23A)$$

$$\sigma_{AgSn} = \sigma_{Ag} C_{Ag} + \sigma_{Sn} C_{Sn} + C_{Ag} C_{Sn} \sum_{j=0}^{m} (a_j + b_j T + c_j T^2)(C_{Ag} - C_{Sn})^j \qquad (24A)$$

$$\Delta\sigma_{CuSn} = C_{Cu} C_{Sn} \sum_{k=0}^{l} (a_k + b_k T + c_k T^2)(C_{Cu} - C_{Sn})^k \qquad (25A)$$

$$\Delta\sigma_{AgCuSn} = X_{Ag} X_{Cu} X_{Sn} \sum_{p=1}^{l} (a_p + b_p T) X_{Ag}^p + (c_p + d_p T) X_{Cu}^p + (e_p + f_p T) X_{Sn}^p \qquad (26A)$$

The concentrations C_{Ag}, C_{Cu} and C_{Sn} in binary alloys Ag – Cu, Ag – Sn and Cu – Sn are calculated according with relations:

Ag - Cu

$$C_{Ag} = \frac{X_{Ag}}{X_{Ag} + X_{Cu}} \qquad C_{Cu} = 1 - C_{Ag} \qquad (27A)$$

Ag - Sn

$$C_{Ag} = \frac{X_{Ag}}{X_{Ag} + X_{Sn}} \qquad C_{Sn} = 1 - C_{Ag} \qquad (28A)$$

Cu - Sn

$$\mathbf{C_{Cu}=\frac{X_{Cu}}{X_{Cu}+X_{Sn}}} \qquad \mathbf{C_{Sn}=1-C_{Sn}} \tag{29A}$$

The surface tension for the Ag-Cu system was calculated from the Butler relation using the thermodynamic parameters from [2000Moo] on the Ag-Cu-Sn phase diagram. Next it was worked out by the equation (23A) and it is as follows:

$$\boldsymbol{\sigma}_{\mathbf{Ag\text{-}Cu}} = \sigma_{Ag}\bullet C_{Ag} + \sigma_{Cu}\bullet C_{Cu}+$$
$$C_{Ag}\bullet C_{Cu}\bullet[(-1161.6 + 0.78595\bullet T- 0.0002083\bullet T^2) +$$
$$(397.6- 1.72431\bullet T + 0.0004032\bullet T^2)\bullet(1-2\bullet C_{Ag}) +$$
$$(-1844 + 1.78776\bullet T- 0.0005071\bullet T^2)\bullet(1-2\bullet C_{Ag})^2+$$
$$(-2380.5 + 1.7489\bullet T- 0.0007162\bullet T^2)\bullet(1-2\bullet C_{Ag})^3+$$
$$(1520.7 - 2.91972\bullet T + 0.0011807\bullet T^2)\bullet(1-2\bullet C_{Ag})^4+$$
$$(8996.6 - 11.3049\bullet T+ 0.0035419\bullet T^2)\bullet(1-2\bullet C_{Ag})^5+$$
$$(-8691.4 +12.297\bullet T- 0.0042904\bullet T^2)\bullet(1-2\bullet C_{Ag})^6-7227.1\bullet(1-2\bullet C_{Ag})^7] \tag{30A}$$

Standard deviation = 0.7 mN/m

T = 500 K - 1473 K

The coefficients a,b,$c_{(i, j, k)}$ in Eqs (23A), (24A) and (25A) are the same as in Eqs (11A), (14A) and (30A). Worked out Eq. (26A) can be written explicit as follows:

$$\begin{aligned}\Delta\sigma_{\mathbf{ter}(X_{Ag},X_{Cu},X_{Sn})} = {} & X_{Ag}\bullet X_{Cu}\bullet X_{Sn}\bullet[(-13226.2 + 5.87379E{+}01\bullet T)\bullet X_{Ag}+ \\ & (-2998.4+ 0.554\bullet T)\bullet X_{Cu}+(-1914.4+ 2.84596 \bullet T)\bullet X_{Sn}+ \\ & (86125.5+ -31.4636\bullet T)\bullet X_{Ag}^{2}+(-1918.5- 0.36594\bullet T)\bullet X_{Cu}^{2}+ \\ & (-1368.4+ 3.24094\bullet T)\bullet X_{Sn}^{2}+(300570 -258.321\bullet T)\bullet X_{Ag}^{3}+ \\ & (1615.4- 1.54048\bullet T)\bullet X_{Cu}^{3}+(146.4+ 1.14017\bullet T)\bullet X_{Sn}^{3}+ \\ & (-1283010+ 862.605\bullet T)\bullet X_{Ag}^{4}+(7101.3-3.00282\bullet T)\bullet X_{Cu}^{4}+ \\ & (3018.3+ -5.1781\bullet T)\bullet X_{Sn}^{4}] \qquad (31A)\end{aligned}$$

Standard deviation = 1.1 mN/m

$X_{Sn} >= 0.7$ T = 500 K-1373 K

12. Annex 2

In this annex are reported the abstracts of the most important publications used in preparation of SURDAT database.

[2006Mos1] Moser Z., Gąsior W., Bukat K., Pstruś J., Kisiel R., Ohnuma I., Ishida K., *Pb – free solders - Wettability Testing of Sn-Ag-Cu Alloys with Bi Additions. Part I,* J. Phase Equilib. Diffus., 27, (2006), 1-6.

Abstract

Maximum bubble pressure, dilatometric, and meniscographic methods were used in the investigations of the surface tension, density, wetting time, wetting force, contact angle, and interfacial tension of liquid alloys of Sn-Ag-Cu eutectic composition with various additions of Bi. Density and surface tension measurements were conducted in the temperature range 250-900 °C. Surface tensions at 250 °C measured under a protective atmosphere of Ar-H_2 were combined with data from meniscographic studies done under air or with a protective flux. The meniscographie data with a nonwetted teflon substrate provided data on interfacial tension (solder-flux), surface tension in air, and meniscographic data with a Cu substrate allowed determinations of wetting time, wetting force, and calculation of contact angle. The calculated wetting angles from meniscographie studies for binary Sn-Ag eutectic and two ternary Sn-Ag-Cu alloys were verified by separate measurements by the sessile drop method under a protective atmosphere with a Cu substrate. Additions of Bi to both ternary alloys improve the wettability and move the parameters somewhat closer to those of traditional Sn-Pb solders.

[2006Mos2] Moser Z., Gąsior W., Pstruś J., Ohnuma I., Ishida K., *Influence of Sb additions on surface tension and density. Experiment vs. Modeling.* Z. Metallkd., 97, (2006), 365-370.

Abstract

Surface tension and density measurements by the maximum bubble pressure and dilatometric techniques were carried out in an extensive range of temperature on liquid alloys close to the ternary eutectic Sn3.3Ag0.76Cu with different Sb content. It has been found that the addition of Sb to Sn, Sn-Sb, to binary eutectic Sn-Ag and to Sn3.3Ag0.76Cu decreases the surface tension and density. The values of the surface tension calculated by the Butler model and by the method based on the binary alloys surface tension data with the ternary and quaternary correction factors were compared with the experimental results. The best agreement between the measured and the calculated values was observed for the model comprising the binary data with the correction factors.

[2006Ohn] Ohnuma I., Ishida K., Moser Z., Gąsior W., Bukat K., Pstruś J., Kisiel R., Sitek J., ***Pb – free solders. Application of ADAMIS data base in modeling of Sn – Ag – Cu alloys with Bi additions. Part II.*** **J. Phase Equilib. Diffus., 27, (2006), 245-254.**

Abstract

The ADAMIS data base was used for calculation of the surface tension of the quaternary Sn – Ag – Cu – Bi liquid alloys by the Butler model. The obtained data were compared with those from the maximum bubble pressure measurements from Part 1. The same thermodynamic data base was next applied for the calculation of various phase equilibria. It was established that the Bi addition to the ternary Sn – Ag – Cu alloys (Sn – 2.6Ag – 0.46Cu and Sn – 3.13Ag – 0.74Cu in at.% (Sn – 2.56Ag – 0.26 Cu and Sn – 2.86Ag – 0.40Cu in mass %) causes lowering of the melting temperature and the surface tension to make the tested alloys closer to traditional Sn – Pb solders. The simulation of the solidification by the Scheil's model showed that the alloys with the higher Bi concentration are characterized by the lifting–off failure because of the segregation of Bi at the solder/substrate boundary. Thus, in modeling of new Pb - free solders, a compromise among various properties should be taken into consideration.

[2005Kis] Kisiel R., Gąsior W., Moser Z., Pstruś J., Bukat K., Sitek J., *Electrical and Mechanical Studies of the Sn-Ag-Cu-Bi and Sn-Ag-Cu-Bi-Sb Lead Free Soldering Materials*, Archs. Metall. and Mater., 50, (2005), 1065-1071.

Abstract

The electrical resistivity and the tensile strength of two near ternary eutectic Sn-Ag-Cu and four solder alloys close to ternary eutectic Sn-Ag-Cu with different Bi contents as well as eight Sn- Ag-Cu-Bi with different Sb contents in the form of wires were investigated. The four-probe technique was used for electrical parameter measurements. Equipment of the author's own construction for the tensile strength measurement was applied. It was found that the additions of Bi and Sb to Sn-Ag-Cu near eutectic alloys increase the resistivity and the tensile strength and that the resistivity of the Sn-Ag-Cu-Bi and Sn-Ag-Cu-Bi-Sb alloys is comparable with those of Pb-Sn solders for the bismuth and antimony content of about 3 atomic percent.

[2004Gas1] Gąsior W., Moser Z., Pstruś J., Bukat K., Kisiel R., Sitek J., *(Sn-Ag)$_{eut}$ + Cu Soldering Materials, Part 1*: *Wettability Studies*, J. Phase Equilib. Diffus., 24 (2004), 115-121.

Abstract

The maximum bubble pressure, dilatometric, and meniscographic methods were used in investigations of the surface tension, density, wetting time, wetting force, contact angles, and interfacial tension of liquid (Sn-Ag)$_{eut}$ and two (Sn-Ag)$_{eut}$ + Cu alloys (Cu at.% = 0.46 and 0.74). The density and surface tension measurements were conducted in the temperature range from 230 to 950 °C, and the meniscographic investigations were carried out at 252 °C. The resultant values of surface tension were compared with those calculated from Butler's model based on optimized thermodynamic parameters and our data from earlier investigations. In an earlier study, experimental data for all investigated compositions (Cu at. % = 1.08 to 6.5) exhibit an increase in the surface tension with increasing temperature, while both ternary alloys of this study show a slight lowering tendency in comparison to (Sn-Ag)$_{eut}$. A more evident decreasing tendency of surface tension and interfacial tension was noted in meniscographic measurements, noting that data of interfacial tension are always lower than surface tension due to the role of the flux. Eight different fluxes were tested to select the lowest interfacial tension for the (Sn-Ag)$_{eut}$. ROLI (3% solids), which is the alcoholic solution of organic compounds and rosin activated by halogens, was recommended. In (Sn-Ag)$_{eut}$ + Cu Soldering Materials, Part II: Electrical and Mechanical Studies, for the same (Sn-Ag)$_{eut}$ and (Sn-Ag)$_{eut}$ + Cu alloys (Cu at. % = 0.46 and 0.74), the electrical resistance and strength measurements will be presented in parallel with printed-circuit boards in wave soldering at 260 °C.

[2004Gas2] Gąsior W., Moser Z., Pstruś J., Ishida K., Ohnuma I., *Surface Tension and Density Measurements of Sn-Ag-Sb Liquid Alloys and Phase Diagram Calculations of the Sn-Ag-Sb Ternary System*, Mater. Trans., 45, (2004), 652-660.

Abstract

The maximum bubble pressure method has been used to measure the surface tension of pure antimony and the surface tension and density (dilatometric method) of Sn-3.8at%Ag eutectic base alloys with 0.03, 0.06 and 0.09 mol fraction of antimony at a temperature range from 550 to 1200 K. The linear dependencies of surface tension and density on temperature were observed and they were described by straight-line equations. Moreover, experimental determination of phase diagram and thermodynamic calculations in the Sn-Ag-Sb system were performed and the resulting optimized thermodynamic parameters were used for modeling of the surface tension. In addition, a non-equilibrium solidification process using the Scheil model was simulated and compared with the equilibrium solidification behavior of a Sn-Ag-Sb alloy.

[2004Gas3] Gąsior W., Moser Z., Pstruś J., ***SnAgCu+Sb Measurements of the Surface Tension and Density of Tin Based Sn-Ag-Cu-Sb Liquid Alloys,*** **Archs. Metall. and Mater., 49, (2004), 155-167.**

Abstract

The maximum bubble pressure method for the determination of the surface tension and dilatometric technique for density measurements were applied in the studies of liquid quaternary Sn-Ag-Cu-Sb alloys close to the ternary eutectic (Sn-Ag-Cu). The investigations of the density were conducted in the temperature range from 513 K to 1186 K and those of the surface tension from 513 K lo 1177 K. The experiments were carried out for the liquid alloy of composition close to the ternary eutectic (Sn3.3AgO.76Cu) and for four quaternary liquid alloys (Sn-3.3Ag-0.76Cu) + Sb alloys (X_{sb} = 0.03, 0.06, 0.09, 0.12 mol fractions). It has been found that both surface tension and density show linear dependence on temperature. The relations describing the dependence of the surface tension and density on concentration were determined. The surface tension, density and molar volume isotherms calculated at 673 K and 1273 K have shown that the antimony addition to the ternary alloy (Sn-3.3Ag-0.76Cu) decreases the surface tension and the density while increase of the molar volume is observed. The maximal decrease of surface tension is slightly higher than 50 mN/m and that for density is about 0.15 g•cm^3. The observed increase of molar volume is about 2.5 cm^3 at the maximal Sb addition equal to 0.12 mole fraction.

[2004Kis] Kisiel R., Gąsior W., Moser Z., Pstruś J., Bukat K., Sitek J., *$(Sn\text{-}Ag)_{eut}$ + Cu Soldering Materials, Part II*: *Electrical and Mechanical Studies*, J. Phase Equilib. Diffus., 24 (2004), 122-124.

Abstract

Electrical (solder resistivity and solder joint resistance) and mechanical (tensile strength and shear strength of solder joints) parameters of the binary eutectic Sn-Ag and two alloys close to the ternary eutectic Sn-Ag-Cu composition were investigated. The four-probe technique was used for the measurement of electrical parameters. Special equipment was constructed for the tensile strength measurements and also for determination of the shear strengths of solder joints between a typical circuit component and a Cu contact on a printed circuit board (PCB). It was found that electrical and mechanical properties of the three alloys studied are comparable to data in the literature for traditional Pb-Sn solders. A joint resistance below 0.3 mΩ (Ω =ohm) and shear strength of above 20 MPa were found for an individual solder joint between a circuit component (in the current study a "jumper" resistor) and a copper surface on a PCB.

[2003Gas1] Gąsior W., Moser Z., Pstruś J., Krzyżak B., Fitzner K., *Surface Tension and Thermodynamic Properties of the Liquid Ag-Bi Solutions*, J. Phase Equilib., 24, (2003), 40-49.

Abstract

With the maximum bubble pressure method, the density and surface tension were measured for five Ag-Bi liquid alloys *(*X_m = 0.05, 0.15, 0.25, 0.5, and 0.75), as well as for pure silver. The experiments were performed in the temperature range 544 - 1443 K. Linear dependences of both density and surface tension versus temperature were observed, and therefore the experimental data were described by linear equations. The density dependence on concentration and temperature was derived using a polynomial method. A similar dependence of surface tension on temperature and concentration is presented. Next, the Gibbs energy of formation of solid Bi_2O_3 as well as activities of Bi in liquid Ag-Bi alloys, were determined by a solid-state electromotive force (emf) technique using the following galvanic cells: *Ni, NiO, Pt/O* $^{-2}$*/W,* $Ag_xBi_{(1-X)}$, $Bi_2O_{3(S)}$*.* The Gibbs energy of formation of solid Bi_2O_3 from pure elements was derived: $\Delta G^{\mathbf{0}}_{f(\alpha-Bi_2O_3)}$ = -598 148 + 309.27T [J • mol^{-1}] and $\Delta G^{\mathbf{0}}_{f(\delta-Bi_2O_3)}$= -548 009 + 258.94T [J • mol^{-1}]; the temperature and the heat of the α → δ transformation for this solid oxide were calculated as 996 K and 50.14 J • mol^{-1}. Activities of Bi in the liquid alloys were determined in the temperature range from 860-1075 K, for five Ag-Bi alloys (X_{Ag} = 0.2, 0.35, 0.5, 0.65, 0.8), and a Redlich-Kister polynomial expansion was used to describe the thermodynamic properties of the liquid phase. Using Thermo-Calc software, the Ag-Bi phase diagram was calculated. Finally, thermodynamic data were used to predict surface tension behavior in the Ag-Bi binary system.

[2003Gas2] Gąsior W., Moser Z., Pstruś J., ***Density and Surface Tension of Sb-Sn Liquid Alloys. Experiment vs. Modeling*****, J. Phase Equilib., 24, (2003), 504-510.**

Abstract

Through the application of the maximum bubble pressure and dilatometric methods, density and surface tension were investigated. The experiments were conducted in the temperature range from 583 K ≤ T ≤ 1257 K. The surface tension was measured for pure antimony and for six liquid Sb-Sn alloys (mole fractions X_{Sn} = 0.2, 0.4, 0.6, 0.8, 0.9, and 0.935 mm^2) and measurements of-the density were only for alloys. It has been observed that both surface tension and density show linear dependence on temperature. The temperature-concentration relations were of both surface tension and density determined with minimization procedures. The surface tension isotherms calculated at 873 K and 1273 K show slight negative deviations from linearity changes, but the observed maximal differences did not exceed 30 mN • m^{-1}. The surface tension calculated from Butler's model was higher than the experimental value for most concentrations and also showed curvilinear temperature dependence. The experimental densities and the molar volumes of the Sb-Sn liquid alloys conform very closely to ideal behavior with differences comparable to the experimental errors.

[2002Liu] Liu X.J., Inohana Y., Ohnuma I., Kainuma R., Ishida K., Moser Z., Gąsior W., Pstruś J., ***Experimental Determination and Thermodynamic Calculation of the Phase Equilibria and Surface tension of the Ag-Sn-In System*****, J. Electron. Mater., 31, (2002), 1139-1151.**

Abstract

The phase equilibria of the Sn-Ag-In system were investigated by means of differential scanning calorimetry (DSC) and metallography. The isothermal sections at 180-600 ºC, as well as some vertical sections were determined. Thermodynamic assessment of this system was also carried out based on the experimental data of thermodynamic properties and phase equilibria using the CALPHAD method, in which the Gibbs energies of the liquid, fcc and hcp phases are described by the subregular solution model and those of compounds are represented by the sublattice model. The thermodynamic parameters for describing the phase equilibria were optimized, and reasonable agreement between the calculated and experimental results was obtained.

The maximum bubble - pressure and dilatometric method have been used in measurements of the surface tension and density of the binary In-Sn and the ternary $(Sn–3.8Ag)_{eut}$+In (5 and 10% at.) liquid alloys, respectively. The experiments were performed in the temperature range from 160 ^{o}C to 930 ^{o}C. The experimental data of the surface tension were compared with those obtained by the thermodynamic calculation of the Butler model.

[2002Mos] Moser Z., Gąsior W., Pstruś J., Księżarek S., *Surface Tension and Density of the (Ag-Sn)$_{eut}$+Cu liquid Alloys*, J. Electron. Mater., 31, (2002), 1225-1229.

Abstract

The maximum bubble-pressure method has been used to measure the surface tension and density of liquid alloys (Ag-Sn)$_{eut}$ + Cu (X_{Cu} = 0.005, 0.020, 0.0375, and 0.065 (mole fraction)). The surface tension and density measurements were curried out in the temperature ranges of 262-942°C and 264-937°C, respectively. The linear dependencies of surface tensions and densities on temperature were observed, and they were described by straight-line equations. It has been found that the additions of Cu to the Ag-Sn eutectic alloy increase the surface tension. Experimental data of the surface tension were compared with those from modeling based on Butler method, using the optimized-thermodynamic parameters from the literature, and a slight tendency contrary to the experimental results was observed.

[2001Gas1] Gąsior W., Moser Z., Pstruś J., Kucharski M., *Viscosity of the Pb-Sn Liquid Alloys*, Archs. Metall., 46 (1), (2001), 23-32.

Abstract

The capillary method was used in the measurements of the viscosity of the lead-tin liquid alloys. The experiments were performed for the lead, tin and five lead-tin alloys of the concentration 0.1, 0.261 (eutectic), 0.5, 0.7 and 0.9 mole fraction of lead and between 521 K and 871 K. The experimental data on viscosity of pure components and liquid Pb-Sn alloys were described by the exponential equation $\eta = A\exp(E/RT)$. The dependence of viscosity on temperature and concentration was modeled by the Kucharski method considered in the calculations the activity coefficients, the partial molar volume of components and the molar volume of liquid alloys. Obtained isotherms of viscosity at 623 K and 823 K have shown nearly linear changes with the concentration and a reasonable agreement with the experimental data. The observed differences when compared with data from the literature do not exceed 15%.

[2001Gas2] Gąsior W., Moser Z., Pstruś J., ***Surface Tension and Density of the Pb-Sn Liquid Alloys*****, J.Phase Equilib., 22, (2001), 20-25.**

Abstract

The maximum bubble pressure and the dilatometric method were used respectively in measurements of surface tension and density of Pb-Sn liquid alloys. The experiments were carried out in the temperature range from 573 K to 1200 K for the pure Pb, pure Sn and 7 alloys of the composition 0.1, 0.2, 0.26, 0.36, 0.5, 0.7 and 0.9 mole fraction of Pb. A straight-line dependence on temperature was observed and fitted by the method of least squares both for the densities and the surface tension. The calculated density isotherm at 673 K showed a positive deviation from the linearity over the entire range of composition, and the same tendency was seen at 1173 K for compositions higher than X_{Pb}=0.26. At the lower concentration of Pb a nearly linear character of isotherm was noted. In the case of the surface tension, both at the lowest and the highest temperatures (673 K, 1173 K), the deviation from linearity with composition was negative, but deviation decreased with increasing temperature. The isotherms of the compositional dependence of surface tension calculated from the Butler model exhibit good agreement with the experimental data.

[2001Mos1] Moser Z., Gąsior W., Pstruś J., ***Density and surface tension of the Ag-Sn liquid alloys*****, J. Phase Equilib., 22, (2001), 254-258.**

Abstract

The maximum bubble pressure method has been used to measure the surface tension of pure tin and seven binary alloys with concentrations of 15,30,40, 60, 75,87.8, and 96.2 at.% Sn. Measurements were performed at the temperature range from 500 to about 1400 K depending on the composition of the investigated alloy. Densities of the Ag-Sn alloys were measured dilatometrically. The linear dependencies of densities and surface tensions on temperature were observed, and they are described by a straight-line equation.

Experimental data of the surface tensions were compared with calculations using Butler's model, which assumes an equilibrium between the bulk phase and the monolayer surface phase. Excess Gibbs energies of silver and tin necessary in calculations were taken from the optimized thermodynamic parameters reported recently from Tohoku University. It is shown that the calculated surface tension data from the optimized thermodynamic parameters of the liquid phase of the Ag-Sn are in good agreement with the experimental results.

[2001Mos2] Moser Z., Gąsior W., Pstruś J., Zakulski W., Ohnuma I., Liu X.J., Inohana Y., Ishida K., ***Density and surface tension of the Ag-In liquid alloys*****, J. Electron. Mater., 30, (2001), 1120-1128.**

Abstract

The phase boundaries of the Ag-In binary system were determined by the diffusion couple method, differential scanning calorimetry (DSC) and metallographic techniques. The results show that the region of the ζ (hcp) phase is narrower than that reported previously. Thermodynamic calculation of the Ag-In system is presented by taking into account the experimental results obtained by the present and previous works, including the data on the phase equilibria and thermochemical properties. The Gibbs energies of liquid and solid solution phases are described on the basis of the sub-regular solution model, and that of the intermetallic compounds are based on the two-sublattices model. A consistent set of thermodynamic parameters has been optimized for describing the Gibbs energy of each phase, which leads to a good fit between calculated and experimental results. The maximum bubble pressure method has been used to measure the surface tension and densities of liquid In, Ag, and five binary alloys in the temperature range from 227 °C to about 1170 °C. On the basis of the thermodynamic parameters of the liquid phase obtained by the present optimization, the surface tensions are calculated using Butler's model. It is shown that the calculated values of the surface tensions are in fair agreement with the experimental data.

[2001Mos3] Moser Z., Gąsior W., Pstruś J., *Surface tension measurements of the Sn-Bi and Sn-Bi-Ag liquid alloys*, J. Electron. Mater., 30, (2001), 1104-1111.

Abstract

The maximum bubble pressure method has been used to measure the surface tension of pure Bi, surface tension and density of liquid binary Bi-Sn alloys (X_{Bi} = 0.2, 0.4, 0.6, and 0.8 molar fractions) at the temperature range from about 500 K to 1150 K. Similarly, there were investigated ternary alloys adding to the eutectic (3.8 at.%Ag-Sn) 0.03, 0.06, 0.09, and 0.12 molar fractions of Bi. The linear dependencies of densities and surface tensions on temperature were observed and they were described by straight-line equations. It has been confirmed that the additions of Bi to liquid Sn and to the eutectic alloy (3.8 at. %Ag-Sn) markedly reduce the surface tension. Experimental data of the surface tension of liquid Bi-Sn were compared with modeling based on Butler's method and a reasonable agreement was observed.

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