EXPERIMENTAL RESULTS OF STUDIES OF THE SURFACE TENSION AND DENSITY FOR DATA BASE OF PB-FREE SOLDERING MATERIALS

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ABSTRACT

Experimental studies of surface tension and density were undertaken by the maximum bubble pressure method and dilatometric technique. The accumulated data for liquid pure components, binary, ternary and multicomponent alloys were used to create of the data base for the Pb-free soldering materials. The data base enables also to compare the experimental results with those obtained by Butler's model and with the existing literature data.

INTRODUCTION

In view of the increasing concern over the health hazards associated with the presence of lead in the environment, very substantial efforts are being made to eliminate lead-base solders. In 1998, the first commercial product soldered with Pb-free material was reported in Japan, as well as other international projects. In 1999 the driving forces for lead-free technology were growing rapidly in Europe. ITRI launched SOLDERTEC, the Lead-Free Soldering Technology Centre, and at the same time recommended the use of Sn-Ag-Cu alloy as a general purpose replacement for Sn-Pb alloy. This line was followed by NEMI, a major industry research group in the US, meeting at the 1999 US IPC Lead-Free Conference "Get the Lead Out", and the Sn-Ag-Cu alloy is now the major alloy in use for lead-free assembly.

In February 2003 the EC published Directive 2002/95/EC-Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment. This requires that by 1st July 2006 at the latest the Member States must ensure that new electrical equipment in major use categories does not contain lead and other hazardous substances. Links were made with Japanese and US research industry organisations, and technology development began to accelerate. Polish centres also initiated the studies on Pb-free soldering materials, which enabled participation in COST 531 and recently in ELFNET-the European Lead-Free Soldering Network comprising 37 Core Members within the Framework 6 Programme for 2004-2006.

In 1997 at the Institute of Metallurgy and Materials Science in Kraków (Poland) the studies were initiated on Pb-free solders comprising:

1. Phase diagrams and melting temperatures
2. Thermodynamic properties
3. Modeling of physical properties
4. Wetting characteristics: surface tension, density, viscosity, wetting angle, wetting force, interfacial tension, correlation between surface tension and interfacial tension.

Experimental studies of the physical properties of liquid solders, such as the surface tension and density were very scarce, and surface tension or viscosity were mainly calculated from thermodynamic modelling basing on the properties of liquid alloys and the data of pure components. Therefore, during the last 7 years there were initiated at the Institute of

Metallurgy and Materials Science systematic measurements of the surface tension by the maximum bubble pressure method, the density was measured by dilatometric technique and the obtained results were used for data base of Pb-free solders.

EXPERIMENTAL RESULTS USED FOR DATA BASE

Surface tension and density measurements were conducted on pure liquid metals, binary, ternary, quaternary and quinary liquid alloys which are listed in Table 1 with references.

TABLE 1. The investigated liquid metals and alloys

METALS	Ref.	BINARY ALLOYS	Ref.	MULTICOMPONENT ALLOYS	Ref.
Pb	1	**Pb - Sn**	1	**$(Sn\text{-}Ag)_{eut}$ +Zn**	*
Sn	2	**Ag - Sn**	2	**$(Sn\text{-}Ag)_{eut}$ +In**	6
In	3	**Ag - In**	3	**$(Sn\text{-}Ag)_{eut}$ +Bi**	4
Ag	3	**Bi – Sn**	4	**$(Sn\text{-}Ag)_{eut}$ +Cu**	8, 9
Bi	4	**In – Sn**	6	**$(Sn\text{-}Ag)_{eut}$ +Sb**	10
Sb	5	**Ag – Bi**	7	**$(Sn\text{-}Ag)_{eut}$ +Cu+Sb**	11
Cu	*	**Sb – Sn**	5	**$(Sn\text{-}Ag)_{eut}$ +Cu+Bi**	12
		Sn – Zn	*	**$(Sn\text{-}Ag)_{eut}$ +Cu+Sb+Bi**	13
		In - Zn	*		

* not published

Most data are connected with the binary eutectic Sn-Ag or when various amounts of a third metal adding to this eutectic. Finally, the higher order systems are composed on the base of the ternary eutectic Sn-Ag-Cu when examining the addition of Bi and Sb. 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 a substitute for traditional Sn-Pb solders.

Experimental results of the surface tension and density performed in the extensive temperature range and concentrations of components (particularly binary systems) were used to create the data base, comprising moreover the modelling of the surface tension by the Butler's method [14]. Modelling of surface tension by this method requires the knowledge of the excess Gibbs energies of the components of liquid alloys and the surface tension data of pure metals. For the development of a Pb-free solder, thermodynamic calculation of the surface tension is an important tool in the design and evaluation of various soldering materials because it significantly decreases the amount of the required experimental work. To construct a more reliable data base thermodynamic assessments as well as experimental work on the phase diagram are important as indicated in the introduction. To be able to perform modelling experimental studies of the surface tension were extended to include phase equilibria in co-operation with Tohoku University in Japan within the group headed by K.Ishida, who presented thermodynamic data base ADAMIS for micro-soldering alloys [15-16].

Having gathered the numerous results of investigated lead-free solders alloys, listed in Table 1, in 2003 at the Institute of Metallurgy and Materials Science of PAS there were taken the preliminary steps to use the experimental data, the density and molar volume to create the

computer data base SURDAT. Next, a computer program for modeling of the surface tension by the Butler's method was added to SURDAT.

PRESENTATION OF THE SURDAT DATA BASE

The functioning of the data base is presented in the scheme in Fig.1.

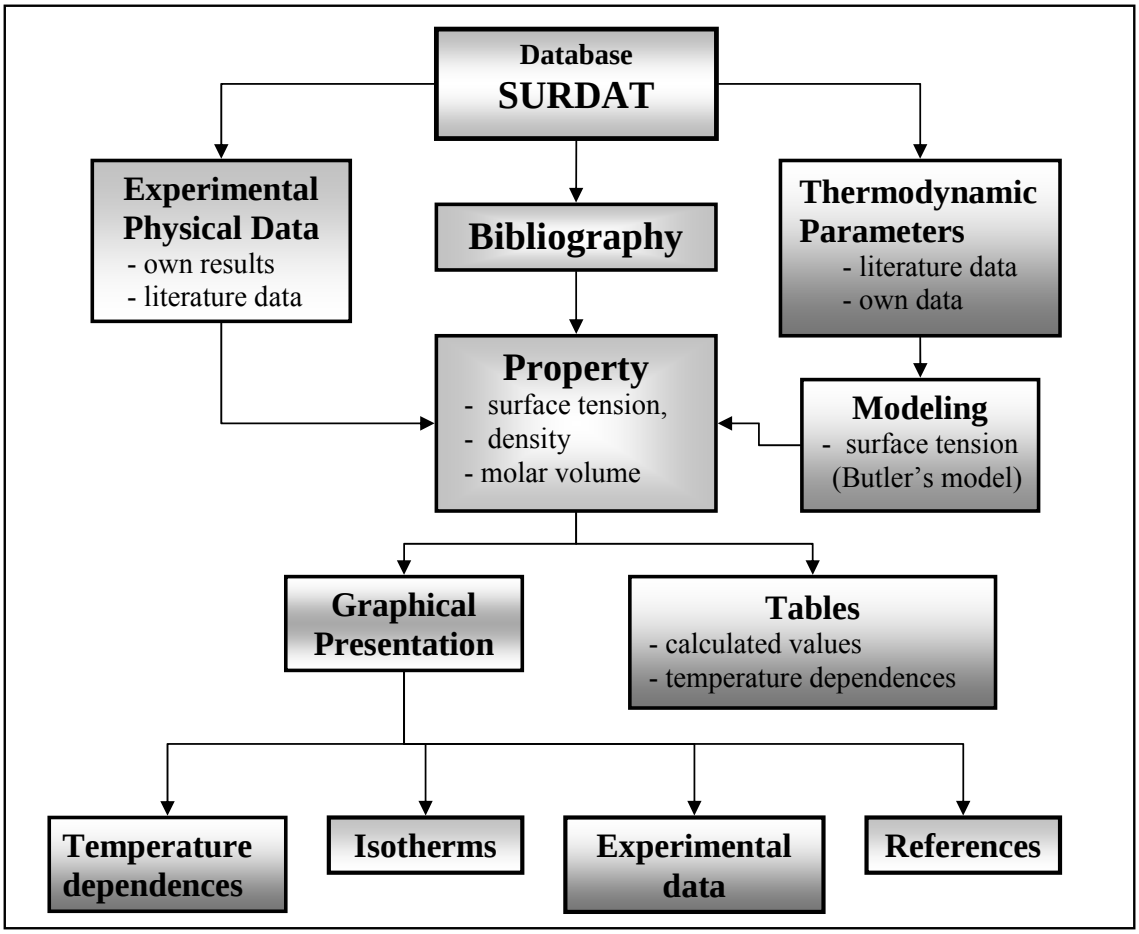

Fig. 1. Scheme of the database functioning.

For some systems the thermodynamic parameters needed for Butler's modelling are taken from literature [11], from the authors thermodynamic studies such as for instance for Ag-Bi liquid alloys [7], but in most cases the authors are using ADAMIS data base [15-16].

The scheme presented below in Fig. 2 shows the use of both data bases SURDAT and ADAMIS for calculation of different properties of alloys. The first version of the presented data base of physical properties of the lead-free solder alloys was shown at the CALPHAD XXXIII Meeting [17].

A short view at the operation of the SURDAT data base is presented in the following section of this article.

After setting in motion the SURDAT software the first window (Fig. 3) gives the information where the SURDAT was composed and in the part "System selection" the kind of the systems has to be chosen to go ahead.

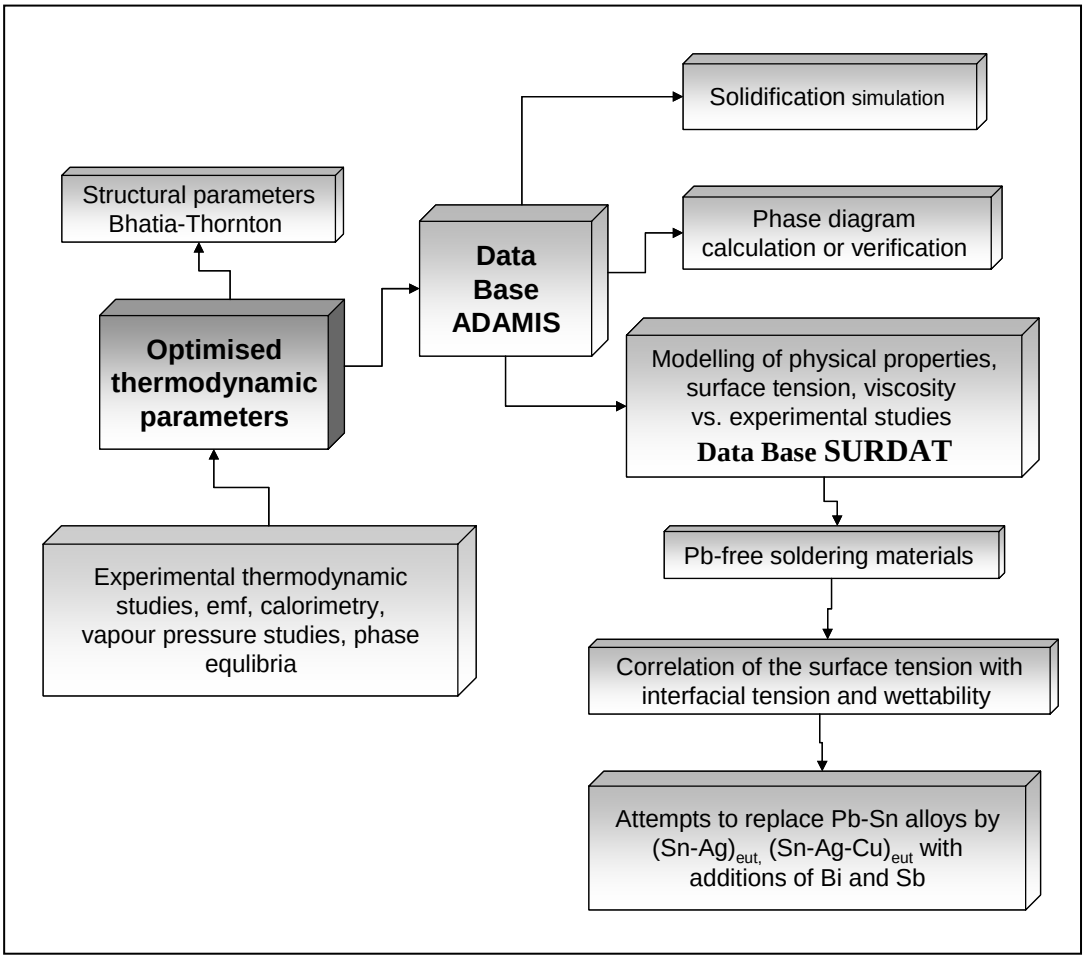

Fig. 2. Presentation of the use of the data bases ADAMIS and SURDAT

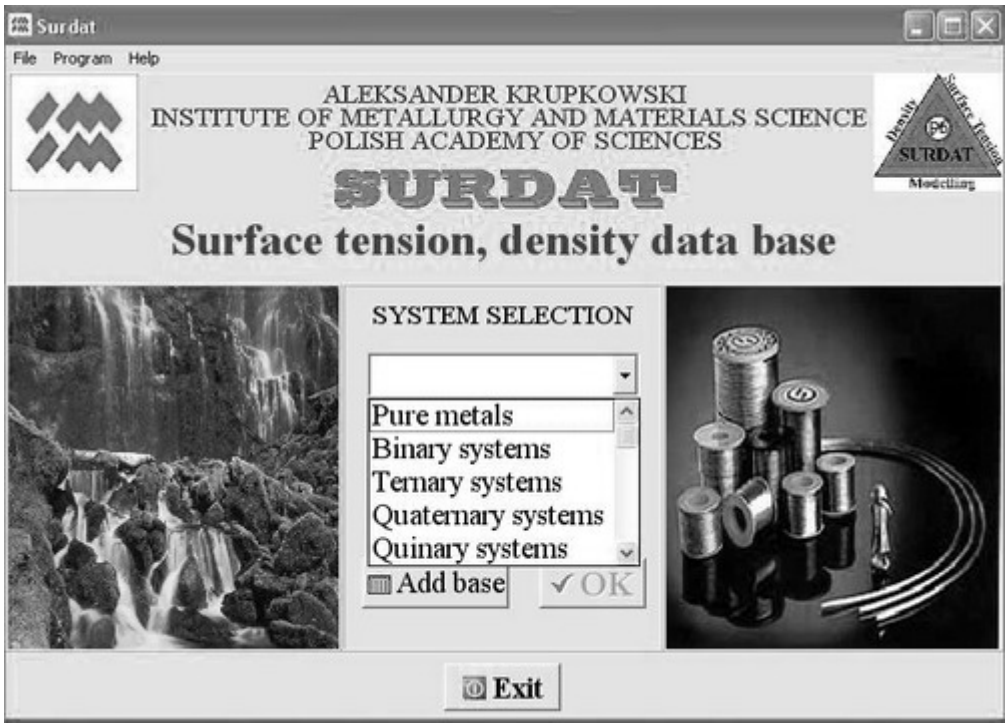

Fig. 3. Selection of the kind of the system in SURDAT data base

There are possible 5 options from pure metals (used in the investigations of lead-free solders) to the quinary systems. In the present version of the SURDAT data base the data for 7 pure metals, 9 binary, 5 ternary, 2 quaternary and 1 quinary systems are available. The surface tension of pure silver and the binary tin-silver alloys obtained from the SURDAT data base are shown on Figures 4 and 5.

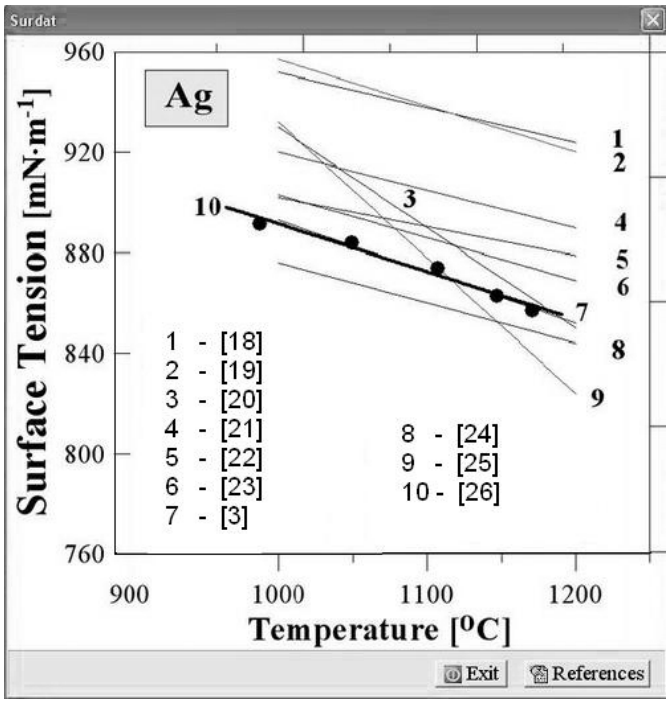

Fig. 4. Comparison of the temperature dependences of the liquid silver accessible in literature. Ref. 7 with experimental points comes from the Krakow's laboratory

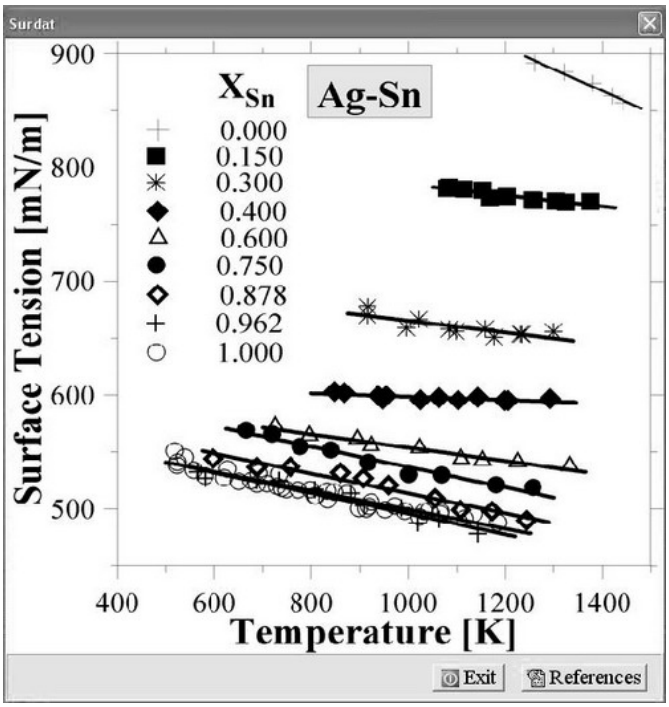

Fig. 5. The temperature dependences of the surface tension for Ag-Sn liquid alloys

In the next part of the paper the application of SURDAT for the presentation mainly of the data of the surface tension for the ternary (Sn-Ag-Cu) alloys in various configurations is shown. The temperature dependences of the liquid $(Sn\text{-}Ag)_{eut}$+Cu alloys are shown on Fig. 6 together with the results for the binary Sn-Ag eutectic.

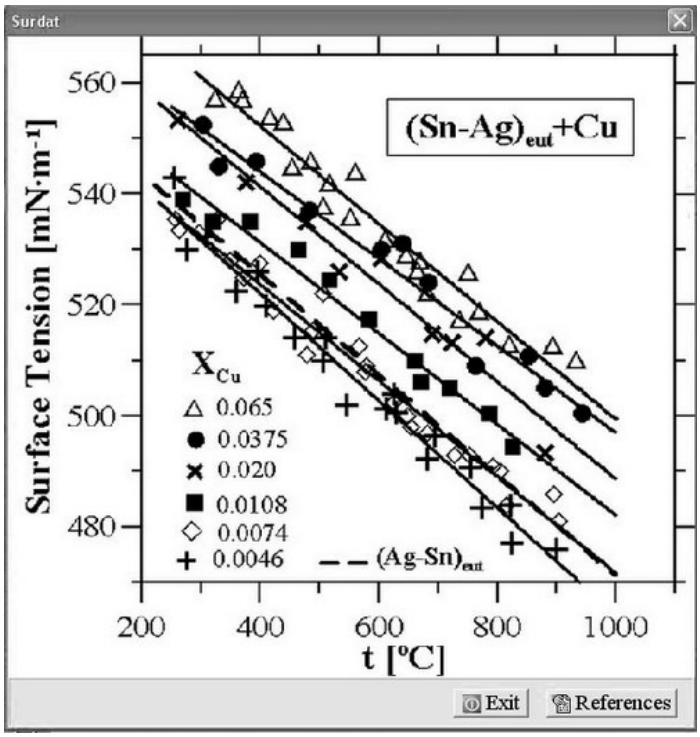

Fig. 6. Temperature dependences of the surface tension of the $(Sn\text{-}Ag)_{eut}$+Cu alloys (least squares lines) together with the experimental results (symbols) [8, 9].

At the next stage of the action of SURDAT data base there are three different possibilities of getting information on the surface tension, density or molar volume by choosing one from the three options; 1) temperature dependences, 2) isotherms and 3) Butler's model (only when the surface tension as the physical property was chosen).

The first option offers the possibility to show and compare in one figure the temperature dependences of the selected physical property data from different papers, in the form of experimental points and least squares lines. If only one author's data are in the data base, Fig. 5 is shown. When for the chosen system the results from different papers are given, there is possibility to see and to compare at one figure all those data.

When the second option is selected, 4 temperatures at most are available and the SURDAT shows the experimental points for each temperature together with the isotherms lines calculated using the equation (worked out by authors), describing the temperature-concentration dependence of the surface tension (Fig. 7).

The last option - modeling of the surface tension by Butler's relation [14]-is realized after selecting: the "Butler model" button, with the available thermodynamic parameters and the experimental data for comparison from various authors. There are possible two additional actions of the data base; calculation of the temperature dependences of the surface tension from thermodynamic parameters or calculation of the isotherms. In both options a comparison of the calculated and the experimental data for the surface tension reported by the selected author can be realized (Fig. 8).

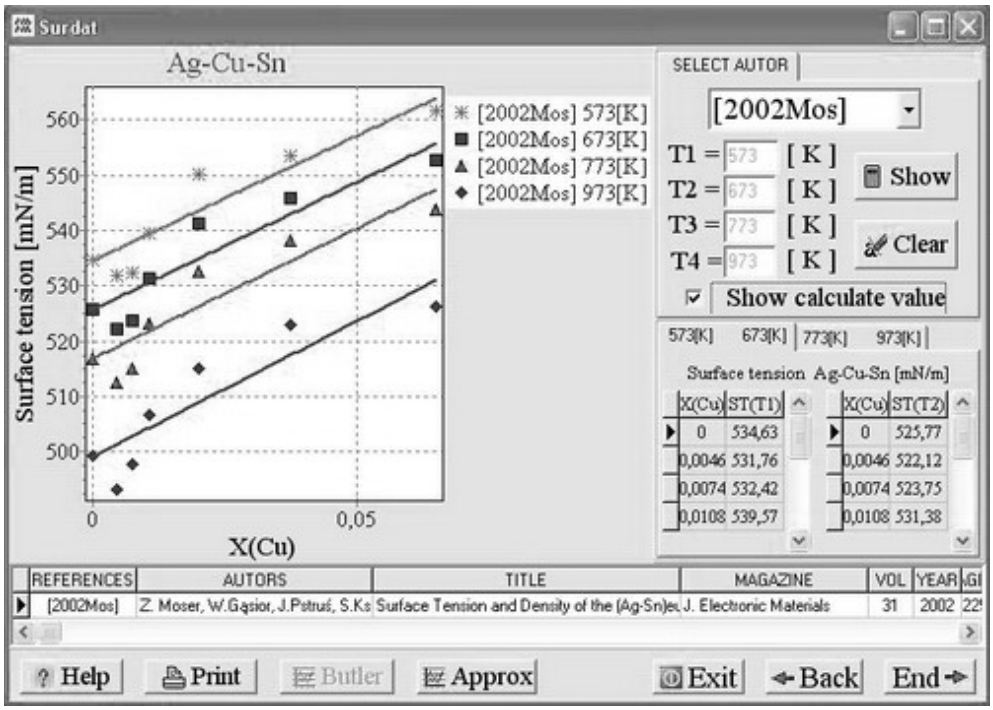

Fig. 7 Isotherms of the surface tension of the $(Sn\text{-}Ag)_{eut}$+Cu calculated at 4 temperatures (573K, 673K, 773K and 973K- lines) compared with the experimental data.

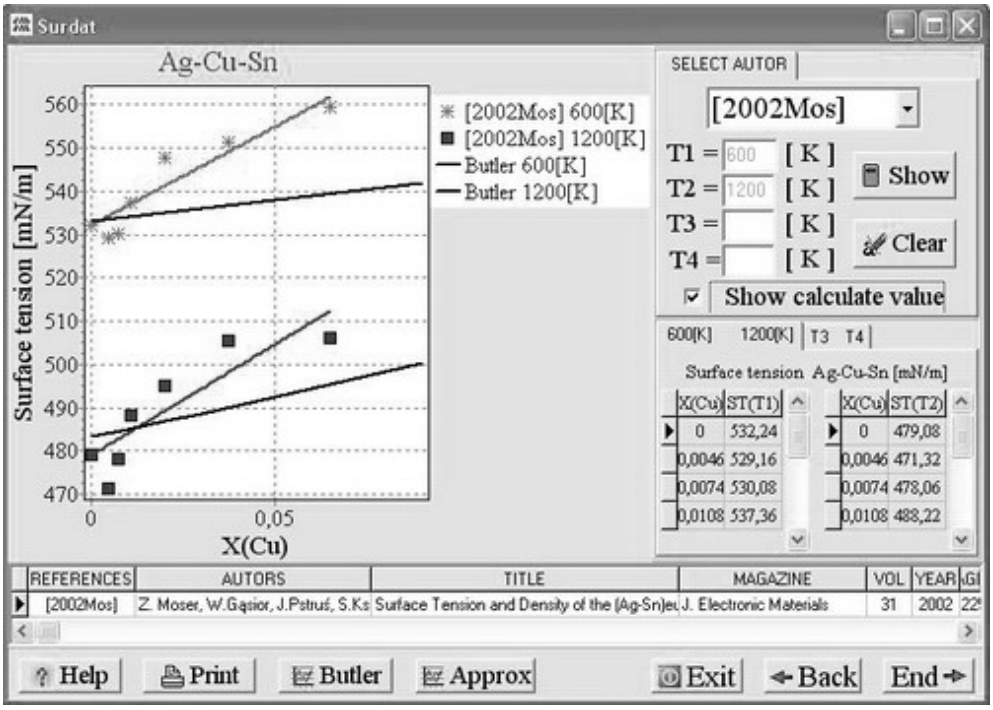

Fig. 8 Comparison of the isotherms calculated from Butler's model (black lines) with those calculated from the linear relation worked out by the authors (grey lines) and the experimental data (symbols) at 600K and 1200K.

Modeling of the surface tension using the thermodynamic data from different papers and the comparison in one figure of the obtained results is also possible.

The same options as for the surface tension are accessible for the molar volume and the density which is shown, as samples, in Fig. 9 and 10.

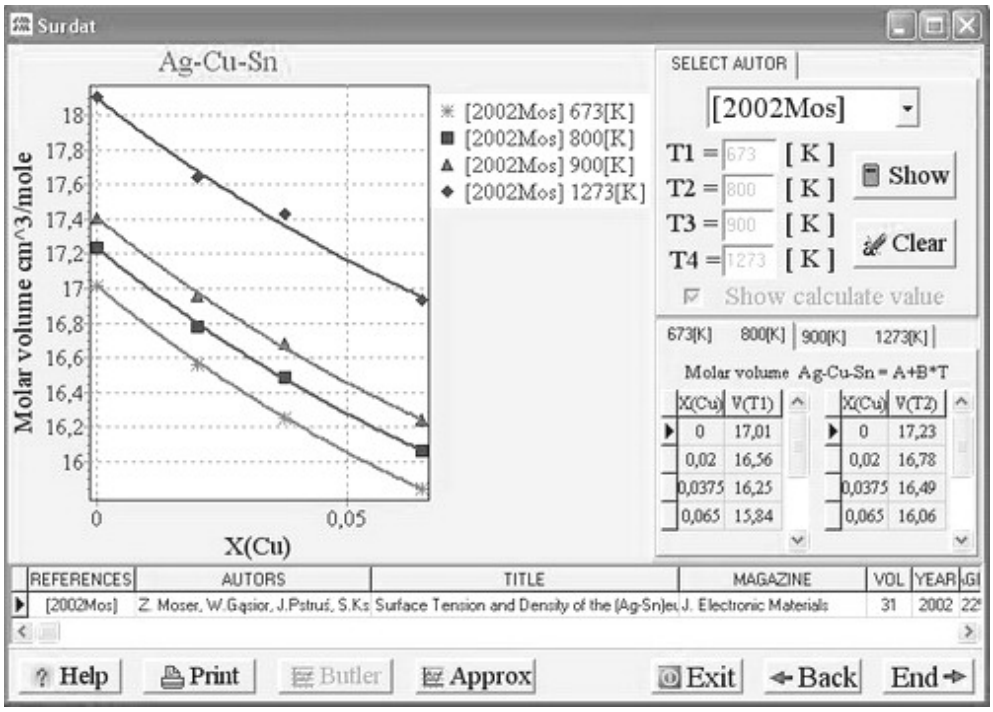

Fig. 9 Isotherms calculated by SURDAT of the molar volume at 4 temperatures (600K, 800K, 900K and 1200K) together with the experimental results (symbols)

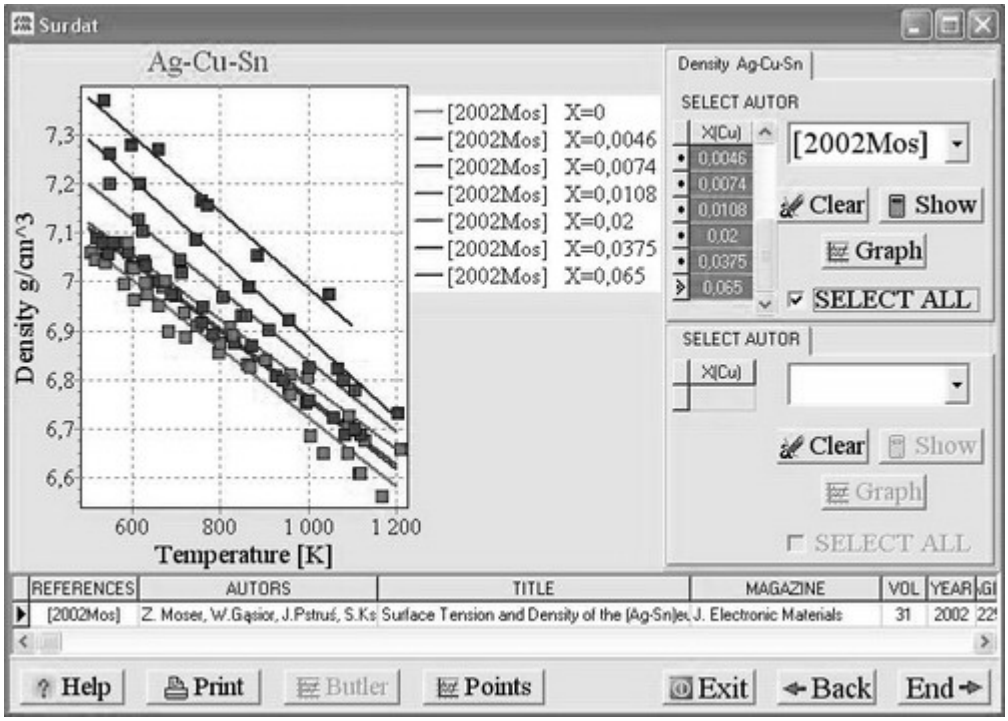

Fig. 10 Temperature dependences of the density for the $(Sn\text{-}Ag)_{eut}$+Cu liquid alloys together with the references

Additional information concerning the analyzed system (references, temperature, concentrations of alloys) can be obtained at every stage of the SURDAT action in the side windows.

CONCLUSIONS

The experimental data of the surface tension, density and molar volume on the lead-free solder alloys and some pure metals obtained by the authors together with those from literature were used for the creation of the SURDAT data base software.

The data base enables to get information on the temperature and isothermal dependences of the surface tension, density and molar volume and to compare those data with the results obtained by the other authors. Additionally, the modeling of the surface tension data from Butler's relation and for the thermodynamic data of different authors can be compared.

Modeling of the surface tension by Butler's relation is performed at the assumption that two parameters characterizing the surface monolayer are constant and that they are equal to $\beta=0.83$ (relation between excess Gibbs free energy in surface and bulk phases) and $L=1.091$ (the correction factor transforming the surface layer calculated from molar volume of liquid alloys into a monoatomic layer with the close-packed structure).

The future development of the SURDAT data base will be concentrated on the creation of the software for calculating the viscosity and the molar volume of liquid alloys from their thermodynamic properties together with the physical property of pure metals. The extension of the data on mechanical and electrical properties is also considered. Variations of the β and L parameters with the temperature are also taken into consideration.

The authors plan to place the SURDAT software at the server of the Institute of Metallurgy and Materials Science of Polish Academy of Sciences to enable its presentation to a broader audience.

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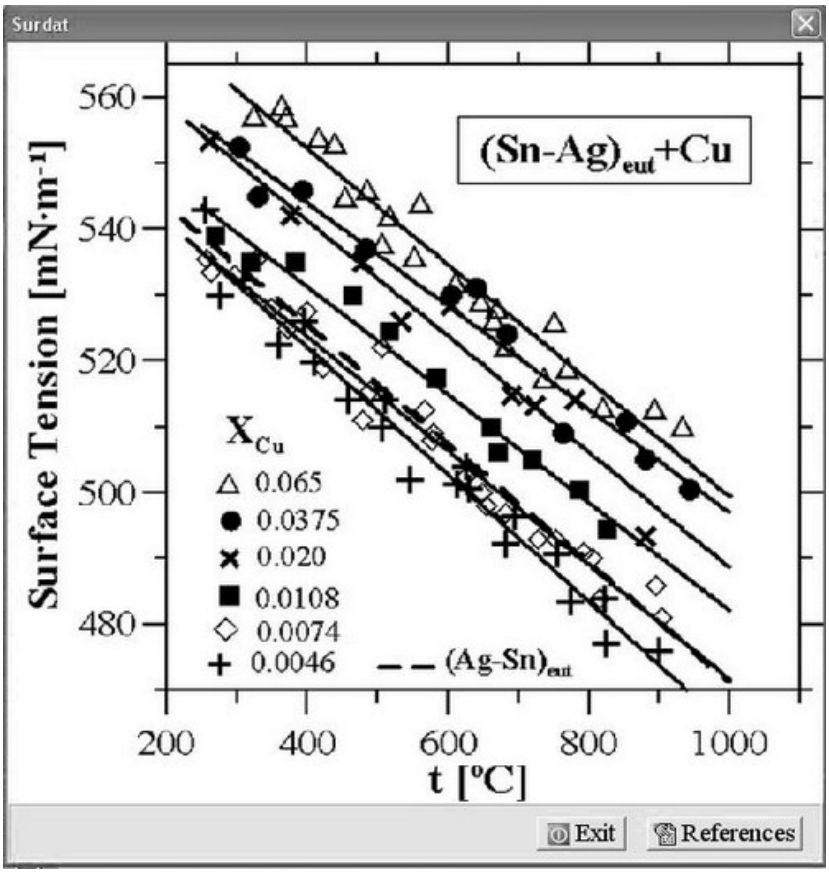
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(Sn-Ag)eut+Cu
Surface Tension [mN·m-1]
560
540
520
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t [°C]
XCu
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0.020
0.0108
0.0074
0.0046
(Ag-Sn)eut
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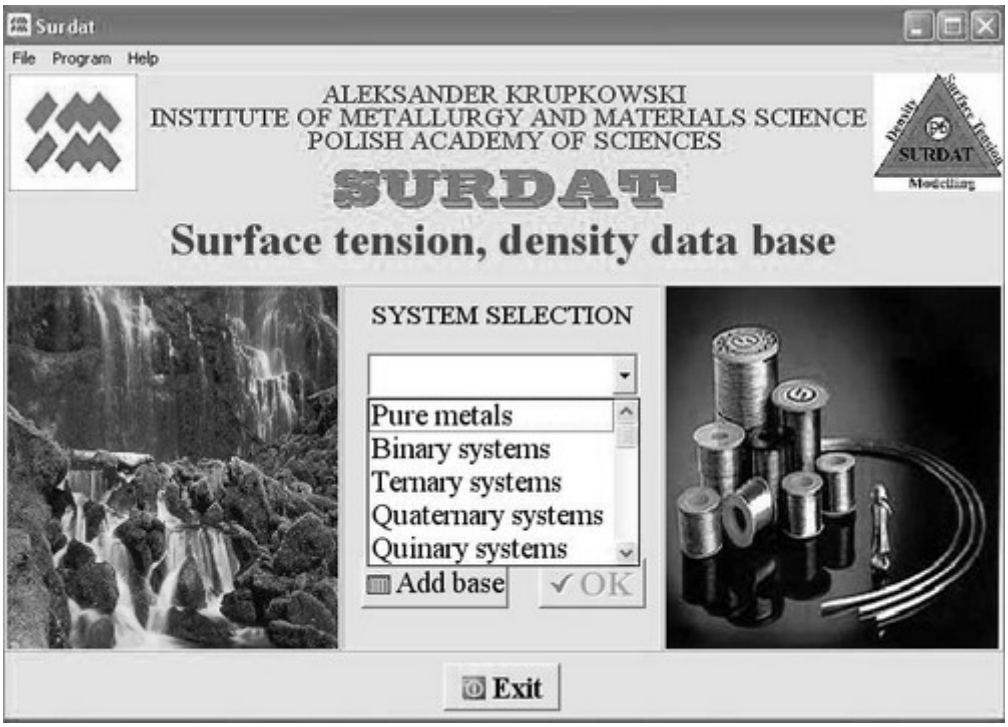
References


Surdat
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SURDAT
Surface tension, density data base
SYSTEM SELECTION
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