Application of Thermodynamics in Pb-Free Soldering Materials

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In experimental thermodynamics of alloys, emf and vapour pressure methods are commonly used for determination of partial functions. They can be recalculated into integral functions, but to increase the precision of splitting integral Gibbs energies into enthalpy and entropy parts, calorimetric measurements are involved.

The calorimetric techniques support enthalpies of mixing and in addition in systems with intermetallic phases, enthalpies of formation. Enthalpies of formation may be obtained from solution calorimetry or from direct reaction method. Both these techniques were discussed in previous studies, when determining enthalpies of formation of intermetallic phases from Al-Ni [1] and Al-Ti [2] systems using the liquid aluminium in solution calorimetry. This method was extended on tin solution calorimetry to determine enthalpy of formation of Ag_3Sn and the partial enthalpy of solution of Ag in liquid Sn, as the thermodynamic properties of the solid phases of the Ag-Sn system are not well known, and Ag-Sn is one of the most basic system for Pb-free soldering materials [3].

Both partial and integral functions with phase equilibria data are used for critical assessments [4] to get the optimized thermodynamic parameters, which are applied for phase diagram calculations and for modelling of physical properties.

In the described field, extensive studies were undertaken during more than 40 years on metallic alloys at the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences, and in recent years they were directed on Pb-free soldering materials. It was also in agreement with our interest to confirm, in studies of alloys, mutual correlations between thermodynamic properties, physical properties, structure mainly of liquid alloys [5] and the character of the phase diagram, experimental or calculated from assessed thermodynamic data. The other tendency is to compare experimental data with modelling and to use the basic data for practical application.

The close co-operation with industrial institutes and with Tohoku University from Japan on two eutectics Sn-Ag and Sn-Ag-Cu, commonly accepted as the substitute for Sn-Pb solders and on other materials, should be noted [6,7] . It is due to environmental problems as since July 1 2006, EU replaces traditional tin-lead solders by Pb-free soldering materials. To meet this demand, studies were undertaken including wettability directly connected with surface tension on tin based alloys, and two listed eutectics. Surface tension and density were determined by the maximum bubble pressure and dilatometric techniques. In addition, the modelling of the surface tension was performed from excess Gibbs energies of liquid components and the surface tension of pure metals. We have found that the Butler's 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 our paper on Ag-Bi liquid alloys [8].

In addition, a series of papers on Sb influence on surface tension and density in quaternary alloys $(Sn\text{-}Ag)_{eut}$ + Cu + Sb resulted in participation in the COST 531 program [9], while the similar parallel studies on Bi and Sb additions to ternary eutectic Sn-Ag-Cu enabled us to get financing for co-operation program with industrial institutes [10].

In co-operation with Tohoku University, Japan (Prof.T.Ishida), we have published several papers comprising thermodynamic properties and partial phase diagrams for Pb-free soldering materials, including also modeling of surface tension. For the same systems we have performed experimental studies of surface tension and density. Our experimental results for pure metals, binary, ternary, quaternary and quinary alloys, the candidates to replace the traditional Sn-Pb solders for Pb-free materials, including also thermodynamic modeling, were used for the SURDAT data base [11,12].

Step by step, we follow from basic studies to confirm the mutual correlations among various properties on the extended materials, to links with industry and to participation in ELFNET international net-work devoted to Pb-free soldering materials.

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