LEAD–FREE SOLDERS ON THE TIN – ZINC – ALUMINIUM BASIS FOR HIGH–TEMPERATURE APPLICATIONS

Jaromír DRÁPALA[a], Aleš KROUPA[b], Bedřich SMETANA[c], Vlastimil VODÁREK[d], Daniel PETLÁK[a], Rostislav BURKOVIČ[a]

Authors: ***Jaromír Drápala, Prof. PhD., Aleš Kroupa, PhD., Bedřich Smetana, PhD., Vlastimil Vodárek, Prof. PhD., Daniel Petlák, MSc. Eng., Rostislav Burkovič, PhD.***

Workplace: ***Vysoká škola báňská – Technical University of Ostrava***

[a] Department of Non-ferrous Metals, Refining and Recycling, tel. +420-597325474, secretary +420-597321273, fax: +420-597321271

[b] Institute of Physics of Materials, Academy of Sciences of the Czech Republic

[c] Department of Physical Chemistry and Theory of Technological Processes

[d] Department of Materials Engineering

Address: ***[a c d] Av. 17. listopadu 15, 708 33 Ostrava – Poruba, Czech Republic***

[b] Av. Žižkova 22, 616 62 Brno, Czech Republic

E-mail: ***Jaromir.Drapala@vsb.cz, kroupa@ipm.cz, Bedrich.Smetana@vsb.cz, Vlastimil.Vodarek@vsb.cz, Daniel.Petlak@vsb.cz, Rostislav.Burkovic@vsb.cz***

Abstract

Six binary Sn–Zn and fourteen ternary Al–Sn–Zn alloys with 0.6 to 3 wt. % Al were prepared experimentally. The alloys were studied metallographically. The micro-hardness and X-ray micro-analysis (EDAX, WDX) of the phases was measured. Temperatures and latent heats of characteristic phase transitions (liquidus, solidus, invariant reactions etc.) were obtained with use of the DTA method. Experiments were performed with Setaram SETSYS 18$_{TM}$ experimental laboratory system for thermal analysis. Samples of selected alloys were analysed at linear heating/cooling rate of 4°C/min in high pure atmosphere of argon. Resulting experimental data were compared with data of known Sn–Zn binary system and Al–Sn–Zn ternary system. For the modelling of phase equilibria from critically assessed data software packages were used: MTDATA, PANDAT and Thermo-Calc.

Key words

lead–free solders, aluminium, zinc, tin, alloys, behaviour, thermal analysis, thermodynamic modelling

Introduction

The production of electronics is an important phenomenon, which cannot be possible without soldering process presently. Lead-free solders of various compositions are used. They are able to substitute the lead based solders in specific applications, but the electronic industry is not satisfied because the lead-free solders often have reliability problems, usually caused by worse mechanical properties, and/or higher tendency to oxidation, higher occurrence of

undesirable intermetallic phases, higher melting temperature. They are also generally more expensive (for example Sn–Ag based solders) or their usage leads to higher technology expenses.

Both the basic and applied research investigates other alloy candidates for the lead-free solders but the results are not satisfactory enough yet. Systems on the Al–Zn base with another alloying element, such as Ga, Ni, Sn, seem to be promising candidates taking also into account that some of the elements represent substrate materials. Optimization of the temperature of soldering process and solder microstructure is important not only from the economical reasons but also from the technological point of view, as a higher temperature means a higher risk for the electronic components and boards.

Coexistence of phases inside the solder materials can be predicted using well-known CALPHAD method, which allows to model equilibrium state of the materials and to predict phase composition of newly developed ones. The results of the CALPHAD method are also important for other scientific applications. This approach can be used as thermodynamic basis for kinetic simulations of phase transformations and development of objects, which are heterogeneous in chemical composition (e.g. solder/7substrate systems, oxidation of solder particles, etc.). The possibility of theoretical calculation of temperature dependence of enthalpy using the CALPHAD method is also very useful, e.g. for investigation of thermal properties of materials via method of differential thermal analysis DTA/DSC.

Aluminium – tin – zinc ternary system

The Zn–Sn binary diagram [1] is of the simple eutectic type. The eutectic reaction takes place at the temperature of 198.5 °C in the alloy containing 85.1 at. % Sn (see point e_4 in the Fig. 2). The Al–Sn binary system [1] is a simple eutectic system. The eutectic reaction takes place at the temperature of 228.5 °C in the alloy containing 97.6 at.% Sn (see point e_3 in the Fig. 2). The equilibrium phase diagram of Al–Zn [1] is a eutectic system involving a monotectoid reaction – see Fig. 1. The eutectic reaction proceeds at 381 °C close to the Zn side (eutectic point has 88.7 at.% Zn). The monotectoid reaction takes place at the temperature of 277 °C.

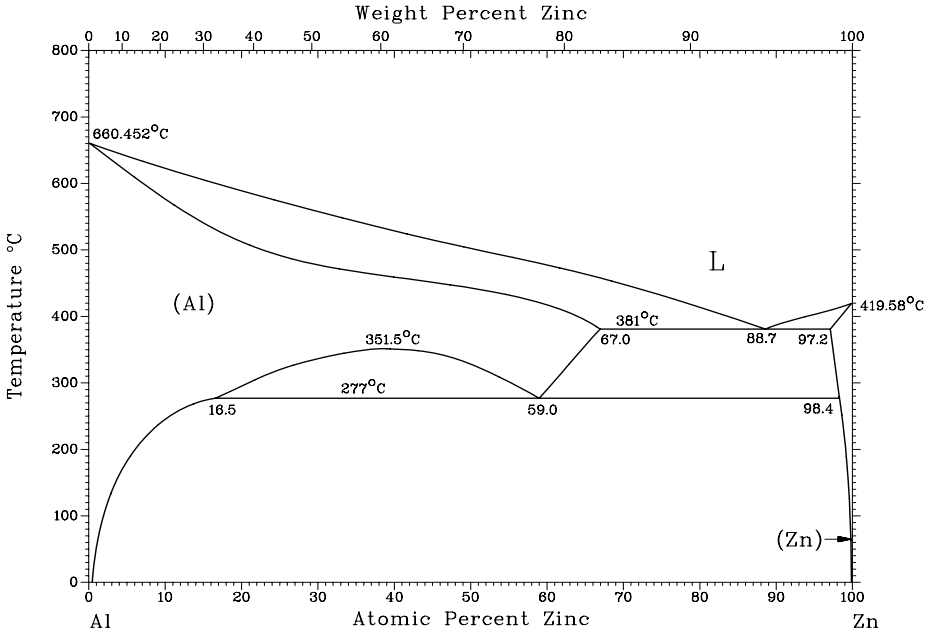

Fig. 1 *Binary diagram of the Al – Zn system [1]*

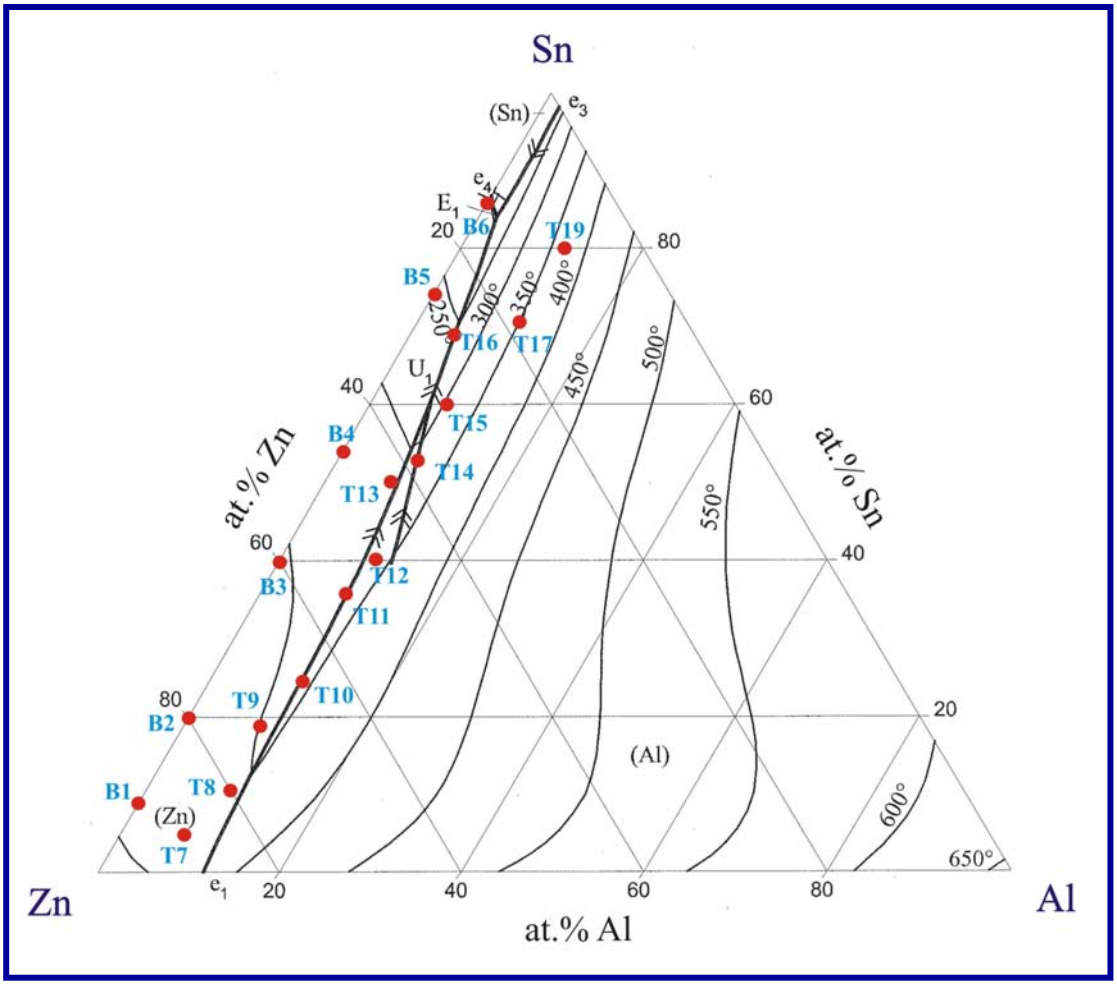

Fig. 2 *Positions of experimental alloys Al–Sn–Zn with the liquidus surface calculated by [6]*

The phase diagrams of the Al–Sn–Zn ternary system were investigated and published [2-8]. Using obtained experimental data and obtained thermodynamic description the phase diagram was calculated [6]. The liquidus isotherms of different experimental investigations agree fairly well, whereas the traces of the three phase equilibria are experimentally less well established. Fig. 2 shows the liquidus surface calculated by [6]. Table 1 presents characteristic reactions in Al–Sn–Zn ternary system [2, 3, 6].

CHARACTERISTIC REACTIONS IN THE Al–Sn–Zn TERNARY SYSTEM (see Fig. 2) Table 1

Reaction	T [°C]	Phase	Composition [at.%]			Author
			Al	Zn	Sn	
U_1 L + (Al)′ = (Al)′′ + (Zn)	277.8	L (Al)′ (Al)′′ (Zn)	6.45 85.82 41.01 1.63	31.79 14.17 58.97 98.24	61.67 0.01 0.02 0.13	[6]
E_1 L = (Al) + (Zn) + (Sn)	195.4 196 198	L L L	- 5.7 2.5	13.86 16.6 15.0	84.0 77.7 82.5	[6] [7] [3]

Experiments, measurements and results

Six binary Sn-Zn and fourteen ternary Al–Sn–Zn alloys with 0.6 to 3 wt. % Al were prepared experimentally (melting in the electrical resistance furnace and casting into a graphite mould). The alloys were studied metallographically, the micro-hardness, their overall chemical composition (ICP-AES and OES on the SPECTROMAX device) and X-ray micro-analysis (EDAX, WDX) of the coexisting phases were measured, too.

Chemical composition of samples is given in Fig. 2 (B – binary alloys, T – ternary alloys). Cast structure with cellular or dendritic formations was apparent from the metallographic study of Sn–Zn and Al–Sn–Zn alloys. It formed due to relatively high rates of the melt cooling. Zn solid solutions precipitated primarily and their volume portion decreased with increasing Sn content. Dendritic formations with light areas of secondarily solidified eutectic were found in some samples. In the Fig. 3 are shown the microstructures of some Sn–Zn–Al alloys.

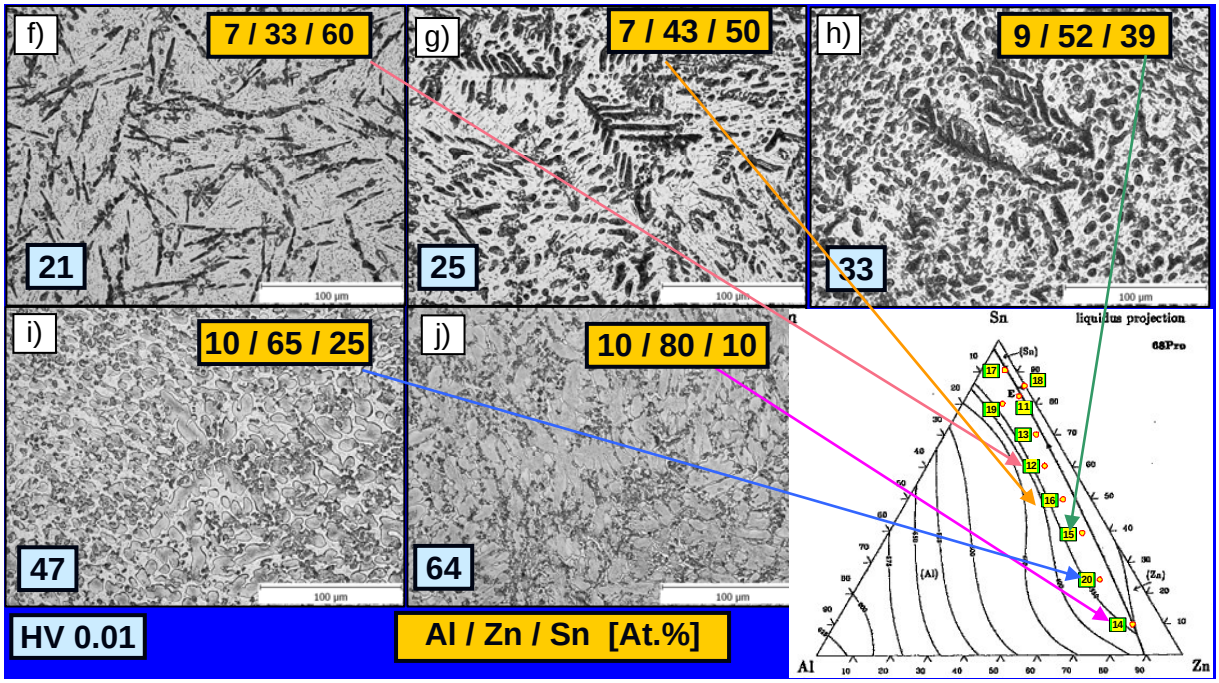

Fig. 3 *Microstructure, chemical composition and micro-hardness HV 0.01 of some Al–Sn–Zn alloys (composition: 1. number – Al content, 2. number – Zn content, 3. number – Sn content in atomic percent, mean values of HV are in the bottom left corner of pictures)*

Vickers micro-hardness test HV was performed – see Fig. 3. It can be concluded from the micro-hardness measurements that the micro-hardness decreases with the rising tin content in all hypoeutectic alloys. Aluminium, however, essentially increases micro-hardness, especially with high zinc contents, when the micro-hardness is nearly double compared to the binary tin–zinc system.

X-ray micro-analysis EDAX was performed as both the surface and point micro-analyses. SEM analysis showed considerable heterogeneity of microstructure which will relate to the formation of non-equilibrium phases in the course of solidification. Mostly two or three types of phases of various chemical compositions were discovered, which was also proved by the following X-ray microanalysis. The phase analyses of the Al–Sn–Zn alloys are presented as an example in Fig. 4. Three typical phases were identified here: white phase contains high

concentration of tin without aluminium, grey phase contains high concentration of zinc without of tin and small black phases contains high concentration of Al + Zn and a certain concentration of oxygen. Oxygen can originate from the preparation of samples (high affinity of aluminium to oxygen at high temperatures of re-melting).

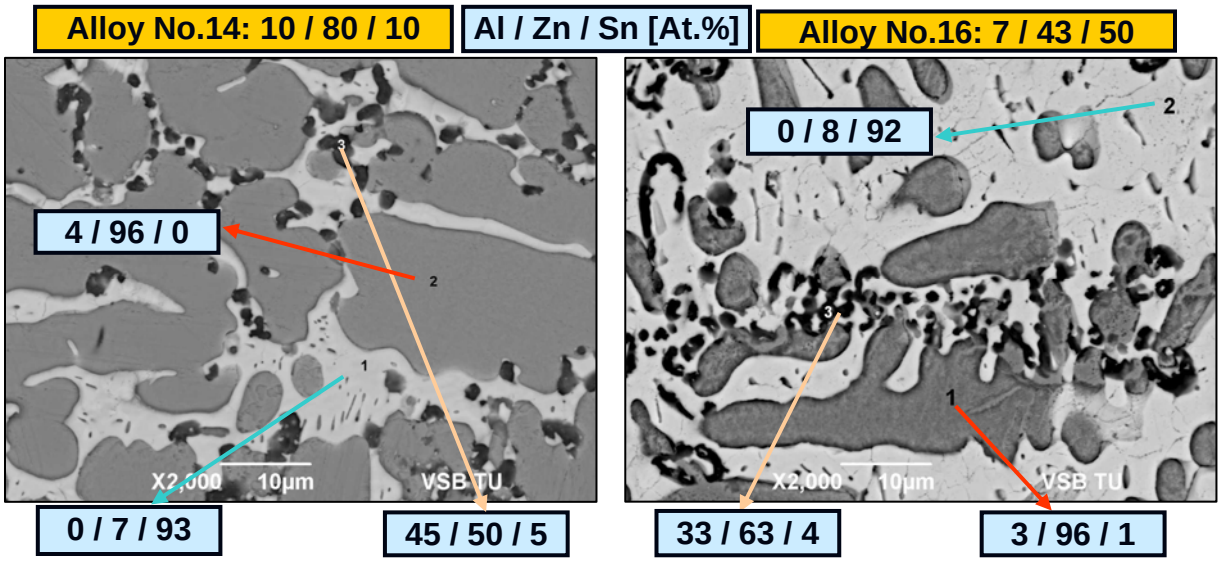

Fig. 4 *X-ray micro-analysis EDAX of phases in the Al–Sn–Zn alloys (composition: 1. number – Al content, 2. number – Zn content, 3. number – Sn content in atomic percent)*

Temperatures of liquidus, solidus and other transformation reactions and latent heats of melting and solidifying were investigated applying the DTA method. Experiments were performed with experimental laboratory system Setaram SETSYS 18_{TM} for thermal analysis. DTA analysis was conducted under an inert Ar atmosphere (purity > 6N). During analysis a constant dynamic atmosphere was maintained in the furnace space (flow of Ar 2 l/h). Analyses of samples were made in corundum crucibles. Prepared samples were analysed at heating and cooling rates of 4°C/min in the temperature range of 20 ÷ 450°C. Two cycles of DTA experiments were performed: heating from 20 to 450°C, then cooling to 100°C and again heating up to 450°C and cooling to room temperature. Second DTA measurements (heating and cooling) were evaluated.

Insufficient data about structure and properties of investigated samples persist at present time. Lack of exact experimental data in the field of phase transformations – significant differences [1-8] exist too. The temperatures of liquidus (T_L), solidus (T_S) and other transformation temperatures and latent heats of melting and solidifying were investigated at heating and cooling. The obtained experimental data were compared with thermodynamic calculations and with the data of known Sn–Zn binary system – see Fig. 5 and Al–Sn–Zn ternary system – see Fig. 6. MTDATA, PANDAT and THERMO-CALC programs were used for modelling of phase equilibria.

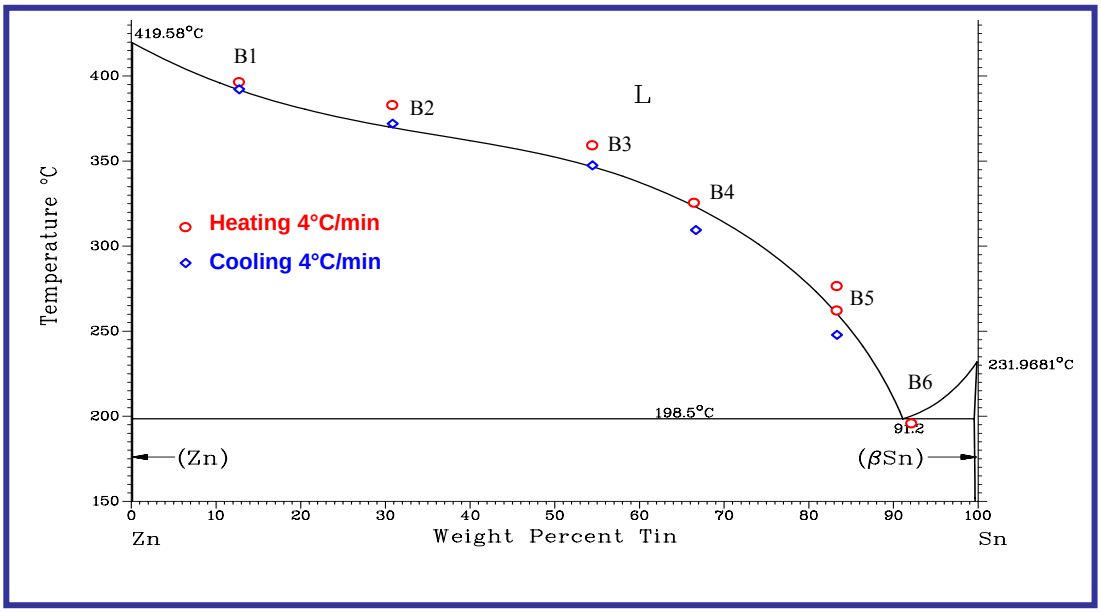

Fig. 5 Experimentally obtained values of phase transformation temperatures (DTA) compared with the Sn – Zn binary system [1]

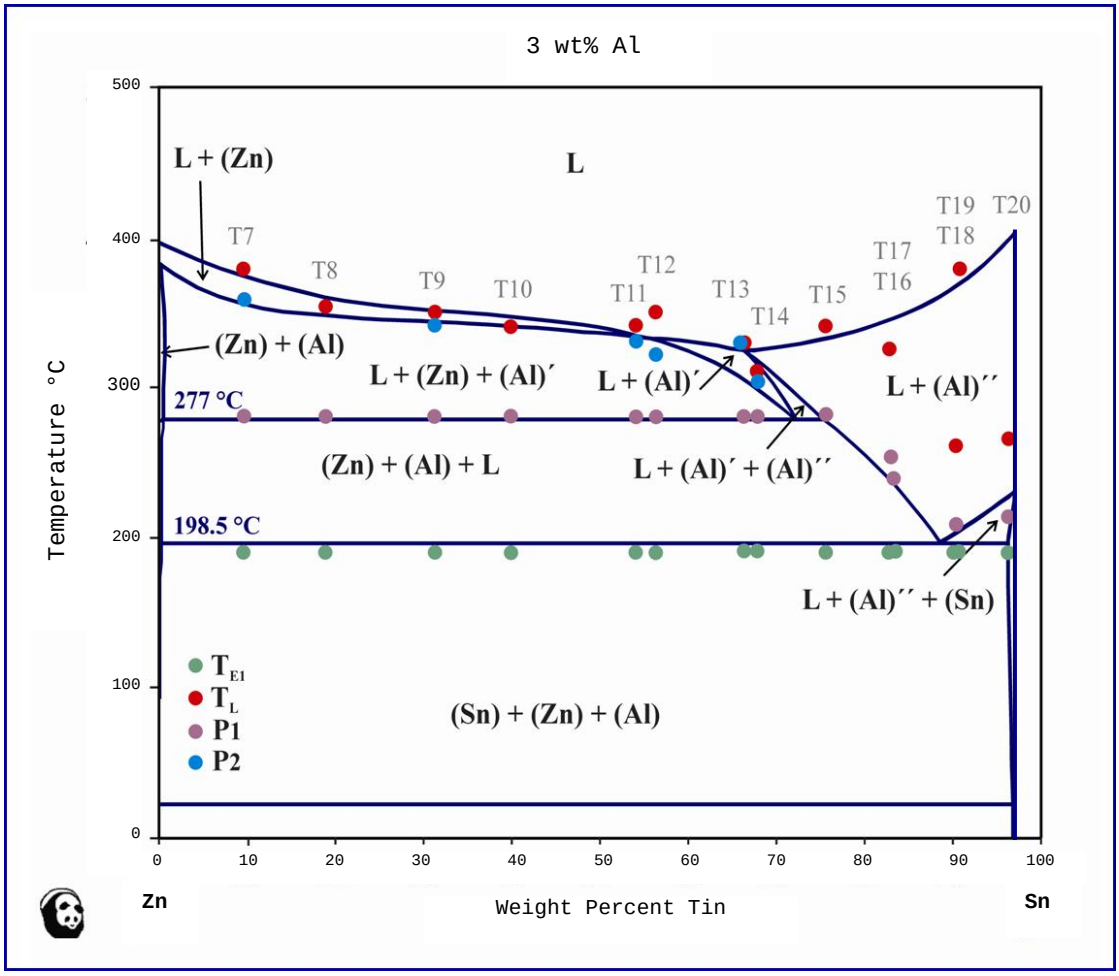

Fig. 6 Experimentally obtained values of phase transformation temperatures (DTA) in the Al–Sn–Zn system with 3 wt% Al compared with the values of PANDAT calculations

Discussion

On the basis of the performed experiments and results obtained by means of DTA measurements it is possible to draw the following conclusions:

- The temperature of eutectic reaction of investigated Sn–Zn binary alloys was found to be 198.0 °C and 198.8 °C respectively, which is in excellent agreement with the widely accepted temperature of eutectic reaction (198.5 °C) [1].
- The temperatures of liquidus T_L of binary alloys, obtained from the heating curves, were slightly higher than those in the published Sn–Zn binary system [1]. This may be caused by the delay of heat transfer in the sample due to a limited thermal conductivity of the sample.
- The temperature of ternary eutectic reaction in the Al–Sn–Zn system was found to be 197.6 °C, which is about 1 °C lower than the temperature of the binary eutectics of the system Sn–Zn (198.5 °C). The decrease of the temperature is caused by the addition of Al.
- The invariant reaction $L+(Al)' \leftrightharpoons (Al)''+(Zn)$ – see point U_1 in Fig. 2 and Table 1 takes place at the temperature 277.8°C [6], which is in good agreement with our DTA analyses.
- The liquidus temperatures correspond to the calculated liquidus curve or are just slightly higher (by a few degrees). The alloys No T18 and T20 content less than 3 wt.% Al, this is why the T_L points lie below the thermodynamic calculated liquidus.

We have found three types of phases in the structure of ternary Al–Sn–Zn alloys using X-ray micro-analysis EDAX: the primary phase with the concentration 3÷4 at.% Sn and 96 at.% Zn without Al, the eutectic phase with 93 at.% Sn and 7÷8 at.% Zn without Al, and tiny oxide phases on the grain boundary with high Al + Zn concentrations. Oxide phases originated from the atmosphere in the course of the melting and cooling processes in the furnace although we used a graphite crucible and the melt was covered by graphite powder.

Conclusion

Some results of the study of Al–Sn–Zn system, which can be a possible lead-free solder candidate for high temperature-applications in electronics and for automotive industry, were presented in this paper. The experimental and thermodynamic study of the binary Sn–Zn and ternary Al–Sn–Zn systems were carried out. The results are summarized in the figures above.

To apply these alloys as high-temperature solders for electronics and automotive industries, it will be necessary to perform further technological tests, such as tests of rezistivity, wettability, solderability, mechanical tests, which are in the state of elaboration. Alloys with higher chemical and structural homogeneity have to be prepared in a furnace under vacuum (respectively in an inert atmosphere) or in evacuated ampoules.

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