Low-temperature alloys for lead-free solders – study of physico-chemical characteristics

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Abstract. New types of lead-free solders on the base of tin with addition of metals Ag, Al, Bi, Cu, In, Mg, Sb, Zn were studied. Various alloys were experimentally prepared by smelting of metals in an inert atmosphere or in vacuum in resistance furnace. Purity of metals was minimally 4N. The specimens of solders were studied metallographically including the micro-hardness measurements, complete chemical analysis (ICP-AES, OES), X-ray micro-analysis of alloys by SEM and EDX in order to determine the composition and identification of individual phases. Significant temperatures and enthalpies of phase transformations were determined by DTA. After long-term annealing of selected alloys in vacuum followed by quenching the structural and chemical microanalyses of the present phases and their limit concentrations were carried out. The achieved results were compared with the thermodynamic modelling of the ternary systems (ThermoCalc, Pandat, MTDATA and databases CALPHAD, COST 531 and COST MP0602). Electrical resistivity, density, magnetic susceptibility and wettability of solders were measured as well.

1. Introduction

Recent EU legislation „Directive WEEE – Waste from Electrical and Electronic Equipments“ and “Directive 2002/95/EC – Restriction of the use of certain Hazardous Substances (RoHS) in electrical and electronic equipments” prohibited the use of lead containing solders in many industries from July 1st, 2006 [1-3]. There is continuing pressure to remove hazardous substances from currently exempt areas. The exemptions are time-limited and undergo regular scrutiny to defend their necessity.

The international cooperative project COST Action MP0602 „High-Temperature Lead-Free Solders“ was initiated in the 2007 with the aim of studying the properties of materials for potential future use as substitutes for high-temperature lead-containing solders (250-350 °C). The main aim of the project was to increase the fundamental knowledge of the crucial properties of alloys that can be used as environmentally friendly alternatives to high-temperature solders. Much of the work of the Action was devoted to a programme of investigation of chemical, physical and mechanical properties, such as melting point, wettability and surface tension of various binary and ternary alloys [4].

Aim of this work was to study of selected binary or ternary alloys on the base of tin and their properties: microstructure, chemical composition of alloys and individual phases in them, micro-hardness, wettability, electrical resistivity, and so on. The achieved results were compared with the thermodynamic modelling of the ternary systems [5].

2. Experiment

Various alloys on the base of tin with addition of metals Ag, Al, Bi, Cu, In, Mg, Sb, Zn were experimentally prepared by smelting pure metals in an electrical resistance furnace an inert atmosphere or in evacuated quartz ampoules. The purity of individual metals was minimally 4N.

The following characteristics were studied: temperatures and enthalpies of phase transformations (DTA, TG, DSC) of individual alloys at the rates of re-heating and cooling of specimens of 4 °C/min,
macro- and microstructural analysis (optical microscopy OM), micro-hardness, chemical analysis: ICP-AES, optical emission spectrometry (OES), X-ray microanalysis of individual phases in the structure of alloys (WDX, EDX), measurement of electrical resistivity of selected alloys in dependence on the temperature, test of wettability with or without use of fluxes. Reactive diffusion at the contact of a solid phase (Cu, Ni, Cu-Zn) with melt of solders was studied too. The theoretically calculated isothermal and isopleths sections (software ThermoCalc, MTDATA and Pandat™) of selected ternary systems at various temperatures and compositions were compared with experimental results (DTA, EDX, ICP-AES, structural analyses).

Metallographic analyses discovered practically fine-grained structure, mostly of a eutectic type, often with present dendritic formations. Results of microstructural and chemical microanalysis of present phases in selected alloys were detected by using of OM and X-ray analysis (EDX, WDX). The some alloys (for example Al-Sn-Zn) were subsequently submitted to long-term annealing in evacuated ampoules. The annealing temperatures were 250, 300 and 350 °C, annealing times 3, 7, 14 and 28 days followed by quenching into water. After them the image analysis of metallographic pictures and chemical microanalysis (EDX) of presented phases were carried out. The obtained results were compared with thermodynamic modelling of individual binary or ternary systems.

3. Results and discussion

3.1. Microstructure, DTA and chemical analyses of aluminum–tin–zinc alloys

The phase diagrams of Sn–Zn and Al–Sn binary systems are a simple one of eutectic type [6]. Equilibrium Al–Zn phase diagram [6] comprises from the eutectic reaction at 381 °C and eutectoid reaction at 277 °C. The theoretical thermodynamic description of the ternary Al–Sn–Zn system based on existing experimental data was published by Fries et al. [7] There are two important invariant reactions in this system: eutectic reaction L ↔ (Al) + (Zn) + (Sn) at the temperature \( T_E = 197.3 \) °C and invariant peritectic reaction L + (Al) ↔ (Al) + (Zn) at the temperature \( T_U = 277.8 \) °C.

Microstructures of specimens acquired by the microscope Neophot 32 using the camera Olympus DP 11 differed very slightly with respect to the history of their preparation. Metallographic analyses discovered practically fine-grained structure, mostly of a eutectic type, often with present dendritic formations. A certain portion of fine lamellar ternary eutectics (Al) + (Sn) + (Zn) with a minority Al presence in all the samples was identified. Needles of primarily precipitated Zn and the secondary Al–Zn alloy containing 9-16 at.% Zn were found in the structures. Results of microstructural and chemical microanalysis of present phases in selected alloy No. 16N are shown in figure 1 by using of OM and X-ray EDX analysis.

The samples of Al–Sn–Zn alloys were subsequently submitted to long-term annealing in evacuated ampoules. The annealing temperatures were 250, 300 and 350 °C, annealing times 3, 7, 14 and 28 days. Figure 2 shows microstructure of sample 16N after the annealing regime 250 °C/28 days followed by quenching into water.

Figure 1. Macro- and microstructure and EDX analysis of alloy No. 16N: 50 Sn 43 Zn 7 Al (at.%).
Figure 2. Microstructure and EDX analysis of alloy No. 16N (annealing 250°C/28 days).

Table 1. DTA analysis (heating rate 4 °C/min) and microhardness $HV_{0.01}$ of Al–Sn–Zn alloys.

| Specimen | Chemical composition (at.%) | $T_E$ (°C) | $T_U$ (°C) | $T_1$ (°C) | $T_2$ (°C) | $T_L$ (°C) | $HV_{0.01}$ eutectic Al-Zn phase |
|----------|-----------------------------|------------|------------|------------|------------|------------|----------------------------------|
| 1        | 7.4 Al, 17.8 Sn, 87.7 Zn    | 197.1      | 279.3      | 360.1      | 385.0      | 64         |                                  |
| 2        | 8.9 Al, 19.4 Sn, 71.7 Zn    | 197.8      | 279.0      | 346.8      | 355.5      | 44         |                                  |
| 3        | 9.2 Al, 35.4 Sn, 55.4 Zn    | 198.9      | 278.3      | 337.3      | 342.3      | 32         |                                  |
| 4        | 11.2 Al, 50.9 Sn, 37.9 Zn   | 198.8      | 278.7      | 294.1      | 324.0      | 27         |                                  |
| 5        | 11.1 Al, 69.4 Sn, 19.5 Zn   | 198.6      | 241.0      | 360.0      | 21         |            |                                  |
| 11       | 3.9 Al, 79.5 Sn, 16.6 Zn    | 196.6      | 207.1      | 263.0      | 20         |            |                                  |
| 12       | 8.8 Al, 60.8 Sn, 30.5 Zn    | 197.4      | 279.8      | 294.2      | 324.4      | 21         |                                  |
| 13       | 6.6 Al, 69.0 Sn, 24.4 Zn    | 197.5      | 258.1      | 324.3      | 20         |            |                                  |
| 14       | 9.9 Al, 10.1 Sn, 80.0 Zn    | 197.2      | 278.1      | 355.7      | 363.1      | 64         |                                  |
| 15       | 9.2 Al, 39.0 Sn, 51.8 Zn    | 197.8      | 278.7      | 324.0      | 348.5      | 33         |                                  |
| 16       | 9.4 Al, 52.9 Sn, 37.8 Zn    | 197.6      | 279.1      | 310.2      | 333.0      | 25         |                                  |
| 17       | 5.7 Al, 87.4 Sn, 6.9 Zn     | 196.9      | 215.1      | 268.0      | 18         |            |                                  |
| 18       | 0 Al, 85 Sn, 15 Zn          | 198.0      |            |            |            |            | 19                  |
| 19       | 8.6 Al, 80.2 Sn, 11.2 Zn    | 198.4      | 207.8      | 379.4      | 21         |            |                                  |
| 20       | 10 Al, 25 Sn, 65 Zn         | 198.1      | 278.2      | 341.4      | 346.0      | 47         |                                  |
| 1N       | 2.5 Al, 85 Sn, 12.5 Zn      | 198.8      |            |            |            |            |                                  |
| 3N       | 4.9 Al, 70.4 Sn, 24.7 Zn    | 197.6      |            | 253.8      | 16         |            |                                  |
| 4N       | 10 Al, 10 Sn, 80 Zn         | 196.7      | 277.3      | 327.1      | 358.8      | 19         | 64                  |
| 10N      | 10 Al, 70 Sn, 20 Zn         | 197.6      |            | 239.0      | 16         | 94         |                                  |
| 12N      | 7 Al, 60 Sn, 33 Zn          | 197.9      |            | 296.5      | 16         | 96         |                                  |
| 15N      | 9 Al, 39 Sn, 52 Zn          | 197.3      | 277.5      | 325.0      | 17         | 83         |                                  |
| 16N      | 7 Al, 50 Sn, 43 Zn          | 197.9      | 277.5      | 313.6      | 16         | 73         |                                  |
| 21N      | 15 Al, 20 Sn, 65 Zn         | 197.5      | 277.6      | 325.3      | 363.4      | 43         | 17                  | 87 |
| 22N      | 25 Al, 40 Sn, 35 Zn         | 197.5      | 277.8      | 297.0      | 406.0      | 18         | 90                  |
| 23N      | 18 Al, 40 Sn, 42 Zn         | 197.6      | 277.8      | 311.6      | 337.0      | 16         | 77                  |
| 24N      | 32.3 Al, 9.8 Sn, 57.9 Zn    | 196.9      | 277.4      | 344.5      | 412        | 446.9      |                                  |
| 25N      | 51.5 Al, 18.7 Sn, 29.8 Zn   | 197.4      | 277.4      | 333.8      | 439        | 356.4      |                                  |
| 26N      | 40.5 Al, 20.5 Sn, 39 Zn     | 197.8      | 277.4      | 302.9      | 332        | 506.5      |                                  |

The differential thermal analysis (DTA), the thermo-gravimetry & differential scanning calorimetry (DG/DSC) were carried out in the device SETARAM SYSTEM 18™. The results of the measurements of the temperatures $T_E$ (eutectic reaction), $T_U$ (invariant peritectic reaction), temperatures of phase transitions $T_1$, $T_2$ in solid state and $T_L$ (liquidus) were acquired at the heating...
rate 4 °C/min, see table 1 and figure 3. The experimentally obtained transition temperatures are presented in the calculated isopleth for 3 wt.% of Al in figure 3. Excellent agreement was achieved in the case of ternary invariant reactions temperatures. The temperature of ternary eutectic reaction $T_E$ in the Sn–Zn–Al system was found to be $197.7 \pm 0.7 ^\circ C$, this value is very close mainly to the value presented in [7]. The mean value of invariant peritectic temperature $T_U$ was found to be $278.6 \pm 0.7 ^\circ C$. Experimental value obtained in this work is about 0.8 °C higher than [7].

Other phase transitions were observed in ternary alloys above the eutectic reaction, majority of these phase transition temperatures, e.g. liquidus temperatures, were in an excellent agreement with thermodynamic calculations.

Microhardness according to Vickers was measured in all the specimens by the microhardness tester LECO applying the load 0.01 N. The results of measurements $HV_{0.01}$ are presented in table 1 as well.

![Figure 3. Vertical section in Al–Sn–Zn ternary diagram for 3 wt.% Al with the experimental values of temperatures (DTA analyses).](image)

3.2. Electrical resistivity of solders

The electrical resistivity is an important property when determining suitable types of lead-free solders. Resistivity of metals is dependent on the purity of individual elements and on the structural perfection of materials. Even a slight amount of impurities can change it considerably. The classical four-point method at room temperature 23 °C was used for the resistivity measurement – see table 2. It was interesting that the electrical resistivity of Al–Sn–Zn alloys was lower then at commercially used solder Sn–Ag–Cu.

Electrical resistivity of Al–Sn–Zn alloys was measured from the room temperature to 500 °C by contactless method in rotating magnetic field [8]. The total uncertainty in resistivity values was ± 5%. The temperature dependencies of resistivity were linear and fitted with linear function in solid and liquid states for all Al–Sn–Zn alloys – see figure 4.
Table 2. Electrical resistivity of selected solders at 23 °C.

| Composition (wt.%) | Resistivity (μΩ cm) |
|--------------------|---------------------|
| Sn – 37 Pb         | 16.2                |
| Sn – 3.8 Ag 0.7 Cu | 11.7                |
| Sn – 2.7 Al 3.3 Zn | 10.8                |
| Sn – 3 Al 41 Zn    | 9.34                |
| Sn – 0.6 Al 7.4 Zn | 9.83                |

Composition of alloys (at.%):
No. 1: Sn – 6.5 Zn 2.5 Al
No. 2: Sn – 12 Zn 8 Al
No. 3: Sn – 25 Zn 5 Al
No. 4: Sn – 43 Zn 7 Al
No. 5: Sn – 65 Zn 10 Al

Figure 4. Temperature dependence of the electrical resistivity for some Al–Sn–Zn alloys.

3.3. Wettability of solders

Wettability is a property of metal surface that expresses the material diffusivity. Formation of an intermetallic compound is a necessary condition of good wetting and linking of the solder and wetted metal. Tested components were suspended on the dynamometer above the vessel with the molten solder. The measurement itself was carried out on the meniscograph solderability tester. The device consists of a measuring head with a spring micro-balance, a holder for gripping the measured object, a soldering bath and electronic control unit. The tested specimens of copper, nickel or brass (Cu-Zn) wires had the diameter 1 mm. Rinsing-less fluxes were used for Al-Sn-Zn solders: types RX (alcoholic flux) and RXZ (semi-aquatic flux), for Sn–Ag–Cu solders: types Epsilon M5, Epsilon 5 and Epsilon 2 from the firm Sluvis, Prague. Cu, Cu-Zn and Ni wires were tested at the temperature 50 °C above the liquid temperature applying various fluxes or without any flux. An example of the curves of wettability measurements is presented in figure 5.

Figure 5. Wettability of a) solder Sn 3.8 Ag 0.7 Cu (wt.%); b) solder Sn 9 Zn 0.6 Al (wt.%)
a) Sn 3.8 Ag 0.7 Cu, wire Ni, flux Epsilon 2  b) Sn 9 Zn 0.6 Al, wire Ni, flux RX
4. Reactive diffusion
This section deals with the problems of dissolution of the solid phase A in the melt B, diffusion of atoms of the melt into the solid phase accompanied by creating new phases and/or chemical reactions and finally by diffusion of atoms from the solid phase into the melt. Those processes usually proceed at the presence of convection in the melt. At the same time the process a significant movement of the interface between the solid phase and the melt takes place, the rate of which depends on the properties of atoms A and B and their interaction, temperature T and time t of the process in question. Furthermore, it depends on the geometric arrangement, on the volume of the melt and conditions enabling or restricting convection in the melt. The relevant phase diagram provides a prediction of newly appearing phases. During the reactive diffusion, due to the rate of the solid phase dissolution in the melt, conditions of the equilibrium state do not have to be always met because of non-stationary processes. During the diffusion of the melt B atoms into the solid phase A new phases form and grow, i.e. the diffusion processes take place in areas with moving interface boundaries. When new phases appear in the course of reactive diffusion, surface and subsurface layers of material of various compositions, properties and thickness also form.

The uni-directional experiment was realized using the „sandwich” specimens. A layer of a tin-based solder was inserted between two Cu plates. Five compositions of lead-free solder alloys were used: pure Sn, Sn97Cu3, Sn95.5Ag3.8Cu0.7, Sn95Sb5 and Sn91Zn9. Two plates of high-purity copper were 0.5 mm thick, the other dimensions were 20 x 10 mm. The Sn-based solders inserted between the two Cu plates were rolled down to the thickness 0.6 mm. Copper plates were covered by a layer of suitable flux. The soldered joint was created using a heating element. The sandwiches were held at the temperature 255 ÷ 285 °C (above liquid temperature) for 40 ÷ 120 seconds. Prepared specimens were subsequently annealed at T = 300 °C for 18, 24, 48 and 92 h.

The η-Cu6Sn5 grows into during annealing at the temperature T = 300 °C on the interface with the Cu. Copper dissolves in liquid Sn-based solder up to the saturation concentration about 4 at.% (2.2 wt.%) Cu. As a consequence of Sn diffusion into solid Cu, phase η grows with time and subsequently phase ε (Cu3Sn, 75 at.% Cu and 25 at.% Sn) appears close to the pure Cu. The specimens were cooled on the air after annealing and the temperature decreased relatively quickly below the eutectic temperature 227 °C. The joint Cu/Sn95.5Ag3.8Cu0.7 is shown in figure 6 after 24 hours of annealing as an example.

**Figure 6.** Microstructure and concentration profiles in the joint Cu/Sn 3.8 Ag 0.7 Cu (wt.%) after annealing at 300 °C for 24 hours.
The growth of phase \( \varepsilon \) should proceed with time according to parabolic law \( \chi_\varepsilon(t) = \alpha \cdot \sqrt{t} \) where \( \chi_\varepsilon(t) \) is the thickness of phase \( \varepsilon \) and \( \alpha \) is the constant which characterizes the rate of phase growth. The values \( \chi_\varepsilon(t) \) can be obtained experimentally using the metallographic pictures from relatively large areas. The evaluated values \( \alpha \) from the metallography and X-ray EDX microanalysis are presented in table 3. They were determined for times \( t = 24 \) and \( 48 \) h. The calculated values \( \alpha \) for Cu/Sn and Cu/Sn 3 Cu joints from EDX measurements were in very good agreement.

Table 3. Evaluation of the rate of growth \( \alpha \) of phase \( \varepsilon \) in „sandwich“ specimens at \( T = 300 \) °C.

| EDX analysis | \( t \) (h) | \( \alpha \cdot 10^6 \) \( \text{(cm/s}^{1/2}\text{)} \) | mean \( \alpha \cdot 10^6 \) \( \text{(cm/s}^{1/2}\text{)} \) | Metallography | \( t \) (h) | \( \alpha \cdot 10^6 \) \( \text{(cm/s}^{1/2}\text{)} \) | mean \( \alpha \cdot 10^6 \) \( \text{(cm/s}^{1/2}\text{)} \) |
|--------------|-----------|---------------------------------|-----------------|------------|-----------|---------------------------------|-----------------|
| Cu/Sn        | 24        | 3.23                            | 3.33            | Cu/Sn     | 18        | 5.84                            | 5.57            |
|              | 48        | 3.43                            |                  |           | 24        | 5.10                            | 4.38            |
| Cu/Sn 3 Cu   | 24        | 3.16                            | 3.25            | Cu/Sn 3 Cu| 24        | 6.23                            | 5.41            |
|              | 48        | 3.34                            |                  |           | 48        | 4.0                             |                |
| Cu/Sn 3.8 Ag | 18        | 6.12                            |                  | Cu/Sn 3.8 Ag| 18        | 6.6                             |                |
| 0.7 Cu       | 24        | 3.42                            | 4.76            | 0.7 Cu    | 24        | 3.63                            | 4.27            |
|              | 48        | 4.30                            |                  |           | 48        | 2.40                            |                |
|              | 92        | 5.21                            |                  |           | 92        | 4.46                            |                |

The tentative calculation of Sn diffusivities at \( T = 300 \) °C based on the growth of the phase \( \varepsilon \) into Cu were performed using Wagner relation [9]. Based on the X-ray analysis of concentration curves we searched for the size of interval \( \Delta x = 2 \) μm, where the Sn concentration in Cu decreased nearly to zero. We can estimate the diffusivity \( D \) from the value \( \Delta x \) and the known time of annealing \( t \) using the equation:

\[
\frac{\Delta x}{2\sqrt{Dt}} \approx 1.5; \quad \text{erfc}(1.5) = 0.034.
\]

Diffusion joint : Cu/Sn, \( t = 48 \) h, \( T = 300 \) °C, \( \Delta x = 2 \) μm, \( D \approx 2.6 \cdot 10^{-14} \text{ cm}^2/\text{s} \).

Diffusion joint : Cu/Sn 3 Cu \( t = 24 \) h, \( T = 300 \) °C, \( \Delta x \approx 2 \) μm, \( D \approx 5.1 \cdot 10^{-14} \text{ cm}^2/\text{s} \).

Diffusion joint : Cu/Sn 9 Zn \( t = 92 \) h, \( T = 300 \) °C, \( \Delta x \approx 2 \) μm, \( D \approx 1.3 \cdot 10^{-14} \text{ cm}^2/\text{s} \).

When observing the growth of phases in system Cu–Sn on planar specimens at the temperature \( T = 300 \) °C a very irregular growth of phase \( \eta \), especially into the melt, was discovered and estimated of the rate of growth of phase \( \varepsilon \) into Cu according to the parabolic law were performed as well for the other lead-free solders.

5. Conclusion
Some results of the study of selected binary and ternary alloys, which can be possible as lead-free solder candidate for high temperature-applications in electronics and for automotive industry are presented in this paper.

For example alloy Sn 31 Zn 2 Al (wt.%) had the lowest electrical resistivity, but wettability and corrosion resistance were worse then solders Sn–Pb or Sn–Ag–Cu. On the other hand, the alloys Sn–In–Cu had the same electrical resistivity as Sn–Ag–Cu solder, but the wettability with Cu and corrosion properties were very good.
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