Contribution to the aluminum–tin–zinc ternary system

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Abstract. The Sn–Zn–Al alloys are one of significant candidates in the proposal of alternative lead-free solders for higher temperature soldering. This paper deals with the study of the aluminum–tin–zinc system. Twenty Sn–Zn–Al alloys together with six binary Sn–Zn alloys were prepared and studied experimentally. Alloys were prepared from pure Sn, Zn and Al (melting and cooling in a vacuum resistance furnace). The specimens 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 Sn–Zn–Al system (computer programs THERMOCALC, MTDATA, PANDAT and databases CALPHAD, COST). Electrical resistivity, density, magnetic susceptibility and wettability of Sn–Zn–Al solders were measured as well.

1. Introduction
The Sn–Zn–Al ternary system can be one of applicable alternative alloys to high lead content Pb–Sn solders, when the soldering process reaches temperatures as high as 300 °C. These solders can be used above all in automotive industry, in heat exchangers and in special applications. Tin – zinc alloys are used as solders for aluminum.

The tin – zinc binary system diagram is of a eutectic type. The eutectic reaction proceeds at the temperature of 198.5 °C and the concentration of 85.1 at.% Sn. The zinc limit solubility in tin at this temperature corresponds to 0.6 at.% Zn, while on the other hand, the tin maximum solubility in hexagonal zinc is only 0.039 at.% Sn [1].

The binary diagram of the aluminum – tin system [1, 2] is also of a eutectic type with a considerably limited solubility in the area of solid solution (Al) and tetragonal (Sn). The tin solubility in (Al) solid solution exhibits a retrograde character with a maximum of approximately 0.026 at.% Sn at the temperature of 625±20 °C [2].

The Al–Zn equilibrium phase diagram [1] represents a eutectic system involving another reaction and the existence of a miscibility gap area in solid phase α (Al). The eutectic reaction proceeds at 381 °C closer to Zn side (the eutectic point corresponds to 88.7 at.% Zn). (Al) solid solution has an extended area of homogeneity interrupted at the temperature of 351.5 °C and the content of 39.5 at.% Zn. Between this temperature and the temperature of 277 °C, (Al) disintegration into two solid solutions occurs: (Al) with a lower Zn content and (Al′) with a high zinc content (up to 59 at.%). The
Zn solubility in (α Al) increases from 2.2 at.% at 110 °C to 16.5 at.% at 277 °C. Above temperature 277 °C the zinc solubility increases from 59±1 at.% Zn at 277 °C to 67±1 at.% Zn at the eutectic reaction. The maximum solubility of Al in (Zn) is 2.8±0.2 at.% Al at the eutectic temperature and decreases along with a decreasing temperature to 1.6 at.% Al at 277 °C and down to 0.07 at.% Al at the room temperature. Then, (Al) + (Zn) two-phase structure can be expected in the equilibrium crystallization of Al–Zn alloys. In Table 1 thermodynamic values and reactions in Al–Sn, Sn–Zn and Al–Zn binary systems are listed.

Table 1. Thermodynamic values of phase transformations of Sn, Zn and Al pure metals and equilibrium compositions of solidus and liquidus at the eutectic or eutectoid reaction in Al–Sn, Sn–Zn and Al–Zn binary systems [1, 2].

| Metal A | $T_m$ (°C) | $\Delta H_m$ (J/mol) | $X_{SE}$ (at.%) | $X_{LE}$ (at.%) | $T_E$ (°C) |
|---------|------------|-----------------------|---------------|---------------|------------|
| Sn      | 232        | 7029                  | 1.0           | 97.6          | 228        |
| Zn      | 419.6      | 7322                  | <0.01         | 97.6          | 228        |
| Al      | 660.5      | 10711                 | 0.6           | 14.9          | 198.5      |

$T_m$ – melting point of metal A  
$\Delta H_m$ – molar enthalpy of fusion for metal A  
$T_E$ – eutectic temperature  
$X_{SE}$ – maximal solubility of element B in A at $T_E$  
$X_{LE}$ – concentration of element B in liquidus at $T_E$  
* – eutectoid reaction

The Al–Sn–Zn ternary system was studied in details by Prowans [3] and later by Nayak [4] and other authors [5, 6]. A revision of the Al–Sn–Zn ternary system and a thermodynamic calculation was performed by Fries [7] (see Figure 1). The latest findings on this system are mentioned on www.msiport.com [8] and www1.asminternational.org [9] proposed by M. Hubert-Protopopescu [10]. When researching this system it was found out that the liquidus areas in the Al–Sn–Zn ternary system including their isotherms differ according to data of authors [3-10] both in a position of the eutectic valley and in a character of the isoliquidus courses. So, there are significant disproportions in describing this system according to various authors. The thermodynamically shaped liquidus area according to Fries [7] is closer to the diagram designed experimentally by Nayak [4]. In Table 2 are summarized the invariant equilibria in the Al–Sn–Zn ternary system.

Figure 1. Thermodynamic calculated liquidus surface of the Al–Sn–Zn ternary system by [7, 10] with the denotation of nine sections for image of isopleths.
Table 2. Thermodynamic invariant equilibria in the Al–Sn–Zn ternary system.

| $T$ (°C) | Phase | Sn (at.%) | Zn (at.%) | Al (at.%) | Ref. |
|----------|-------|-----------|-----------|-----------|------|
| **L**    | (Al)  | 61.76     | 31.79     | 6.45      | [7]  |
|          | (Al') | 0.01      | 14.17     | 85.82     |      |
|          | (Zn)  | 0.13      | 98.24     | 1.63      |      |

| $T$ (°C) | Phase | Sn (at.%) | Zn (at.%) | Al (at.%) | Ref. |
|----------|-------|-----------|-----------|-----------|------|
| 277.8    | L     | 61.76     | 31.79     | 6.45      |      |
|          | (Al)  | 0.01      | 14.17     | 85.82     |      |
|          | (Al') | 0.02      | 58.97     | 41.01     |      |
|          | (Zn)  | 0.13      | 98.24     | 1.63      |      |

On the basis of structural analyses, SEM and x-ray analysis EDX and DTA, the aim of this paper was to examine validity of the published diagrams, to perform thermodynamic calculations of phase equilibria after long-term isothermic annealing of specimens of selected alloys. Other properties of the selected Al–Sn–Zn alloys, such as resistivity, density, magnetic susceptibility and wettability are tested as well.

2. Assessment of the Al–Sn–Zn ternary system

Figure 2 shows isothermal cross-sections through the ternary Al–Sn–Zn system at the temperatures of 300 °C to 270 °C according to [7-11]. The diagram in Figure 2 b) is beside character of the existence of (Al) + (Al') + (Zn) phases area, which penetrate deep inside the diagram at the expense of three-phase (Al) + (Al') + L area in the cross-section at 290 °C. Comparing the cross-sections at the temperatures of 300 °C and 280 °C, it is obvious that the cross-section at 290 °C is improperly plotted in term of the coexistence of phases. Sebaoun [11] studied the Al–Sn–Zn phase diagram using the reactive diffusion with preparing three diffusion pairs: Zn-10 wt.% Sn/Al, Zn-28 wt.% Al/Sn and Al-10 wt.% Sn/Zn (see lines g, h and i in Figure 1), which were annealed for a period of 3 up to 6 hours at the temperatures of 270, 280 and 290 °C. Following annealing, the specimens were water-quenched rapidly. From structural and chemical microanalyses (SEM/EDX) the respective diffusion routes were found out, on the basis of which a modified Al–Sn–Zn diagram was created (see the isothermal cross-sections in Figure 2 b), c) and d). The following phases were found out: (Al), (Al'), (Zn) and a solidified tin-rich melt. In all cases the tin solubility in (Al') phase was < 0.8 at.% Sn. That’s why the isothermal cross-section in Figure 2 b) has been explicated incorrectly.
Figure 2. Isothermal sections in Al–Sn–Zn ternary system at temperatures 300 °C by [7, 10] and at 290 °C, 280 °C a 270 °C by [11].

Figure 3. Vertical sections in Al–Sn–Zn ternary system a) red line „a“ in Figure 1 [7, 10]; b) green line „b“ in Figure 1 [3]; c) light blue line „c“ in Figure 1 [3]; d) orange line „f“ in Figure 1 [11].
Figure 3 depicts 4 different isoplethic sections in the ternary Al–Sn–Zn system which has been marked out in Figure 1. Figure 3 a) shows a cross-section for 50 at. % Sn according to authors [7, 10]. On confronting this diagram with isothermal cross-sections in Figure 2, we may state that the given vertical cross-section corresponds to reality. In the diagram in Figure 3 b) Prowans [3] has marked out two areas with a congruent designation (Al) + (Zn) + L, though a phase transformation occurs at the temperature of 275 °C. However, this contradicts the Gibbs phase rule as well as laws of thermodynamics. Therefore we added two thermodynamically conforming curves into the diagram in the temperature area of 275 to 350 °C. The succession of phase formation in Figure 3 b) left to right is as follows: (Al) + L → (Al) + (Al") + L → (Al") + L → (Zn) + (Al") + L → (Zn) + L. The isopleth section in Figure 3 b) conforms to the Sebaoun ideas – see Figure 2 b), however, considering the diagrams in Figures 2 a), c) and d), the tin solubility in the area of (Al) + (Al") phases is negligible, so there is a disproportion here again. In Figure 3 b), the authors’ scheme is plotted as the red curve and (Al) + (Al") + L area includes both the existing yellow tinged area above the temperature of 278 °C and the white area (marked with a green arrow), which has been considered an area of the coexistence of (Al) + (Al") phases according to [3, 11]. In Figure 3 d) all the existing phases are not complemented either. For example for the temperature of 300 °C, the succession of phase formation left to right is as follows: (Al") → (Al") + L → (Al) + (Al") + L → (Al) + L → L. In Figure 3 b), the authors have complemented the missing curves for the area of the coexistence of (Al") phase – the red curve and for (Al") + L area – the violet curve. These complemented isopleth sections have a considerable significance for understanding the succession of phase formation during crystallization of particular alloys.

3. Experiment

3.1. Experimental samples
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 graphite mould). The purity of the initial metals was 3N5 at minimum. Next alloys with different ratios of individual elements Al, Sn and Zn (marked with the letter N – see Table 3) were prepared experimentally by smelting of pure metals in an electrical resistance furnace in evacuated quartz ampoules. These Al–Sn–Zn alloys were melted at the temperature of 750 °C in a muffle furnace, held on this temperature for 15 minutes, overturned for homogenization and held on the temperature for another hour. Finally were the samples overturned again and left in the furnace to cool down until the temperature of 70 °C was reached [12 - 15]. The selected specimens were also subjected to long-term annealing in evacuated ampoules at temperatures of 250, 300 and 350 °C for periods of 3, 7, 14 and 28 days followed by water quenching. The alloys were studied metallographically after casting and after homogenization annealing, their micro-hardness was measured, their overall chemical composition was analysed (ICP-AES and OES on the SPECTROMAX device) and X-ray micro-analysis (EDX, WDX) of the coexisting phases was performed, too.

3.2. Differential thermal analysis
The differential thermal analysis (DTA) of all the specimens was performed on the SETARAM SYSTEM 18\textsuperscript{TM} apparatus. The analyses were carried out twice at the speed of heating as well as cooling 4 K/min. Table 3 presents the final results of the DTA measurements of liquid temperatures $T_L$ and eutectic transformation $T_E$ of all the specimens including the determination of phase transformation enthalpies. The eutectic reaction temperature in binary alloys was 199 °C, while in all the ternary alloys it was $T_E = 197.7 \pm 0.7$ °C. Another invariant reaction was found at the temperature of $T_U = 278.6 \pm 0.7$ °C in some specimens. It was caused by the aluminum presence in the area of medium and high Zn concentrations. Further transformations $T_1$ and $T_2$ occur in ternary alloys between the temperatures 278 °C and liquid, which requires a more detailed analysis utilizing further methods.
The experimentally obtained transition temperatures are presented in the calculated isopleth for 3 wt.% of Al in Figure 4. Excellent agreement was achieved in the case of ternary invariant reactions temperatures [16-18].

Table 3. Nominal chemical composition of Al–Sn–Zn alloys (charge) and results of DTA analysis (heating rate 4 °C/min).

| Specimen | Sn (at.%) | Zn (at.%) | Al (at.%) | $T_E$ (°C) | $T_U$ (°C) | $T_1$ (°C) | $T_2$ (°C) | $T_L$ (°C) |
|----------|-----------|-----------|-----------|------------|------------|------------|------------|------------|
| 1        | 5.5       | 87.2      | 7.3       | 197.1      | 279.3      | 360.1      | 385.0      |
| 2        | 18.2      | 73.8      | 8         | 197.8      | 279.0      | 346.8      | 355.5      |
| 3        | 33.7      | 57.4      | 8.9       | 198.9      | 278.3      | 337.3      | 342.3      |
| 4        | 52.9      | 37.1      | 10        | 198.8      | 278.7      | 294.1      | 324.0      |
| 5        | 70.8      | 18.2      | 11        | 198.6      | 241.0      | 360.0      |
| 6        | 5.8       | 94.2      | 0         | 199.1      |            |            | 397.0      |
| 7        | 19.1      | 80.9      | 0         | 199.4      |            |            | 382.0      |
| 8        | 35.5      | 64.5      | 0         | 198.9      |            |            | 357.3      |
| 9        | 56.2      | 43.8      | 0         | 198.8      |            |            | 323.5      |
| 10       | 75.7      | 24.3      | 0         | 198.9      |            |            | 272.6      |
| 11       | 82.5      | 15        | 2.5       | 196.6      | 207.1      |            | 263.0      |
| 12       | 60        | 33        | 7         | 197.4      | 279.8      | 294.2      |            |
| 13       | 70.5      | 24.8      | 4.7       | 197.5      | 258.1      |            | 324.3      |
| 14       | 10        | 80        | 10        | 197.2      | 278.1      |            | 355.7      | 363.1      |
| 15       | 39        | 51.8      | 9.2       | 197.8      | 278.7      |            | 324.0      | 348.5      |
| 16       | 50        | 43        | 7         | 197.6      | 279.1      |            | 310.2      | 333.0      |
| 17       | 91        | 6.5       | 2.5       | 196.9      |            | 215.1      |            | 268.0      |
| 18       | 85        | 15        | 0         | 198.0      |            |            |            |            |
| 19       | 80        | 12        | 8         | 198.4      | 207.8      |            |            | 379.4      |
| 20       | 25        | 65        | 10        | 198.1      | 278.2      |            | 341.4      | 346.0      |
| 1N       | 85        | 12.5      | 2.5       | 198.8      |            |            |            |            |
| 3N       | 70.4      | 24.7      | 4.9       | 197.6      |            |            |            | 253.8      |
| 4N       | 10        | 80        | 10        | 196.7      | 277.3      | 327.1      |            | 358.8      |
| 10N      | 70        | 20        | 10        | 197.6      |            |            |            | 239.0      |
| 12N      | 60        | 33        | 7         | 197.9      |            |            |            | 296.5      |
| 15N      | 39        | 52        | 9         | 197.3      | 277.5      |            |            | 325.0      |
| 16N      | 50        | 43        | 7         | 197.9      | 277.5      |            |            | 313.6      |
| 21N      | 20        | 65        | 15        | 197.5      | 277.6      | 325.3      | 363.4      | 439.6      |
| 22N      | 40        | 35        | 25        | 197.5      | 277.8      | 297.0      | 318.6      | 406.0      |
| 23N      | 40        | 42        | 18        | 197.6      | 277.8      | 311.6      |            | 337.0      |
| 24N      | 9.8       | 57.9      | 32.3      | 196.9      | 277.4      | 344.5      | -412       | 446.9      |
| 25N      | 18.7      | 29.8      | 51.5      | 197.4      | 277.4      | 333.8      | -439       | 536.4      |
| 26N      | 20.5      | 39        | 40.5      | 197.8      | 277.4      | 302.9      | -332       | 506.5      |
3.3. Microhardness
The Vickers microhardness test HV was performed. The results of HV 0.1 measurements (load 100 g) are plotted in Figure 5 in dependence on the tin content for both the binary Sn–Zn system and ternary Al–Sn–Zn alloys containing 3 wt.% Al. It can be concluded from measurements that the microhardness decreased with the rising tin content in all hypoeutectic alloys. However, aluminum increased microhardness substantially, especially with high zinc contents, when the microhardness value was nearly double compared to the binary tin-zinc system.

Figure 4. Vertical section in Al–Sn–Zn ternary diagram for 3 wt.% Al with the experimental values of temperatures (DTA analysis).

Figure 5. Dependence of the microhardness HV 0.1 on the tin content in binary Sn–Zn system and ternary Al–Sn–Zn alloys containing 3 wt.% Al.
3.4. Metallographic study

The metallographic analyses showed basically 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 was identified in all the samples. Needles of primarily precipitated Zn and the secondary Al–Zn alloy containing 9÷12 at.% Zn were found in the structures – see Figures 6 and 7.

Figure 6. SEI/EDX structural and phase analysis of the sample 16N (7 at.% Al, 43 at.% Zn, 50 at.% Sn), liquid temperature $T_L = 314\,^\circ C$.

Figure 7. Microstructural and phase analysis of the sample 16N after annealing at 250 °C in evacuated ampoule followed quenching into water.

In Figure 6 on the lefts shown a microstructure of the alloy 16N (charge: 7 at.% Al, 43 at.% Zn, 50 at.% Sn) after casting – initial state. In Figure 6 on the right is presented a microstructure with eutectic composition. Main part was formed by pure tin, on the thin lamellas of pure zinc were sometimes seen particles of (Al) solid solution. Area fraction of the Zn + (Al-Zn) phase in eutectic was 9.6 %. Microhardness of the eutectic was $HV_{0.01} = 15$. In Figure 7 is shown microstructure of the alloy 16N after long-time heat treatment at the temperature 250 °C – 3 and 28 days. It can see a matrix with eutectic and two phases (Al) with 10 – 12 at.% Zn and (Zn) with 3 at.% Al. Presence of tin in these phases has not been observed. In Figure 8 is shown a microstructure of the alloy 15N (charge: 9 at.% Al, 52 at.% Zn, 39 at.% Sn) after annealing at the temperatures 300 °C/14 days and 250 °C/28 days. In the microstructure were found: ternary eutectic with high content of tin, then solid solution (Zn) with aluminum (3 and 6 at. %). At temperature 250 °C was in structure present a phase (Al) with 11 at.% Zn and at 300 °C was found a phase (Al") with 62.3 at.% Zn.
Figure 8. SEI/EDX structural and phase analysis of the sample 16N (7 at.% Al, 43 at.% Zn, 50 at.% Sn), liquid temperature $T_L = 314 ^\circ C$.

3.5. Isothermal diffusion in ternary system Al–Sn–Zn

Figure 9. SEM/EDX microanalysis of the diffusion couple: pure tin-alloy 24N (32 at.% Al, 58 at.% Zn, 10 at.% Sn) after vacuum annealing 300 $^\circ C$/6 hours followed by quenching into water.
Phases formed by isothermal diffusion in the Al–Zn–Sn ternary system have been studied at 300 °C for the three various couples (Al–Zn–Sn)-Sn. The experiment completes a study using direct together with differential thermal analysis, and provides better understanding of isothermal equilibria. Comparing the results allows different possible diffusion paths to be proposed, and EDX microprobe analysis of phases in isothermal equilibrium gives detailed information on the Al–Zn–Sn phase diagram. As an example we show a profile of the diffusion couple: pure tin-alloy 24N (32 at.% Al, 58 at.% Zn, 10 at.% Sn) after vacuum annealing 300 °C/6 hours followed by quenching into water – see Figure 9. Region A was before the heat treatment a pure tin. During annealing diffused here Zn and Al from alloy 24N. We found in the structure: eutectics, needles of pure Zn and phase (Al) with c. 18 at.% Zn. Transition region B contained: ternary eutectic, pure Zn and phase (Al) with c. 15 at.% Zn. Region C with high concentration of Zn contained minority portion of eutectic and two phases: (Al) with c. 15 at.% Zn and (Al") 48 at.% Zn. It means that in region C were at the temperature 300 °C in equilibrium three phases: (Zn) + (Al) + (Al").

4. Thermodynamic modeling of Al–Zn–Sn ternary system
Theoretically calculated isothermal sections (software MTDATA) at 300 and 250 °C in the Al–Sn–Zn ternary system are presented in Figure 10. The positions of the chemical compositions of some alloys are noted in these diagrams together with the results of area structural analyses of individual phases. We found in all the studied alloys the presence of the ternary eutectic (Sn) + (Zn) + (Al) with high concentration of tin. Then long needles of pure zinc were found in the microstructure of alloys. Next phases were: solid solutions (Al) with content about 8-12 at.% Zn and in some cases a solid solutions (Al") with 50-60 at.% Zn.

On the basis of the DTA, structural and EDX analyses of Al–Sn–Zn alloys after crystallization and after long-time annealing in evacuated ampoules (250, 300 and 350 °C; times 3, 7, 14 and 28 days) followed by quenching into water were observed the proportions of the individual phases in the structure. The results of the phase equilibria for annealing temperatures 300 and 250 °C are presented in Figure 10 (examples for alloys 4N, 15N and 16N). The positions of the chemical compositions of some alloys are noted in these diagrams on the basis of results of area structural analyses of individual phases [16, 17].
5. Physical and technological properties of Al–Sn–Zn alloys

5.1. Electrical resistivity
Resistivity of the selected specimens of Al–Sn–Zn alloys was measured by two methods: the contact method (two-point and four-point) in accordance with DIN/IEC 468 [19] and the contactless method for measuring in a rotating magnetic field. The specimens were adapted to a unified shape in order to ensure reproducibility of the measurements. The results of the contact method measurements are shown in Table 4. It was found out that resistivity in the Al–Sn–Zn alloys was lower than in P5 solder of SAC type commonly used today.

Resistivity of metals depends on purity of particular elements and on structural indefectibility of materials. It can be changed significantly even by a negligible amount of impurities. Comparing the results of our own measurements of resistivity with literary data, for example for Sn–Pb alloy $\rho = 14.4 \, \mu\Omega\cdot\text{cm}$ according to [20] and 15.0 $\mu\Omega\cdot\text{cm}$ according to [21], or 14.27 $\mu\Omega\cdot\text{cm}$ [22] compared to 15.3 $\mu\Omega\cdot\text{cm}$ resistivity measured in our experiment (see Table 4).

### Table 4. Electrical resistivity ($\mu\Omega\cdot\text{cm}$) of solders

| Alloy | Composition (wt.%) | Resistivity ChU | Resistivity CTU |
|-------|--------------------|----------------|----------------|
| P5    | Sn95.5 Ag3.8 Cu0.7 | 11.98          | 11.7           |
| P6    | Sn63 Pb37          | 15.26          | 16.2           |
| 5     | Sn84 Al2.7 Zn13.3  | 10.8           |                |
| 15    | Sn56 Al13 Zn41     | 9.34           |                |

Notes: ChU – measured at Charles University in Prague, CTU – Czech Technical University in Prague

### Table 5. List of alloys for measurements.

| Sample no. | Zn (at.%) | Sn (at.%) | Al (at.%) | $T_L$ (°C) |
|------------|-----------|-----------|-----------|------------|
| 17         | 6.5       | 91        | 2.5       | 268        |
| 19         | 12        | 80        | 8         | 379        |
| 13         | 25        | 70        | 5         | 324        |
| 16         | 43        | 50        | 7         | 333        |
| 20         | 65        | 25        | 10        | 346        |
From this follows that the values measured in our experiment were by 12% higher than literary data in average. This may be caused by an initial condition of our specimens which were deformed by cold rolling to foils of 0.2 mm thickness and were not annealed for internal defects reduction before the measurements. Nevertheless, the results can be considered objective and comparable to one another because all the specimens had the same geometric shape, dimensions and processing history. The resistivity temperature dependences (see Figure 11) were linear in all the Al–Sn–Zn alloy specimens and were fitted with a linear function: \( \rho = \rho_T [1 + \beta(T - T_L)] \), where \( \rho_T \) stands for the molten metal resistivity at \( T_L \) temperature, \( \beta \) stands for the temperature coefficient of specific resistance. Temperature dependences \( \rho(T) \) were also linear for the solid phase and were fitted with a similar linear function. \( \rho(T) \) curves almost merged with each other during heating as well as cooling in the liquid state (molten metal). Certain hysteresis was observed in some specimens during the change from the solid to liquid state and vice versa. The total uncertainty for determination of resistivity values was determined \( \pm 5 \% \) [23, 24].

Figure 11. Temperature dependence of the electrical resistivity of some Al–Sn–Zn alloys.

5.2.Density
Figure 12 shows the temperature dependence of density for five Sn–Zn–Al alloys. Alloy no. 17 (high Sn content) exhibits the highest density. It is not without interest that a pair of alloys no. 19 and 13 and alloys no. 16 and 20 have approximately the same density at different zinc contents (see Table 5).

Figure 12. Temperature dependence of density of some Al–Sn–Zn alloys in liquid state.
5.3. Magnetic susceptibility
Magnetic susceptibility $\chi$ was measured using the Faraday method during heating and subsequent cooling at a rate of 3 K/min in a helium atmosphere in BeO crucibles [23, 24]. Pressure in the vacuum chamber was $10^{-3}$ Pa. In all the measurements it was found out that the Al–Sn–Zn alloys featured only low susceptibility to the outer magnetic field, therefore the uncertainty in susceptibility absolute values was on ± 10 % level. For all the specimens $\chi > 0$ up to $T = 200$ to 210 °C (the solid phase area) and above this temperature $\chi < 0$ (for specimen no. 20 $\chi < 0$ at $T > 140$ °C, however, a decrease was also observed at 210 °C). Other anomalies were not found at liquid temperatures, however, worth noting are temperature regions $T = 380$ to 460 °C and 530, or 580 °C, where susceptibility was constant, which was an evidence of certain structural rearrangements. The graph (see Figure 13) shows here evidently a step change of $\chi$ during the transition from the solid state to liquid.

**Figure 13.** Temperature dependence of the magnetic susceptibility of Al–Sn–Zn alloy no. 17.

5.4. Wettability
Wettability is defined as an ability of a molten solder to adhere to a surface of the material being joined in the presence of a flux at a specified temperature. A formation of an intermetallic compound is an essential condition of good wettability and the bond between a solder and a wetted metal.

The wetting balance method was used, enabling to obtain accurate quantitative results and observing also a non-equilibrium situation. A tested component was suspended on a dynamometer above a pot filled with a molten solder. The measurement of wettability was carried out on Meniscograph Solderability Tester GEC in CTU in Prague. The apparatus consists of a measuring head with a spring microbalance, a holder for clamping the tested object, a solder bath and an electronic control unit [25].

Regarding relatively small amounts of solder specimens, the measuring apparatus was modified in the part of the molten bath, so that the alloy amount needed to perform the test was reduced to approximately 8 cm$^3$. Crucibles, made of stainless steel and graphite, were used for this purpose. A small crucible with a specimen of the Al–Sn–Zn alloy was lowered and dipped into the main Pb–Sn solder bath (the eutectic composition) of a volume of c. 250 cm$^3$ in the tester pot and clamped in holders made of stainless material laid over the original pot.

Eight specimens were selected for the Al–Sn–Zn alloys wettability testing. Three types of fluxes were used for testing of wettability of solders with various substrates on a meniscograph. Almost for all the tested combinations: a solder, a material, a flux – a perfect wetting of a specimen by a solder has not occur. Non-wetting of the specimens of Cu and Ni wires resulted from the used type of fluxes, which appeared insufficient in term of the used measurement temperatures of molten solders. An example of a non-wettable course is depicted in Figure 14.
6. Discussion

When testing resistivity of solders, it was found out that the Sn–Zn–Al alloys had ρ values lower than Pb–Sn solder and even lower than the best known alternative solder SAC, whereas the presence of aluminum supported the resistivity decrease. Our prepared specimens were deformed by rolling before the testing, which resulted in an increase of ρ by approximately 12% in comparison with the non-deformed condition. A linear increase in resistivity in the solid as well as in the liquid state (molten metal) was observed from temperature dependences ρ(T) in five investigated alloys – see Figure 11. According to expectations, a resistivity step increase occurred in all the solders in the area of the eutectic reaction temperature. Complicated reactions at phase transformations occurred in specimens of alloys no. 16 and 20 with high zinc contents (Table 5). A certain hysteresis degree was evident on the curves. The lowest ρ value was exhibited by alloy no. 20 with a high Al content (10 at.%).

A linear decrease ρ(L)(T) was observed from temperature dependences of molten metal densities in the above mentioned five specimens – see Figure 11 which was in conformity with theoretical assumptions. An interesting finding was that alloys no. 19 and 13 and alloys 16 and 20 nearly overlaid one another, which was caused by the presence of aluminum in a suitable ratio to Sn and Zn.

The magnetic susceptibility measurement confirmed that this method was sensitive to structural and phase transformations, too. Here also, a jump of χ values at the eutectic temperature and a certain degree of hysteresis behavior during heating and cooling of the specimens became evident (Figure 13).

Three types of fluxes were used for testing of wettability of solders with various substrates on a meniscograph. Cu and Ni wires (1 mm diameter) were applied as substrates and 8 Sn–Zn–Al alloys were tested. The measurements proved that nickel exhibited higher wettability with the solders used, however, the measurements results showed low wettability in general compared to common Pb–Sn, SAC and Sn-Cu solders. Here the presence of aluminum in the alloy had a negative effect; aluminum has a tendency to form oxides on solder surfaces and their dissolution using the particular fluxes failed. The results of measured courses of wetting forces “on plateau” (Figure 14) imply that the Sn–Zn binary alloys can be preferred to aluminum containing alloys. These conclusions were confirmed also by the results of a subjective image analysis. It can be stated that solders not containing aluminum are better solderable. The solderability decreases with an increasing proportion of aluminum in a soldering alloy. An issue remains to find an applicable flux even for these types of alloys. In this case, it will be advisable to use nitrogen as the inert atmosphere for testing.
7. Conclusion
The presented paper deals with a complex study of the Al–Sn–Zn ternary system both in term of phase equilibria and structural and mechanical characteristics depending on the alloy chemical composition and a method of heat treatment (a condition after crystallization or long-term annealing in vacuum at three different temperatures and time periods followed by subsequent rapid cooling – quenching). Further, measurements of resistivity, density, magnetic susceptibility and wettability of the selected alloys were carried out. Some results are presented in relevant tables and graphs. The alloys were also subjected to various corrosion tests not mentioned in this paper [26, 27].

For further applications it will be necessary to perform other technological tests of solderability to find out an optimal flux and to optimize the chemical composition of the Al–Sn–Zn based lead-free solder for particular soldered materials, especially for aluminum alloys.

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