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Ternary invariant point at 403 and 455 °C in the Al–Sb–Zn system

A DTA and DSC studies

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Abstract The temperature and location of the invariant eutectic point at 403 °C in the zinc-rich corner of the Al–Sb–Zn system was determined. However, the experimentally determined temperature was found to be lower than the thermodynamically predicted one. Differential thermal analyses, differential scanning calorimetry, and quantitative microstructural analyses were used to determine this specific reaction. The determined ternary eutectic reaction, $L \rightarrow \alpha\text{-}Sb_2Zn_3 + AlSb + \eta\text{-}Zn$, represents the last solidification path in the phase region of Sb–AlSb–Zn. Before a ternary eutectic reaction takes place, another reaction is also possible near the Sb–Zn binary system, a quasi-peritectic reaction at 455 °C: $L + \beta\text{-}Sb_2Zn_3 \rightarrow AlSb + \alpha\text{-}Sb_2Zn_3$. A scanning electron microscope equipped with an energy-dispersive spectrometer was used for the microstructural analyses. The phase identification was conducted with X-ray diffractometry. The experimental data were compared to the thermodynamic predictions made with the CALPHAD method using the SSOL4 database.

Keywords Thermal analysis · Al–Sb–Zn ternary system · Lead-free alloys · Thermodynamic

Introduction

Lead is a toxic element, and problematic for human health and the environment. However, lead-based alloys often have useful properties, and as such are commonly used for solders in the automobile industry and elsewhere. One of the main applications of lead is adopted in the hot-dip galvanizing industry, where small amounts of the element are added to improve the fluidity of a zinc-rich metal melt. Nevertheless, zinc–antimony coatings (as replacements for lead) and aluminum additions are already in use to a limited extent for the protection of iron sheets against corrosion. Several investigations were made on the phase identification of such zinc-rich coatings on a steel surface by Zapponi et al. [1] and Peng et al. [2]. They found intermetallic phases in the zinc-rich matrix after solidification, i.e., AlSb, Sb_2Zn_3, and Sb_3Zn_4. However, only by understanding the solidification in the zinc-rich corner of the Al–Sb–Zn ternary system can a more complex study of other quaternary systems (like Al–Fe–Sb–Zn) be made.

Our investigation was focused on the zinc-rich corner in the region near the Sb–Zn system. The experimental data are important for optimizing the lead-free phase diagrams predicted using the CALPHAD approach [3]. Nevertheless, optimizations could also be made using a classic calorimetric method on lead-free-based systems [4, 5].

The Sb–Zn system has three intermetallic compounds: SbZn, Sb_3Zn_4 (with γ, β and α modifications), and Sb_2Zn_3 (with α and β modifications). Investigations of the Sb–Zn system and of specific intermetallics (such as the Sb_3Zn_4 phase) are becoming increasingly interesting in the field of thermoelectric materials [6]. In the zinc-rich corner of the Sb–Zn system, the solidification is finished with the binary eutectic reaction: $L \rightarrow \alpha\text{-}Sb_2Zn_3 + \eta\text{-}Zn$ at 414 °C and 1.25 at.% Sb. In the region between 59.5 at.% Zn and 96.1 at.% Zn, a peritectic reaction is expected, where $L + \beta\text{-}Sb_2Zn_3 \rightarrow \alpha\text{-}Sb_2Zn_3$ takes place with its location at 460 °C and 60 at.% Zn. The temperatures and denotations were adopted from Okamoto [7].

The Al–Sb system has only one compound at 50 at.% Sb. The high congruent melting point is at 1058 °C. The AlSb

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phase has a major influence on the position of the eutectics in the Al–Sb system; these are at 657 °C and 0.4 at.% Sb, and 627 °C and 98.5 at.% Sb. Both degenerated eutectics are the starting points of monovariant lines toward the zinc-rich corner: L → AlSb + (Al), L → AlSb + (Sb) [8].

The Al–Zn–Sb system was investigated by Zhu et al. [9] at 450 °C, a typical galvanizing temperature. In the Zn–AlSb–Sb_2Zn_3 region, two intermetallic phases were found at 450 °C: AlSb and Sb_2Zn_3. The investigation made by Klančnik and Medved [10] focused on the solidification in the vicinity of the Al–Zn binary system. Here, no ternary phases were found. Solidification in the AlSb–Zn–Sb_2Zn_3 phase region is expected to be finished with a ternary eutectic, according to thermodynamic predictions made using the CALPHAD approach. This invariant reaction should appear at 409.6 °C with the reaction: L → (Zn) + α-Sb_2Zn_3 + AlSb. The calculation was made with the help of SSOL4 database. The possible existence of this reaction was first noticed by Köster [11].

The aim of our investigation was to determine the position of the ternary eutectic's invariant point and its temperature and to confirm the presence of a ternary peritectic or quasi-peritectic reaction. Both differential thermal analysis (DTA) and differential scanning calorimetry (DSC) heating and cooling curves were taken into account for the temperature determination.

Materials and experimental procedures

All the samples were prepared using elements with a purity of 99.99 mass%. A resistance furnace was used for the melting, which was done in a pure corundum crucible with a graphite cover. The melting involved multi-cycling and turning of the samples to prevent gravity segregations. Using this technique, the prepared samples were relatively homogeneous. The graphite cover was used as protection against rapid evaporation at high temperatures (<850 °C). Argon (99.999 vol.%) was also used to protect against oxidation.

The average mass of the prepared alloy was between 10 and 15 g. The average mass of the samples used in the DTA was up to 1 g. The temperatures determined using the DTA 701 from Bähr had an accuracy of ±3%. In the case of a simultaneous thermal analysis (DSC), an STA 449 Jupiter from Netzsch was used. The accuracy of the determined temperatures was 0.25%.

The microstructures were observed using back-scattered electrons (BSEs) on a JEOL 5610 scanning electron microscope (SEM) and an energy-dispersive spectrometer (EDS). X-ray powder diffraction analyses were used for the phase identification. The measurements were made at the National Institute of Chemistry, Slovenia, with a PANalytical X'Pert PRO apparatus and CuKα = 1.5406 Å radiation.

The DSC and DTA experiments were conducted under a protective shield of argon gas with 99.999 vol.% purity. An empty corundum crucible was used as a reference. The heating and cooling rates were 10 K/min. Lower rates were not used to minimize the evaporation of the zinc at higher temperatures. The temperature was recorded with a PtRh–Pt thermocouple.

The thermodynamic calculations were performed using Thermo-Calc software 5 with the SSOL4 database and the Pandat software at the Technical Faculty in Bor, University of Belgrade, Serbia.

The chemical compositions of the investigated samples are given in Table 1.

Results and discussion

Sb–Zn binary phase diagram

Based on the Sb–Zn binary phase diagram of Okamoto [7], the prepared sample of this study should start to solidify with primary crystals of β-Sb_2Zn_3. If the solidification is indeed in this region, then it should be above the peritectic reaction (>460 °C) with the following reaction: β-Sb_2Zn_3 + L → α-Sb_2Zn_3.

The obtained DSC heating spectra were characterized by several endothermic peaks, where the first melting peak is related to the crossing of the eutectic line. The DSC curves are presented in Fig. 1. Using the DSC heating and cooling curves, the eutectic temperature was determined to be 409 °C with the reaction: L ↔ α-Sb_2Zn_3 + η-Zn (Fig. 1a). This temperature is close to the eutectic temperature in the Sb–Zn phase diagram published by Massalski, i.e., 411 °C [12]. A temperature of 409 °C was determined with DSC in the study of Liu et al. [13]. A temperature of 458 °C is related to the peritectic reaction: α-Sb_2Zn_3 → L + β-Sb_2Zn_3, while a temperature of 458 °C was determined using the Peak-Separation program from Netzsch. The last peak represents the melting of the primary β-Sb_2Zn_3 phase with a melting maximum at approximately 500 °C. The eutectoid reaction: α-Sb_3Zn_4 + η-Zn → α-Sb_2Zn_3, was not noticed.

Table 1 Compositions of the investigated samples in the Al–Sb–Zn ternary system/at%

Sample	Composition
ZS1	15Sb85Zn
AZS3	6.69Al12.2Sb81.13Zn
AZS14	1.2Al27.1Sb71.6Zn
AZS7	2.65Al5.25Sb92.1Zn
AZS12	0.56Al3.89Sb95.55Zn

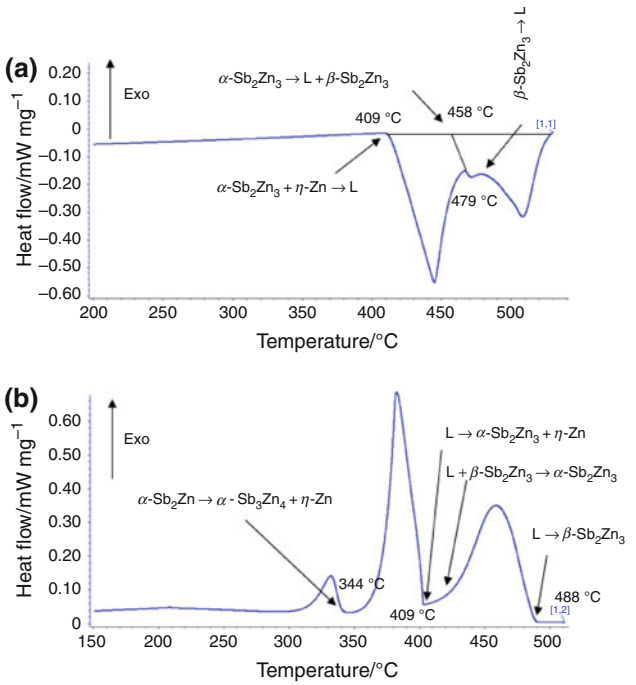

Fig. 1 The DSC heating (**a**) and cooling (**b**) curves of the ZS1 sample

The solidification of the sample ZS1 starts at 488 °C (Fig. 1b). The peritectic reaction was also confirmed by cooling. The temperature of 344 °C is related to the decomposition of α-Sb_2Zn_3 into α-Sb_3Zn_4 and η-Zn. According to the phase diagram of Okamoto [7], the decomposition should have already started at 405 °C. Based on our results and the results from Adjadj et al. [14], it can be concluded that during cooling, this decomposition can be observed at much lower temperatures (344–360 °C) than those proposed in the existing phase diagrams and determined from the heating segments: 405, 409, and 408 °C [7, 12, 13].

Ternary quasi-peritectic reaction

From the data from Okamoto [7] and our own study, we know that the peritectic reaction will occur in the Sb–Zn system in the region of 60–96.1 at.% Zn at 460 °C and at 458 °C, respectively. Taking into account the Sb–Zn phase diagram based on Massalski [12], the peritectic reaction β-Sb_2Zn_3 + L → α-Sb_2Zn_3 will occur at 455 °C. If the position of the monovariant line is indeed close to the Sb–Zn binary system, then rather similar temperatures are expected from a thermal analysis of the prepared samples in the Al–Sb–Zn ternary system.

In the Sb_2Zn_3–AlSb quasi-binary cut, a saddle point is expected with a monovariant line (L + β-Sb_2Zn_3 + AlSb) going toward the monovariant line (L + β-Sb_2Zn_3 + α-Sb_2Zn_3) from the Sb–Zn binary system into the invariant point of the quasi-peritectic (U) or peritectic reaction (P). The solidification is not yet finished in both cases if there is some remaining liquid phase that solidifies with the second invariant point—the ternary eutectic reaction.

The ternary peritectic reaction (P) was predicted using the SSOL4 database to be at 446.71 °C and with the reaction: L + β-Sb_2Zn_3 + AlSb → α-Sb_2Zn_3. The calculation was also made using the Pandat software, where the Al–Sb binary system was taken from the SGTE (2004) database, the Al–Zn binary system from Mey [15], and the Sb–Zn binary system from Liu et al. [13]. The quasi-peritectic reaction at 453.7 °C was predicted with the reaction: Liquid + β-Sb_2Zn_3 → AlSb + α-Sb_2Zn_3.

Two samples were prepared for the investigation of the quasi-peritectic or peritectic reaction, i.e., AZS14 and AZS3. The BSE micrograph of AZS3 with the related phase analysis is shown in Fig. 2. A decomposed α-Sb_2Zn_3 phase (α-Sb_3Zn_4 + η-Zn) was found as part of the ternary eutectic phase, a part of the solidification on the monovariant line (large white phase in Fig. 2) and as a quasi-peritectic phase found on the AlSb phase.

Figure 3a shows the sample AZS14 that was heated as in the previous experiment at a rate of 10 K/min. The eutectoid reaction α-Sb_3Zn_4 + η-Zn → α-Sb_2Zn_3 was not observed and is expected to be close to the ternary eutectic reaction. The temperature of 403 °C represents the ternary eutectic reaction: AlSb + α-Sb_2Zn_3 + η-Zn → L.

The temperature of 455 °C, also determined with the AZS3 sample, is related to the quasi-peritectic reaction resulting from having lower temperatures than the peritectic reaction in the Sb–Zn system. Also, an intense peak was obtained at 480 °C where AlSb and β-Sb_2Zn_3 are melting in a reaction related to the crossing of the (AlSb + β-Sb_2Zn_3) monovariant line. The last small peak at 566 °C is related to the melting of the primary AlSb phase.

The liquidus temperature was determined to be 578 °C (Fig. 3b). The second major peak from the DSC cooling curve is a combination of two peaks. The first peak, as already discussed, is an amount of heat released by the solidification of the AlSb and β-Sb_2Zn_3 phases. The second solidification is directly related to the quasi-peritectic reaction at 455 °C. The remaining liquid solidifies at 403 °C. The decomposition of the α-Sb_2Zn_3 phase was determined at 364 °C. With the AZS3 sample, the decomposition of the α-Sb_2Zn_3 phase was obtained at a temperature of 349 °C, similar to the binary alloy ZS1. Figure 4 shows the morphology of the AZS14 sample with the decomposed quasi-peritectic α-Sb_2Zn_3 phase growing on the AlSb phase.

The recommended reaction from the metallographic analysis, and thermal analysis is not peritectic (P) but quasi-peritectic (U), where the reaction L + β-Sb_2Zn_3 → AlSb + α-Sb_2Zn_3 takes place. A peritectic (P) reaction is not

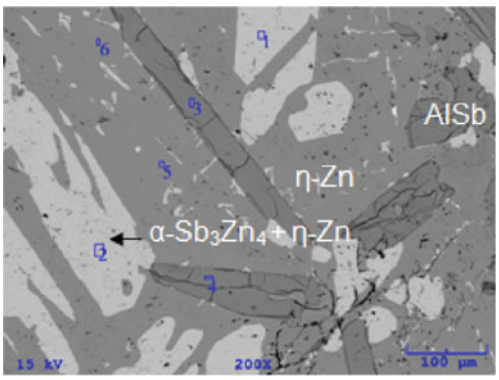

Fig. 2 BSE micrograph of the AZS3 sample and the related EDS

	Al/at.%	Zn/at.%	Sb/at.%
1	0.53	51.35	48.11
2	0.36	52.08	47.56
3	40.04	2.19	57.76
4	40.13	1.42	58.43
5	/	100	/
6	0.12	99.88	/

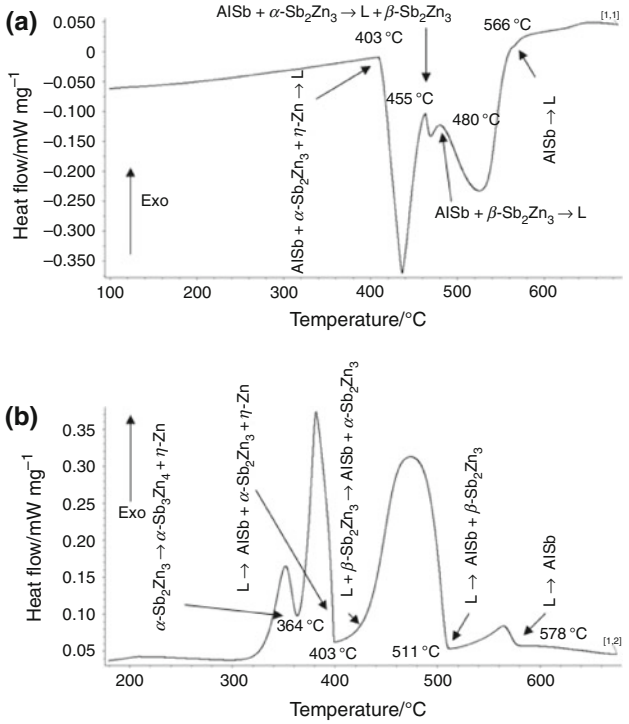

Fig. 3 DSC heating (**a**) and cooling (**b**) curves of the AZS14 sample

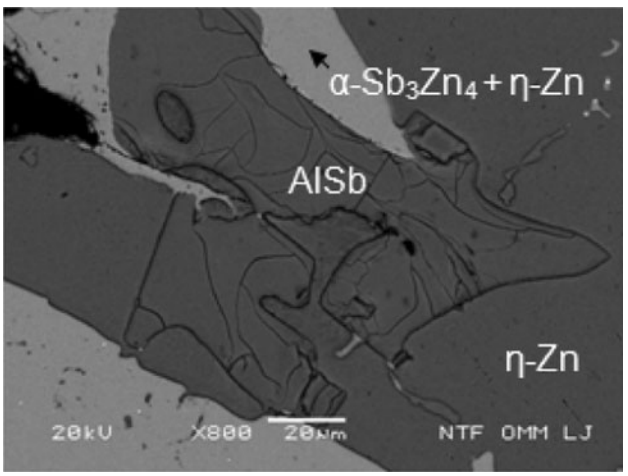

Fig. 4 BSE micrograph of the decomposed quasi-peritectic phase in the ASZ14 sample

recommended since α-Sb_2Zn_3 is not a new (ternary) phase in this system, and the formation of the Sb_2Zn_3 phase is not uniform on the AlSb phase but grows randomly from the AlSb interface. Also, the peritectic temperature in the Sb–Zn system is higher than the one determined in the ternary system and confirms the tendency of combining two monovariant lines rather than splitting them. Nevertheless, the

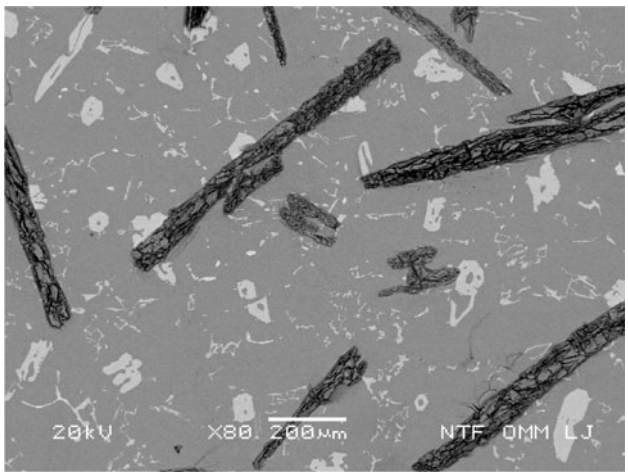

Fig. 5 BSE micrograph of the AZS7 sample

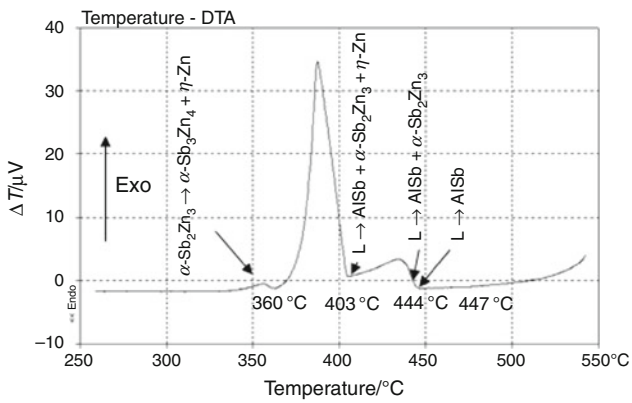

Fig. 6 DTA cooling curve of the AZS12 sample

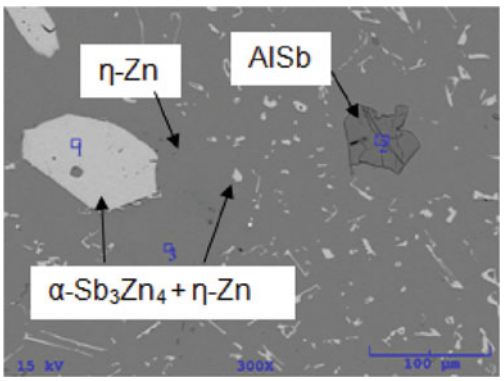

Fig. 7 BSE micrograph of the solidified AZS12 sample

	Al/at.%	Zn/at.%	Sb/at.%
1	0.607	52.498	46.894
2	36.746	2.216	61.038
3	0.152	99.849	/

region where the quasi-peritectic reaction is present without the ternary eutectic is expected to be small if the Sb–Zn phase diagram is taken into account. This means that the β-Sb_2Zn_3–α-Sb_2Zn_3–AlSb region is very narrow compared to the α-Sb_2Zn_3–AlSb–Zn phase region. This also means that in the α-Sb_2Zn_3–AlSb–Zn region a second invariant reaction is expected to occur after the first one.

Ternary eutectic reaction

Solidification in the Sb_2Zn_3–AlSb–Zn region is finished with a ternary eutectic reaction. It is also expected that the AlSb phase will be the primary phase and in a larger region. According to thermodynamic calculations the ternary eutectic reaction should appear at 409.6 °C. According to the data of Köster [11], the crossing through the ternary eutectic plane is at 414 °C. In our experimental study and from thermodynamic calculations, it was determined that the eutectic has a lower temperature than the one determined by Köster. Samples AZS7 and AZS12 were prepared to be close to the estimated ternary eutectic invariant point. From Fig. 5, it is clear that in the AZS7 sample the AlSb phase is a primary phase with a larger fraction of the ternary eutectic. The decomposed α-Sb_2Zn_3 was found to be smaller in size than in the samples AZS3 and AZS14.

During the solidification of AZS12, Fig. 6, the first peak appears at 447 °C where the AlSb phase starts to precipitate from the liquid phase. The location of AZS12 is close to the monovariant line where the solidification of the AlSb and α-Sb_2Zn_3 phases appears at practically the same temperature as the primary AlSb phase, i.e., 444 °C.

The solidification peaks determined at 444 and 447 °C are small in comparison to the ternary eutectic peak determined at 403 °C. This confirms the close proximity of the ternary eutectic point. The microstructure of the AZS12 sample consists of a large fraction of the ternary eutectic $(AlSb + \alpha\text{-}Sb_2Zn_3 + \eta\text{-}Zn)_{eut}$ where the α-Sb_2Zn_3 starts to decompose at 360 °C.

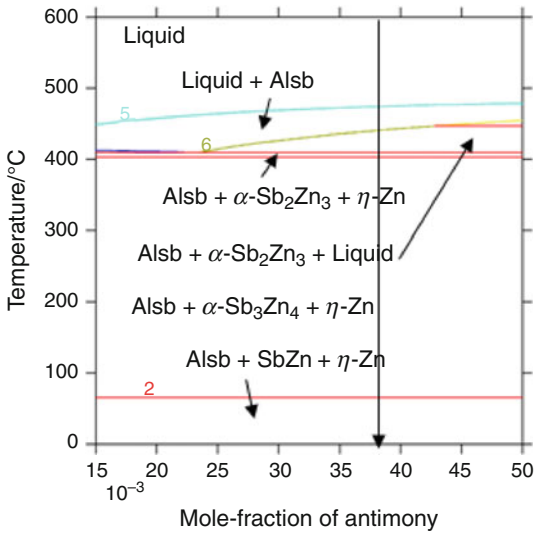

Fig. 8 Isopleth phase diagram for the AZS12 sample

The micrograph in Fig. 7 shows two "primary" solidifications, i.e., AlSb and α-Sb_2Zn_3. This corresponds to the solidification near the monovariant line, as discussed before.

An example of a thermodynamic calculation made with Thermo-Calc software and the SSOL4 database is presented in Fig. 8 for the AZS12 sample. The thermodynamic prediction shows a small temperature interval that suggests the existence of the Liquid + AlSb primary solidification. After this primary solidification, the α-Sb_2Zn_3 solidifies until the eutectic plane is reached. The η-Zn phase also appears as a part of the ternary eutectic. The decomposition of the α-Sb_2Zn_3 appears immediately after reaching the eutectic plane. Based on our past experience, we know that these temperatures can be pushed down to lower values when using a cooling rate of 10 K/min. Thermodynamic calculations predicted the decomposition of the α-Sb_3Zn_4 phase into SbZn and η-Zn in all the investigated samples. However, because the reaction

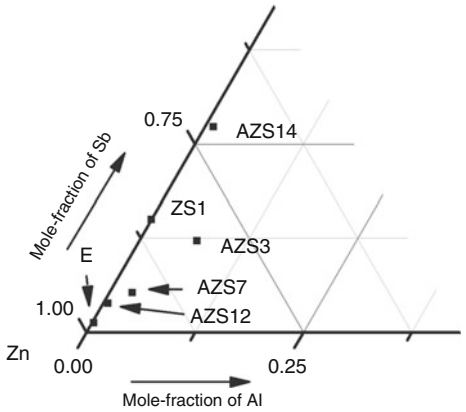

Fig. 9 Zinc-rich corner in the Al–Sb–Zn ternary system

Table 2 Experimentally determined and calculated liquidus temperatures

Sample	Calculated T_{Liq}/°C	Experimental T_{Liq}/°C	Primary phase
AZS3	639	641	AlSb
AZS14	544	578	AlSb
AZS7	559	574	AlSb
AZS12	477	447	AlSb

depends on diffusion, the intermetallic SbZn phase is not formed under such experimental conditions.

The EDS analysis clearly shows that a small aluminum solubility is present in the decomposed α-Sb_2Zn_3 phase as well as in the zinc-rich η phase.

The estimated location of the ternary eutectic point (E) is at 0.26 at.% Al, 1.24 at.% Sb and 98.5 at.% Zn. The temperature of the ternary eutectic is 403 °C (using only the heating curve, the temperature is 408 °C) and is close to a binary eutectic in the Sb–Zn system. The location of the investigated samples and the location of the ternary eutectic E are shown in Fig. 9. The thermodynamic predictions as well as our experimental data revealed that the primary solidification in the investigated samples starts with the AlSb primary phase, Table 2.

Conclusions

The DSC curves of the investigated samples in the AlSb–Sb_2Zn_3–Zn region revealed the presence of two invariant reactions—the ternary quasi-peritectic and the ternary eutectic—as predicted by the thermodynamic calculations. The ternary eutectic reaction will appear at a temperature of 403 °C with the following reaction: L → AlSb + α-Sb_2Zn_3 + η-Zn, and the invariant point (E) at 0.26 at.% Al, 1.24 at.% Sb, and 98.5 at.% Zn. The quasi-peritectic reaction at 455 °C was determined with the reaction: L + β-Sb_2Zn_3 → AlSb + α-Sb_2Zn_3. It was found that the eutectic temperatures are lower than the predicted ones, which is the result of the effect of the cooling rate and the presence of experimental error.

With a cooling rate of 10 K/min the decomposition of the α-Sb_2Zn_3 will appear at the average temperature determined by the thermal analysis, i.e., at approximately 358 °C. The formation of the SbZn phase was retained for the solidified microstructures in the investigated samples.

In all the investigated samples, the AlSb phase was found to be a primary phase, as predicted by the calculations.

In all the investigated samples, three phases were found in the solidified microstructure: AlSb, η-Zn, and α-Sb_3Zn_4.

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