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TERNARY INVARIANT POINT AT 374 °C IN THE THREE PHASE REGION AlSb-Al-Zn INSIDE THE Al-Sb-Zn TERNARY SYSTEM

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Abstract

Al-Sb-Zn ternary system was investigated in the three phase region Al–AlSb-Zn, using differential thermal analysis (DTA), differential scanning calorimetry (DSC) and scanning electron microscope equipped with energy dispersive spectrometer (SEM-EDS). The position and temperature of the invariant eutectic L → AlSb + β-Al + η - Zn point inside Al-AlSb-Zn region was experimentally determined. To confirm the obtained results X-ray powder diffraction analysis or XRD was also done. All results were compared to the calculated isopleth phase diagrams using Thermo-Calc software (TCW 5). All calculations were done using the SSOL4 data base.

Keywords: Al-Sb-Zn system; Phase equilibrium; Ternary eutectic; Lead free alloys.

1. Introduction

Lead-containing materials are widely present in almost every manufacturing process in the electronic industry. For a possible replacement of lead with other alloys [1], especially in the case of soldering processes and/or hot dip galvanization, knowing the constitution of the phase diagram with its invariant points is crucial.

Zinc alloys are nowadays used for protection of steel against corrosion. Aluminium and antimony are both alloying elements used frequently in the hot-dip galvanizing processes [2, 3]. The requirements for a uniform appearance (which depends on the solidification morphology and a possible segregation

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effect of phases), weldability and also corrosion resistance of the formed coatings and/or solders led to the investigation of the Al-Sb-Zn ternary system.

Zinc-rich aluminium alloys are commonly used also as foundry alloys especially for producing castings with low tolerance. Normally they are produced by classical gravity or pressure die casting [4]. In order to improve mechanical properties of Zn-Al alloys some studies are focused on the examination of the microstructure resulting in different additions of other elements [5]. As such, antimony also becomes very interesting.

Our investigations are considered to be a contribution to the European COST MP0602 Action to understand the phase relationship of lead-free Al-Sb-Zn materials with corresponded invariant points.

2. Literature review

2.1. The Al-Zn binary system

Al-Zn binary system is a rather simple system with one eutectic point at 381 °C [6, 7]. The solidification can start with a α-Al or β-Al primary phase. Primary β phase is a zinc-rich phase and by cooling below the monotectoid temperature the β phase decomposes into α phase and η-Zn phase. The latest investigations of β-phase was done by Sandoval [8]. He found out that the β phase has a triclinic structure produced by distortion of the primitive rhomboedral unit cell in the fcc structure. Authors like Aragon [9] are taking aluminium solution on Zn-rich side as a structure which corresponds to fcc structure, with one of the ternary axes slightly stretched.

2.2. The Al-Sb binary system

In the Al-Sb system only one stoichiometric compound is known, the so-called aluminium antimonide, AlSb. The AlSb compound crystallizes in a sphalerite lattice with the constant a = 6.136 A. The Al-Sb phase diagram has two eutectics both in the aluminium-rich and the antimony-rich corner. AlSb compound has a much higher melting point (1058 °C) compared to aluminium and antimony [10]. Welker, Veszelka etc. [11, 12] have studied the Al-Sb system and the AlSb compound. The latest critical assessment was done after Yamaguchi [13]. Nevertheless the position of the liquidus line in this system is still not well known [14].

2.3. The Sb-Zn binary system

Recent differential calorimetric analysis on this system was done by Adjadj 2006 [15]. Three compounds are typical for this system: SbZn, Sb_2Zn_3 and Sb_3Zn_4. Both Sb_3Zn_4 and Sb_2Zn_3 phases exist in different polymorphic transformations (Table 1). From Okamoto [16] the crystal structure data is presented in table 1.

2.4. The Al-Sb-Zn ternary system

Experimental investigations in the literature are very scope about the Al-Sb-Zn ternary system. The investigation done by Zhu and others [17] was focused on the region near Al-Zn and Zn-Sb sub binaries at temperature 450 °C. No ternary phases were found. Based on the microstructure, EDS and XRD it seems that the AlSb phase can

Table 1. Sb-Zn crystal structure data

Phase	X Zn	Pearson symbol	Space group	Struckturbericht designation	Prototype
Sb	0	hR2	R_3m	A7	α-As
SbZn	0.5	oP16	Pbca	B_e	CdSb
γ-Sb_3Zn_4	0.558	/	/	/	/
β-Sb_3Zn_4	0.559	/	/	/	/
α-Sb_3Zn_4	0.571	oP28	Pmmn	/	/
β-Sb_2Zn_3	0.595	oI*	/	/	/
α-Sb_2Zn_3	0.6	oP32	Pmmn	/	/
Zn	1	hP2	$P6_3/mmc$	A3	Mg
*denotations of the stochiometric formula are taken by Okamoto [16]					

equilibrate with all phases in the ternary system. No solubility of antimony was found in the α-Al phase as a result of EDS limitations. They determined that AlSb phase has a small zinc solubility with aprox. 2.1 at.% in it. The presence of AlSb was also determined near the Al-Zn sub binary system in the aluminium-rich corner. There were no ternary phase present as mentioned in our previous work [18]. Publication dealing with the constitution of the zinc rich corner of Al-Sb-Zn system was published in 1942 by Köster [19]. A possible existence of the AlSb-Zn quasi-binary cut was mentioned. Köster found out that the AlSb phase was the primary phase in all compositions he investigated and confirmed that the AlSb phase exists widely inside the Zn rich corner.

According to Köster [19] the prediction was that solidification inside the AlSb - η-Zn - β-Al phase region is finished with the ternary eutectic reaction at temperature 380°C. Using SSOL4 database the thermodynamic calculation predicts a ternary eutectic at 380.7 °C with the following reaction: L → (Al) + (Zn) + AlSb. No experimental parameters were described under which circumstances these temperatures were determined (heating cooling rates etc.). To confirm this result, eight samples were prepared, marked A1 - A8.

3. Experimental

Samples were prepared in a corundum crucible. Each sample was carefully weighed and mixed together before the melting started. The total mass for each of the samples was 15 g. To prevent any oxidation and evaporation of elements a carbon cover was used. No mass losses were recorded during melting. Each melting started with a slow heating in the resistance furnace under argon protection. After shaking and stirring the metal melt with a ceramic rod, the sample was left at the same temperature for at least two hours. Experimental compositions of the prepared alloys are listed in table 2.

Homogenization was done with a sealed

Table 2. Experimental composition of specimens in the Al-Zn-Sb ternary system

Alloy	Sample name	composition
A1	AZS1	0.2Al0.1Sb0.7Zn
A2	AZS4	0.172Al0.078Sb0.751Zn
A3	AZS6	0.17Al0.083Sb0.738Zn
A4	AZS11	0.253Al0.0012Sb0.74Zn
A5	AZS8	0.732Al0.008Sb0.26Zn
A6	AZS10	0.84Al0.0014Sb0.15Zn
A7	AZS9	0.746Al0.014Sb0.24Zn
A8	AZS13	0.77Al0.13Sb0.1Zn

and evacuated quartz sample. To prevent any reduction of quart with aluminium, a corundum crucible was used.

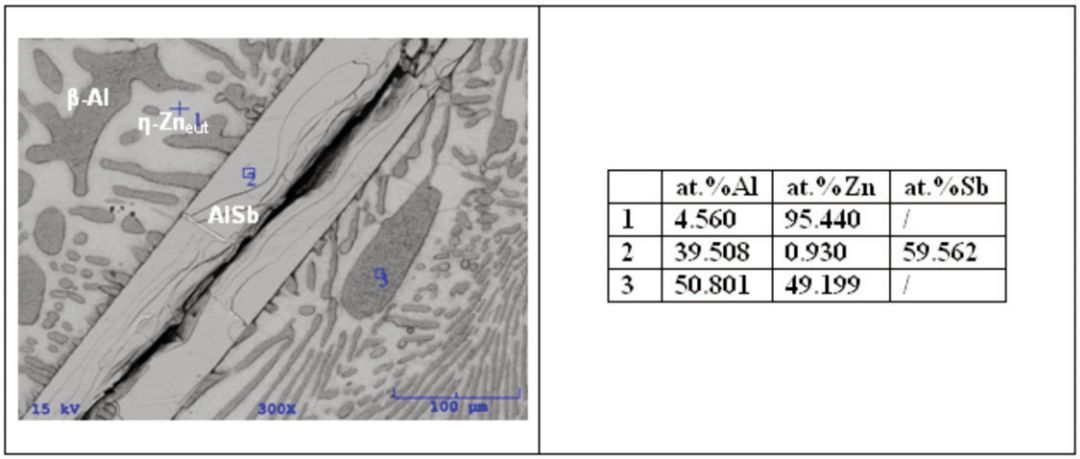
The characteristic temperatures were determined with DTA 701 from Bähr with an accuracy of ± 3% and with STA 449C Jupiter from Netzsch with an accuracy of ± 0.25%. The characteristic temperatures (monotectoid reaction, invariant reaction) were defined using the linear tangential on the side of the minimum or maximum of the peak, depending on the heating/cooling segment of the peak and its intersection point with the base line. For the invariant reaction, an average was taken for the precise determination of the invariant point. The evaluation of the characteristic temperature of the monotectoid reaction is presented by two temperatures determined at heating and at cooling segment. Liquidus temperatures were determined with the last melting maximum and from the first deviation of the DSC/DTA base line by cooling the sample. The measurements were done under argon protection with both the heating and cooling rate of 10 K/min to avoid the intensive zinc evaporation which was already recorded at a heating/cooling rate of 5 K/min. In both cases an empty corundum crucible was used as a reference. In order to conduct a chemical analysis of possible phases, an investigation of the microstructure was made with a JEOL 5610 electron microscope and an energy dispersive spectrometer (EDS).

Investigations were done mostly using a micrograph recorded with back scattering electrons (BSE). The experimental precision for composition determination using EDS was up to 0.1 at%. The X-ray powder diffraction analysis is an important method in identifying the crystal structure of a phase in an alloy. The measurement was done at the National institute of Chemistry Slovenia with the PANalytical X`Pert PRO apparatus, with CuKα = 1.5406 Å and the Siemens D 5000 apparatus also with the following radiation: CuKα = 1.5406 Å.

4. Results and discussion

With the investigation of Al-Zn samples in our previous work [18], we have established that a monotectoid reaction is present and that the effect was determined to be in the temperature range between 276 and 281 °C. A similar effect was expected and also determined inside the Al-Sb-Zn ternary system. In order to investigate the β-Al phase before decomposition, sample AZS 4 was homogenized for 10 days at 330 °C.

No decomposition of β-Al to α-Al and η–Zn was found at 330 °C, figure 1. Decomposition of the β-Al phase was determined with DTA/DSC in the temperature range between 261 and 286 °C. From the results of the EDS analysis one can also conclude that the zinc rich phase η-Zn



	at.%Al	at.%Zn	at.%Sb
1	4.560	95.440	/
2	39.508	0.930	59.562
3	50.801	49.199	/

Figure 1. BSE micrograph of AZS4 homogenized at 330 °C for 10 days

dissolves at 4.56 at.% of aluminium at temperature 330 °C. In the Al-Zn binary system, after Massalski [6], the zinc rich phase dissolves at aprox. 2.5 at.% of aluminium at the same temperature. A small solubility of zinc in the AlSb phase was also confirmed, 0.93 at.% Zn, as already published by Zhu et al. [17]. A small solubility was also determined by others alloys. The XRD analysis confirmed the presence of all three main phases in AZS4: β-Al, η-Zn and AlSb, figure 2.

Examples of DTA heating and cooling curves are represented in figure 3. The first

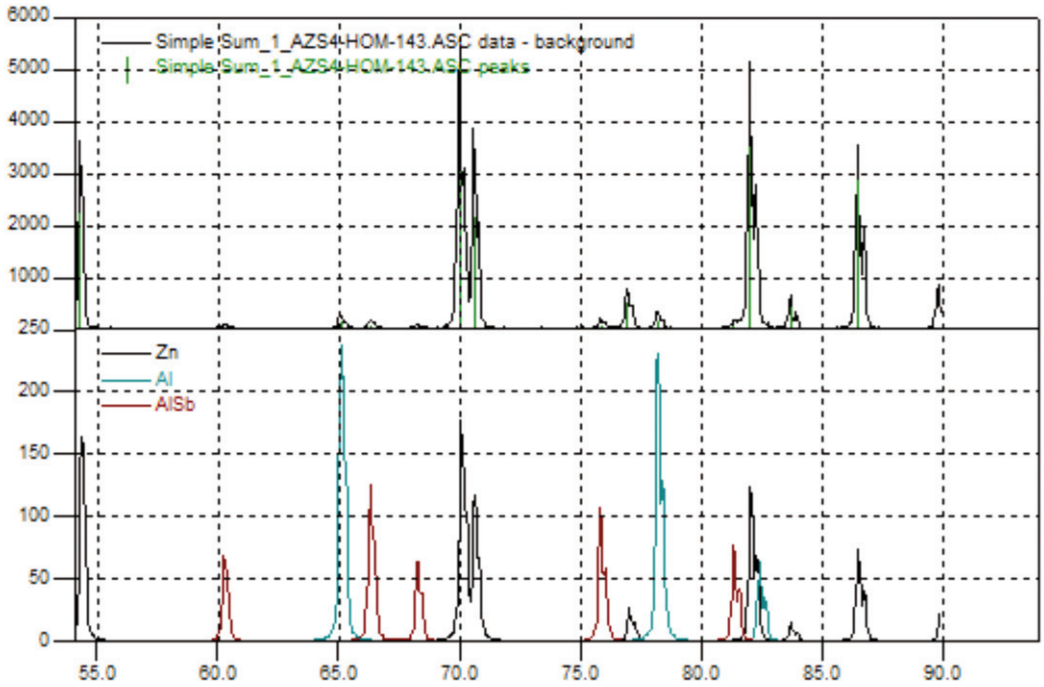
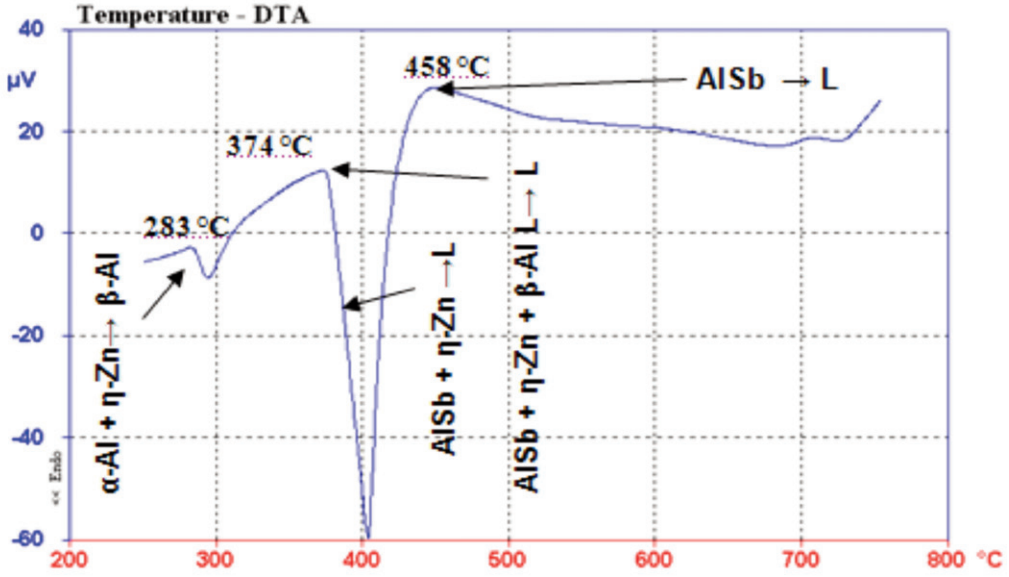
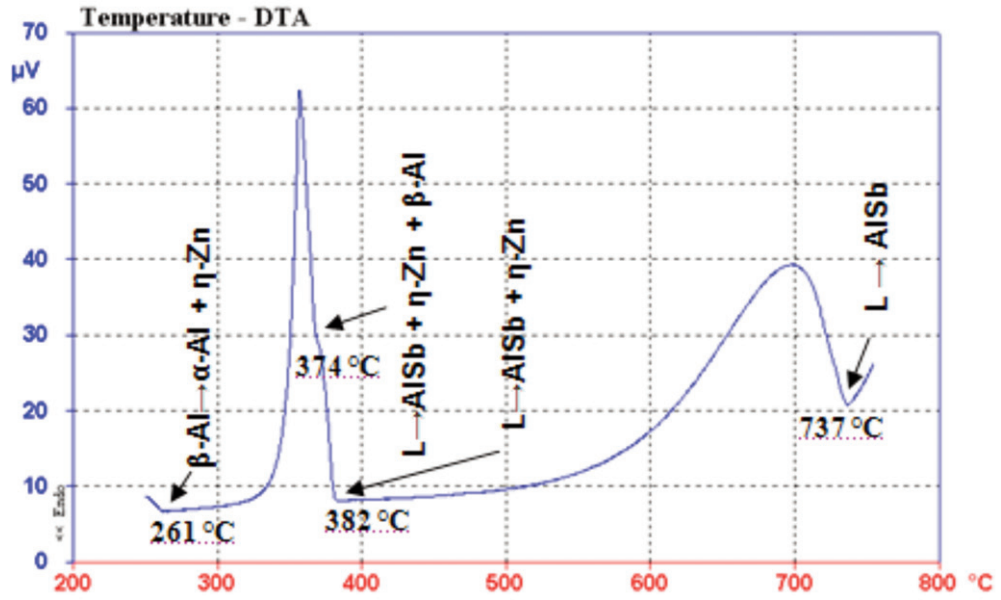


Figure 2. XRD pattern of the sample homogenized AZS4



a)



b)

Figure 3. DTA heating (a) and cooling curve (b) of AZS1 alloy

thermal effect determined by heating is related to the monotectoid reaction (α-Al + η-Zn → β-Al) at 283 °. At 374 °C a ternary eutectic reaction takes place (AlSb + β-Al + η-Zn → L). The temperature of 458 °C is related to the melting of the primary AlSb phase. We have noticed from the heating curve, that the melting of this phase is not uniform (several endothermal peaks). This is a result of size variation of the AlSb phase.

From the DTA cooling curve, the solidification of AlSb was determined to be at 737 °C. Only one continuous peak is present and confirms a more uniform growth of the AlSb phase. Secondary solidification appeared at 382 °C with a passing monovariant line L→AlSb + η-Zn. This is also recognized in the microphotographs, figure 4a. Solidification is finished at 374 °C with a ternary reaction L → (η-Zn + AlSb + β-Al). Temperature 261 °C is related to the monotectoid reaction.

Similar results were obtained with AZS4 and AZS6 sample, figure 4 b, c. The DTA heating curve of the sample AZS4 revealed four thermal effects, figure 5. The first one at 286 °C and related to the monotectoid reaction as already discussed. The second peak was determined when the four-phase eutectic plane at 374 °C was crossed. The third peak appeared when crossing the three-phase region L + β-Al + AlSb and further with the two phase region L + AlSb at 453 °C. Solidification of the primary AlSb phase started at 696 °C. Only one peak was determined with the DTA solidification curve at temperature 374 °C. The metallographic analysis shows no anomalous zinc rich η phase, which confirms a different solidification path. Decomposition of β-Al was determined with the cooling curve to be at 262 °C, similar to the AZS1 sample. Characteristic temperatures of monotectoid and ternary eutectic reactions as well as

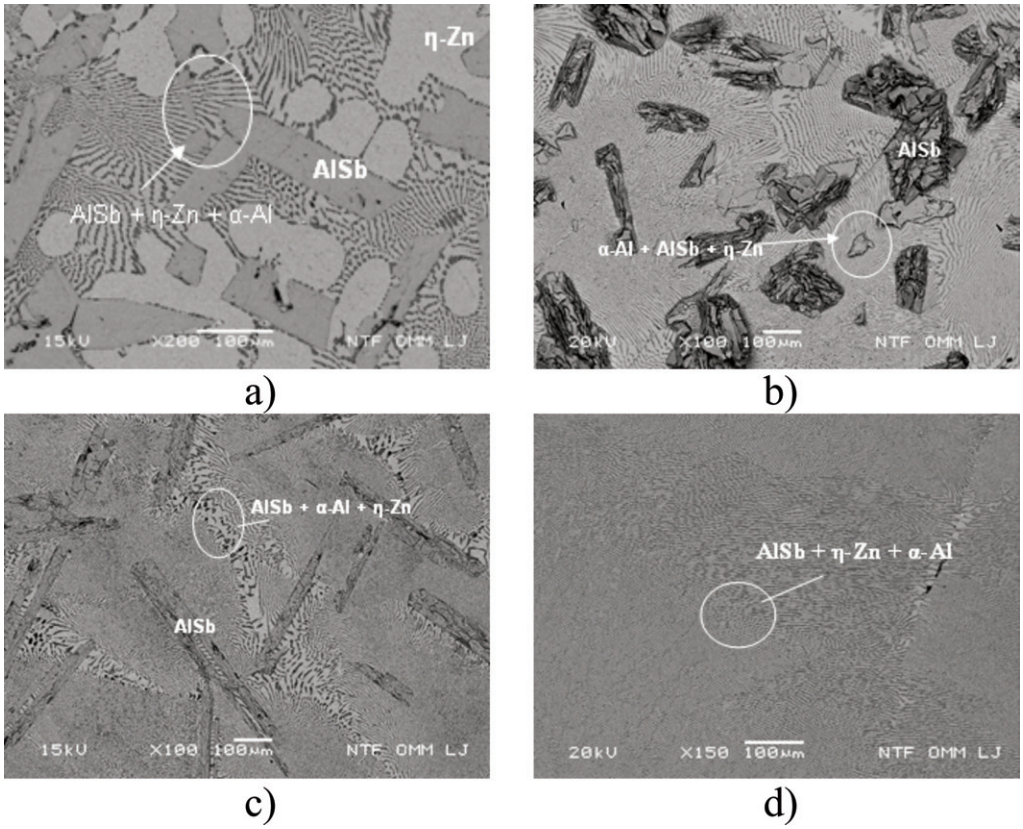
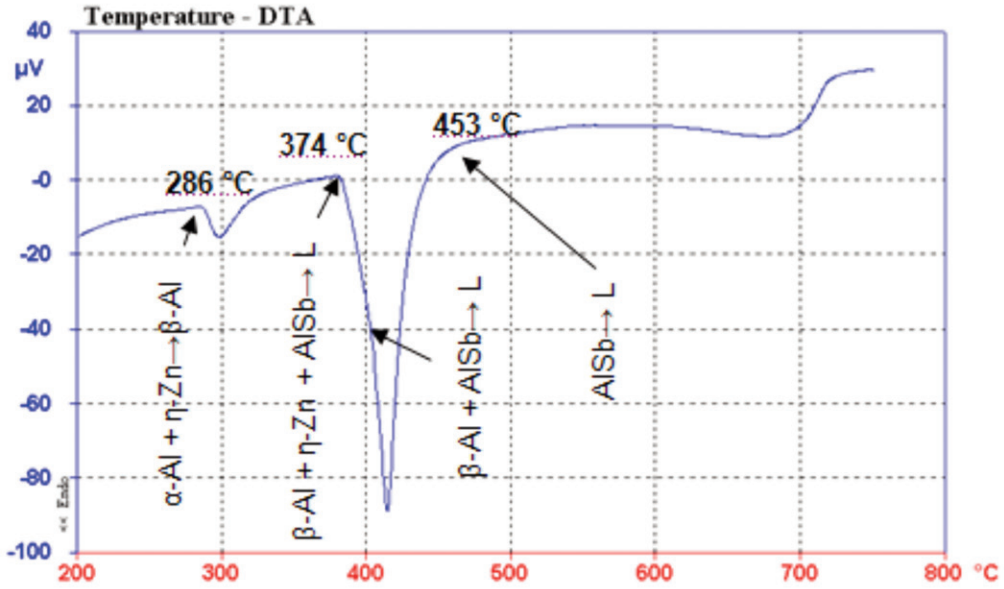


Figure 4. Microphotographs of selected samples in Zn-rich corner: (a) AZS1, (b) AZS4, (c) AZS6 and (d) AZS11

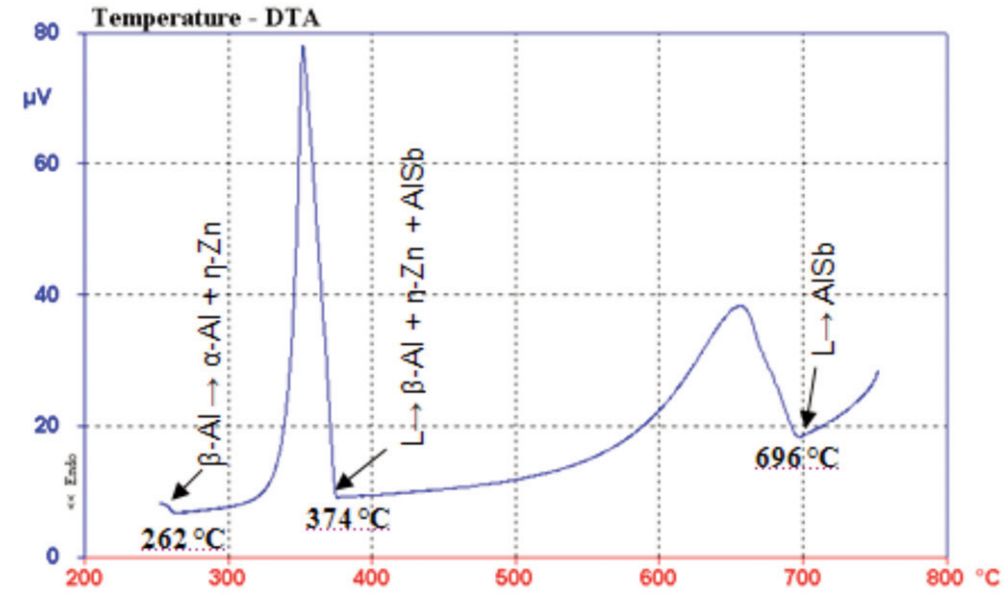
primary solidifications of other investigated samples are gathered in table 3. XRD of the non-homogenized sample AZS 6 confirms the presence of all three phases: AlSb, α-Al and η-Zn, figure 8.

The AZS11 sample's composition is located close to the ternary eutectic point. Four peaks were determined using DTA heating and cooling curves, figure 6. There were no typical peaks noticed for the primary solidification of the AlSb phase.

As discussed, the solidification of AZS11



a)



b)

Figure 5. DTA heating (a) and cooling (b) curve of AZS4

does not start with the AlSb phase but with the aluminium phase: β-Al. This is also seen in the microphotograph in figure 4d. The first examination of the sample revealed that the location of the invariant point is close to the Al-Zn binary system, see table 3. Nevertheless by further elemental mapping of the sample AZS11 revealed that the solidification of primary β-Al points on location of the eutectic point should be closer to the zinc rich-corner than what was at first proposed (0.283Al0.0016Sb0.715Zn), table 4.

Figure 7 shows that the solidification started in the β-Al phase region. The AlSb phase appeared as part of the remaining liquid for the ternary reaction L → β-Al + η-Zn +

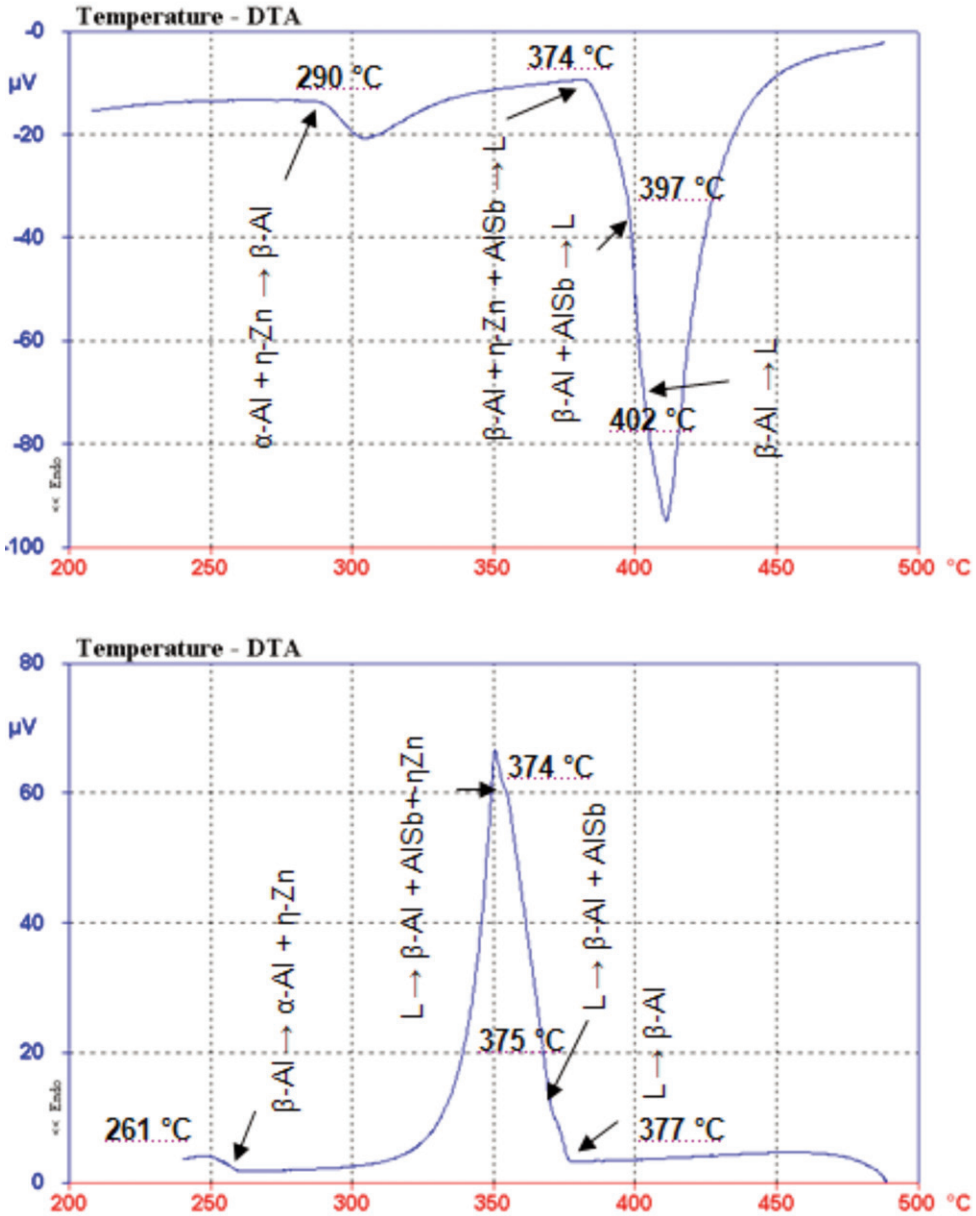


Figure 6. DTA heating and cooling curve of AZS 11

AlSb.

Thermodynamic calculation also predicts the solidification of the AZS11 sample in the β-Al region, figure 9. After primary solidification of β-Al, both $AlSb_{eut}$ and $\beta\text{-}Al_{eut}$ start to solidify. The remainder of the liquid solidifies according to the ternary reaction already discussed above. This is in good

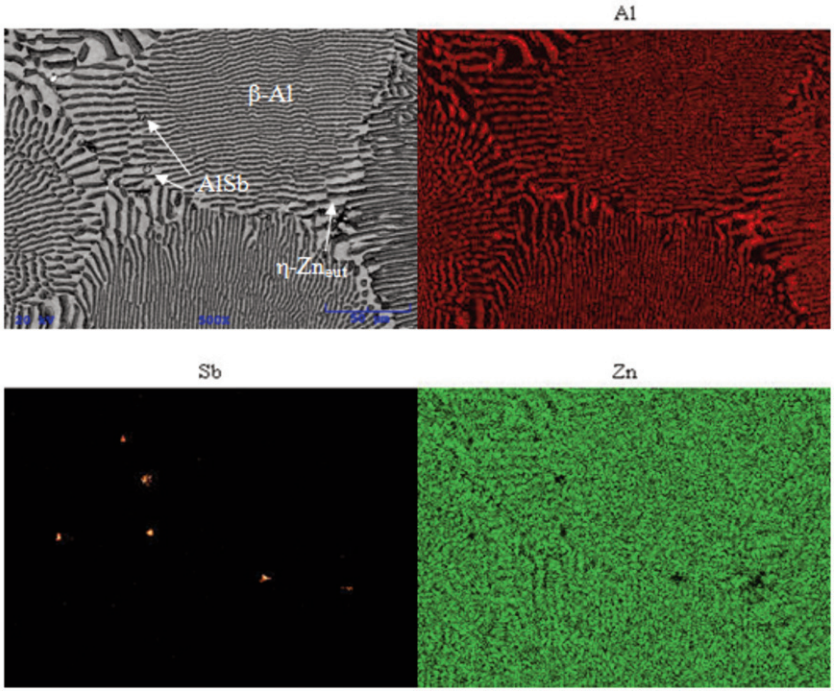


Figure 7. Elemental mapping of sample AZS11

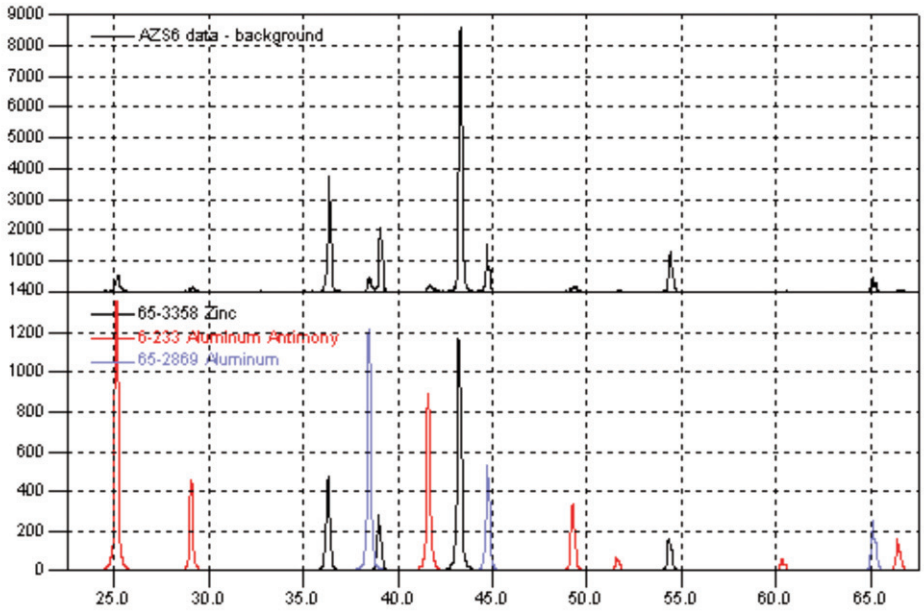


Figure 8. XRD pattern of the sample AZS6

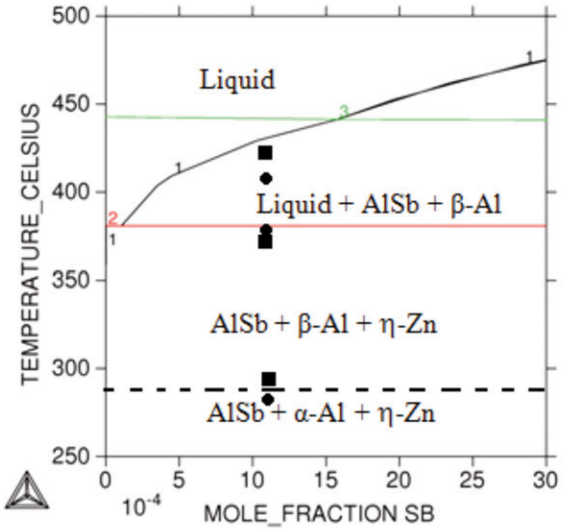


Figure 9. Isopleth phase diagram of AZS11: - - experimental, — predicted, ● cooling, ■ heating

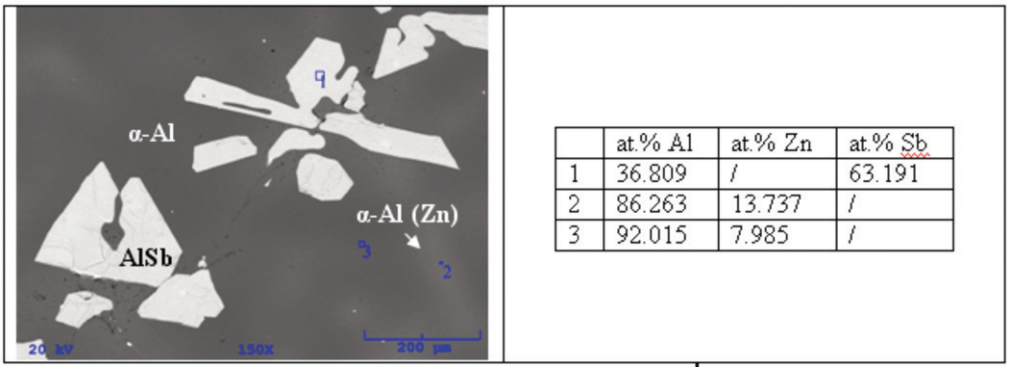
correlation with our experimental data. The ternary reaction will undergo only in the β–Al – AlSb - η-Zn phase region. No ternary eutectic was found in samples AZS13, AZS8, AZS9 and AZS10. The microphotography of the AZS13 sample shows an example of solidification in the α–Al + AlSb region. No solubility of zinc in the AlSb phase was found in the case of AZS13. Nevertheless in the case of AZS9, AZS10 and AZS8 a small solubility of zinc was confirmed in the AlSb phase.

A good correlation was determined also in the cases of AZS13, AZS8, AZS9 and AZS10 with thermodynamic calculation and experimental work. An example of an isopleth phase diagram is represented in figure 11. Primary solidification of the AlSb phase was predicted with no ternary eutectic reactions. The Zn-rich phase appears only when passing the solvus line. From metallographic analysis and from our previous work [18] we know that the formation of the zinc-rich phase can be suppressed, figure 10. In this case instead of a η-Zn phase we have zinc enriched grain boundaries, α-Al (Zn), see figure 10, 11.

As is seen from table 3, the β-Al phase will undergo decomposition into α–Al + η-Zn in average at 261 °C. When heating the β-Al phase will appear in average at around 286 °C. Theoretical liquidus temperatures determined from the DSC/DTA heating curves deviates from the temperature determined from DSC/DTA cooling curves as a result of a mass depended relation and as such is not averaged.

The location determined using metallographic analysis and peak separation of DTA and DSC peaks are revealed in table 4.

The predicted ternary reaction is at a temperature of 380 °C with the composition close to the Al-Zn binary eutectic. The



	at.% Al	at.% Zn	at.% Sb
1	36.809	/	63.191
2	86.263	13.737	/
3	92.015	7.985	/

Figure 10. Microphotograph of AZS 13 with related EDS analysis

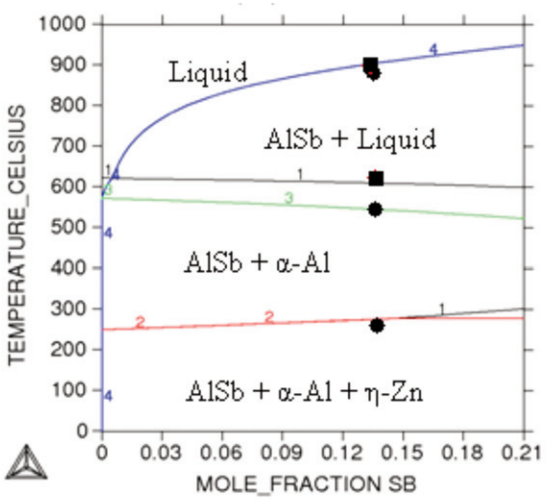


Figure 11. Isoplethe phase diagram of AZS13: ● heating, ■ cooling

location of this point, using Thermo-Calc software (TCW5) was only estimated as a result of a small antimony content (~0.01 at.%Sb). This is in agreement with the experimental results, where at 0.12Al0.0016Sb0.87Zn a ternary reaction in the three phase region AlSb-Al-Zn takes place. Nevertheless, the determined temperature of the invariant point is lower than predicted and to some extent related to the cooling rate used and a possible experimental error.

The compositions and proposed eutectic

Table 3. Characteristic temperatures of Al-Sb-Zn ternary alloys

Sample	T / °C	Type of reaction
AZS1	283, 261	Monotectoid
	374	Ternary eutectic
	724, 737	L → AlSb
AZS4	286, 262	Monotectoid
	374	Ternary eutectic
	689, 696	L → AlSb
AZS6	286, 262	Monotectoid
	374	Ternary eutectic
	685, 693	L → AlSb
AZS11	290, 261	Monotectoid
	374	Ternary eutectic
	411, 377	L → β-Al
AZS8	274	Monotectoid
	/	Ternary eutectic
	592, 577	L → AlSb
AZS10	/	Monotectoid
	/	Ternary eutectic
	623, 610	L → AlSb + α-Al
AZS9	277	Monotectoid
	/	Ternary eutectic
	590, 585	L → AlSb
AZS13	/	Monotectoid
	/	Ternary eutectic
	818, 822	L → AlSb

Table 4. Ternary invariant point

T / °C	Reaction	Composition
374 °C	L→β-Al*+η-Zn+AlSb	(0.283Al0.0016Sb0.715Zn)**
		(0.12Al0.0016Sb0.87Zn)***

*β-Al decomposes at lower temperatures to α-Al + η-Zn
** Location of ternary invariant point using only results from metallographic analysis
*** Location of ternary invariant point using results from metallographic analysis, peak separation of DTA curves and projection from AlSb to Al-Zn binary eutectic.

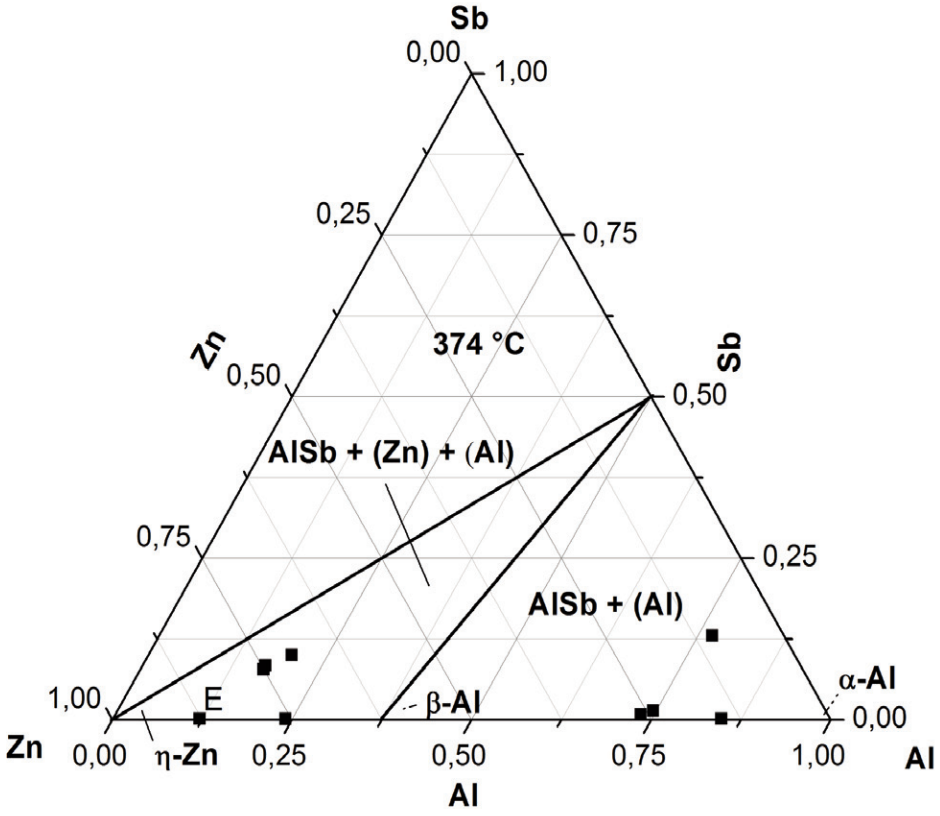


Figure 12. The 374 °C isothermal section with compositions of alloys

location are presented with figure 12.

5. Conclusion

In this study we confirmed that the AlSb phase has a great influence on the constitution of the Al-Sb-Zn ternary phase diagram. One ternary invariant point was determined with the ternary reaction L → AlSb + β - Al + η - Zn where the composition of the ternary point is 0.12Al0.0016Sb0.87Zn. The temperature of the ternary point is 374 °C. Using only the metallographic analysis makes the determination of the ternary invariant point problematic, which results in a problematic evaluation of the primary AlSb phase from the eutectic one. A small solubility of zinc in AlSb was also determined. The monotectoid reaction β - Al ↔ α - Al + η - Zn was determined to be in average at 286 °C by heating and 261 °C by cooling. By homogenization of AZS4 at 330 °C, the solubility of aluminium in zinc-rich phase η - Zn was determined to be 4.56 at.% of aluminium. This confirms a small extension of the zinc-rich region (η - Zn) from binaries into the ternary system.

Acknowledgments

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