Silver – Tin – Zinc

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Introduction

The ternary Ag-Sn-Zn system was investigated by [1994Kar, 1996Kar, 1997Hua, 1997Wnu, 1999Oht, 1999Ohn1, 1999Ohn2, 2001Vas, 2002Vas]. [1994Kar, 1996Kar] determined thermodynamic properties of the Ag-Sn-Zn alloys from electromotive force measurements. In the experiments, the liquidus temperatures of the alloys along the sections with Ag:Sn atomic ratios of 3:1, 1:1 and 1:3 were measured. Using vapor pressure measurements [1997Wnu], determined the activity of Zn in alloys, where the total content of Zn and Ag was less than 30 at.%.

According to [1997Hua], differential scanning calorimetry suggested that the ternary eutectic was at the composition 3.8Ag-1.8Zn-Sn (at.%). Addition of 1.8 at.% Zn reduced the eutectic temperature of the Sn-3.8Ag (at.%) eutectic by 4°C (217°C) [1997Hua].

[1999Oht, 1999Ohn1, 1999Ohn2] studied the Ag-Sn-Zn phase diagram over the entire concentration range by calculations based on the CALPHAD approach, together with experimental results from differential scanning calorimetry and electron probe microanalysis. The liquidus surface, two isothermal sections at 420 and 190°C and five vertical sections were presented. [1999Oht, 1999Ohn1, 1999Ohn2] also determined the invariant equilibria with the liquid phase. The composition and eutectic temperature in the Sn rich alloys was at 4.03Ag-1.62 Zn-94.35Sn (at.%) and 216.4°C according to [1999Oht, 1999Ohn1, 1999Ohn2] and was in good agreement with [1997Hua]. The liquidus surface of [1999Oht, 1999Ohn1, 1999Ohn2] was unusual in having two separate fields of the primary γ phase, but was accepted by later investigators.

[2001Vas] constructed a complete isothermal section of the Ag-Sn-Zn system at 380°C, using optical and scanning electron microscopy, X-ray analysis, microhardness measurements and differential scanning calorimetry. The isothermal section constructed by [2001Vas] was in general agreement with those of [1999Oht, 1999Ohn1, 1999Ohn2], although there were discrepancies with the α + L and α + L + β fields. [2001Vas] established the non-zero solubility of Zn in the binary Ag-Sn phases, and believed this was a reason for the discrepancy.

The Ag-Sn-Zn isothermal section [2001Vas] was confirmed by later work [2002Vas], where diffusion couples were used to study the phase equilibria at 380°C.

[2003Ohn] reported a thermodynamic database for micro-soldering alloys, including those of the Ag-Sn-Zn system, which mentioned the successful application of thermodynamics for calculating phase diagrams [1999Oht, 1999Ohn1, 1999Ohn2]. An additional vertical section was constructed in accordance with [1999Oht, 1999Ohn1, 1999Ohn2].

Binary Systems

The boundary binary systems Ag-Sn, Ag-Zn and Sn-Zn are taken from [Mas2].

Solid Phases

No ternary phases were observed in the system. The terminal solid solutions and the binary phases of the system are described in Table 1. The solubilities in Table 1 are shown after [2001Vas] because this work is the most detailed, and is considered the most reliable.

Invariant Equilibria

Based on calculations [1999Oht, 1999Ohn1, 1999Ohn2], the invariant reactions associated with the full liquidus surface are shown in Table 2. The reaction scheme is shown in Fig. 1, and is constructed considering the four-phase invariant reactions suggested by [1999Oht, 1999Ohn1, 1999Ohn2], as well as three-phase invariant reactions connected with the four-phase invariant reactions shown on the liquidus surface, but not described by [1999Oht, 1999Ohn1, 1999Ohn2]. The peritectic nature of the three–phase

invariant reactions shown on the scheme was determined from the vertical sections of [1999Oht, 1999Ohn1, 1999Ohn2], although their temperatures remain unknown. However, some of the invariant reactions seem to be missing, although they can be inferred from existence of the three-phase invariant reactions, connected with transformation of the β phase into ζ in the solid state during cooling in the binary Ag-Zn system [Mas2]. The assumed binary system Sn-Zn [Mas2] had a eutectic transformation at a higher temperature (198.5°C) than that of the four-phase transition reaction with L, (Zn), (βSn) and ε(Ag-Zn) at 193.7°C [1999Oht, 1999Ohn1, 1999Ohn2] (Table 1), which is assumed to be the ternary eutectic, E_2. However, [1999Oht, 1999Ohn1, 1999Ohn2] assumed this reaction to be the transition one because the Sn-Zn phase diagram used then had the eutectic temperature at 181°C.

Liquidus Surface

Figures 2 and 3 show the liquidus surface of the Ag-Sn-Zn phase diagram constructed after [1999Oht, 1999Ohn1, 1999Ohn2] with some corrections according to the accepted binary phase diagrams [Mas2]. Taking into account the accepted Sn-Zn phase diagram, the corresponding composition of the liquid phase in the four-phase invariant reaction with the phases (Zn), (βSn) and ε(Ag-Zn) is shown as eutectic E_2.

Isothermal Sections

Figure 4 shows isothermal section at 380°C. It is constructed after [2001Vas, 2002Vas] considering results of these works to be the most reliable. Compared to [1999Oht, 1999Ohn1, 1999Ohn2] which gave the isothermal sections at 190°C and 420°C, [2001Vas, 2002Vas] used more detailed experiments and, in general, confirmed the results of [1999Oht, 1999Ohn1, 1999Ohn2], which were obtained mainly by calculations.

Temperature – Composition Sections

Figures 5 and 6 show two vertical sections of the Ag-Sn-Zn phase diagram. They are reproduced after [1999Oht, 1999Ohn1, 1999Ohn2] with minor corrections according to the accepted binary phase diagrams Ag-Sn and Sn-Zn [Mas2].

Thermodynamics

[1994Kar, 1996Kar] determined the partial free energies of Zn in 30 liquid Ag-Sn-Zn alloys as a function of composition and temperature. These data were used by [1999Oht, 1999Ohn1, 1999Ohn2], together with their own measurements to obtain a self-consistent thermodynamic assessment. The derived thermodynamic parameters were incorporated in the database for micro-soldering alloys [2003Ohn] thus enabling many useful subsequent calculations. [1998Pen] compared experimental free energy and enthalpy of mixing values [1994Kar, 1996Kar] with those calculated using different models for the extrapolation of thermodynamic functions from binary subsystems, and found some large discrepancies. [1997Wnu] measured the activity of Zn in Ag-Sn-Zn alloys at 630°C, describing the activity coefficient of Zn as:
$\ln f_{Zn} = 0.414 - 0.424(\pm 0.13) \cdot x_{Zn} - 1.063(\pm 0.20) \cdot x_{Ag}; \quad x_{Zn} + x_{Ag} < 0.30$

Notes on Materials Properties and Applications

The Sn rich alloys of the Ag-Sn-Zn system are considered as the basis of non-toxic lead-free solders for electronic assemblies [1994McC, 1997Hua, 1997Lee, 1999Oht, 1999Ohn1, 1999Ohn2, 2001Vas, 2002Che, 2002Tsa, 2003Cha1, 2003Cha2, 2003Ohn, 2003Son2].
[1997Hua, 1997Lee] gave a review on the lead-free solder alloys for electronics, together with their properties, including those of the Ag-Sn-Zn system.
Ag based alloys containing Sn and Zn after internal oxidation are of interest as materials for electrical contacts [1993Dev].
[2002Tsa] studied thermal expansion coefficients and melting ranges of the Sn rich alloys containing 15.2 at.% Zn and 0-3.58 at.% Ag. The thermal expansion coefficient was determined to be in the range

18-22 $10^{-6}\cdot K^{-1}$ when the Ag content was less than 2.05 at.%, and in the range 24-27$\cdot 10^{-6}\cdot K^{-1}$ when the Ag content was greater than 2.05 at.%. The onset of melting (~198°C) did not change significantly with increasing Ag content. The melting range increased with increasing Ag content from 7.7°C for the binary alloy 15.2Zn-Sn (at.%), up to 27.4°C for the alloy 3.58Ag-15.2Zn-Sn (at.%).
[2001Vas] reported microhardness measurements of the Ag-Sn-Zn alloys. [2003Son2] studied mechanical properties of the Sn rich Ag-Sn-Zn alloys containing 15.2 at.% Zn and 0.51 - 3.58 at.% Ag. Addition of Ag decreased the strength and increased the ductility of the alloys.

Miscellaneous

[1956San] studied effect of Sn on the evaporation rate of Zn in the Ag-Zn alloys at 650°C in vacuum, and the addition of 0.19 at.% Sn to alloy of 34.5 at.% Zn decreased evaporation rate of Zn.
[2003Son1] investigated behavior of intermetallic compounds in the molten Ag-Sn-Zn alloys for solders during cooling and remelting.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Ag) < 961.93	*cF*4 $Fm\bar{3}m$ Cu	a = 408.57	pure Ag at 25°C [Mas2] dissolves up to 32.1 at.% Zn and 11.5 at.% Sn [Mas2]
(Zn) < 419.58	*hP*2 $P6_3/mmc$ Mg	a = 266.50 c = 494.70	pure Zn at 25°C [Mas2] dissolves up to 5.0 at.% Ag and 0.039 at.% Sn [Mas2]
(βSn) 231.9681 - 13	*tI*4 $I4_1/amd$ βSn	a = 583.18 c = 318.18	pure Sn at 25°C [Mas2] dissolves up to 0.09 at.% Ag and 0.6 at.% Zn [Mas2]
(αSn) < 13	*cF*8 $Fd\bar{3}m$ C(diamond)	a = 648.92	[Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ζ, AgZn < 274	*hP*9 $P\bar{3}$ ζ, AgZn	*a* = 763.60 *c* = 281.79	37.0 to ~ 51.2 at.% Zn [Mas2, P] dissolves up to ~1 at.% Sn at 190°C [1999Oht]
β, AgZn 710 - 258	*cI*2 $Im\bar{3}m$ W	*a* = 315.58	36.7 to 58.6 at.% Zn [Mas2, P] dissolves up to ~13 at.% Sn at 380°C [2001Vas]
γ, Ag_5Zn_8 < 661	*cI*52 $I\bar{4}3m$ Cu_5Zn_8	*a* = 934.07	58.5 to 64.7 at.% Zn [Mas2, P] dissolves up to ~2.6 at.% Sn at 380°C [2001Vas]
ε (Ag-Zn) < 631	*hP*2 $P6_3/mmc$ Mg	*a* = 282.27 *c* = 442.74	~66.2 to 89 at.% Zn [Mas2, P] at 22.5 at.% Ag [P] dissolves up to ~0.2 at.% Sn at 380°C [2001Vas]
ζ (Ag-Sn) < 724	*hP*2 $P6_3/mmc$ Mg	*a* = 294.36 *c* = 478.45	11.8 to 22.85 at.% Sn [Mas2, 1987Kar] at 16.0 at.% Sn [P]
ε, Ag_3Sn < 480	*oP*8 *Pmmn* βCu_3Ti	*a* = 596.82 *b* = 478.02 *c* = 518.43	at 23.7 to 25 at.% Sn [Mas2, 1987Kar] dissolves up to ~6 at.% Zn at 380°C [2001Vas]

Table 2: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Ag	Sn	Zn
L + β ⇌ γ	?	p_5	L	12.69	52.62	34.69
L + β ⇌ ζ(Ag-Zn)	?	p_8	L	5.66	91.13	3.21
L + γ ⇌ β (Sn)	?	p_{10}	L	1.95	94.98	3.07
L + γ ⇌ β + ε(Ag-Zn)	560	U_1	L	28.67	11.26	60.07
L + β ⇌ γ + ε(Ag-Zn)	482	U_2	L	11.83	49.28	38.89
L + ζ(Ag-Sn) ⇌ (Ag) +Ag_3Sn	437.2	U_3	L	51.11	38.21	10.68

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Ag	Sn	Zn
L + β ⇌ (Ag) + ζ(Ag-Zn)	266.3	U_4	L	6.37	90.60	3.03
L + β ⇌ γ + ζ(Ag-Zn)	252.5	U_5	L	3.99	92.45	3.56
L + (Ag) ⇌ ζ(Ag-Zn) + Ag_3Sn	240.8	U_6	L	5.42	92.43	2.15
L + γ ⇌ (βSn) + ζ(Ag-Zn)	217.7	U_7	L	2.82	94.66	2.52
L ⇌ (βSn) + ζ(Ag-Zn) + Ag_3Sn	216.4	E_1	L	4.03	94.35	1.62
L + γ ⇌ (βSn) + ε (Ag-Zn)	209.7	U_8	L	0.42	91.87	7.71
L ⇌ ε(Ag-Zn) + (βSn) + (Zn)	193.7	E_2	L	0.04	85.70	14.26

The composition of liquid in p_5 is taken from Fig. 2, the compositions of liquid in $p_{8,}$ p_{10} and E_2 are taken from Fig. 3 [1999Oht]

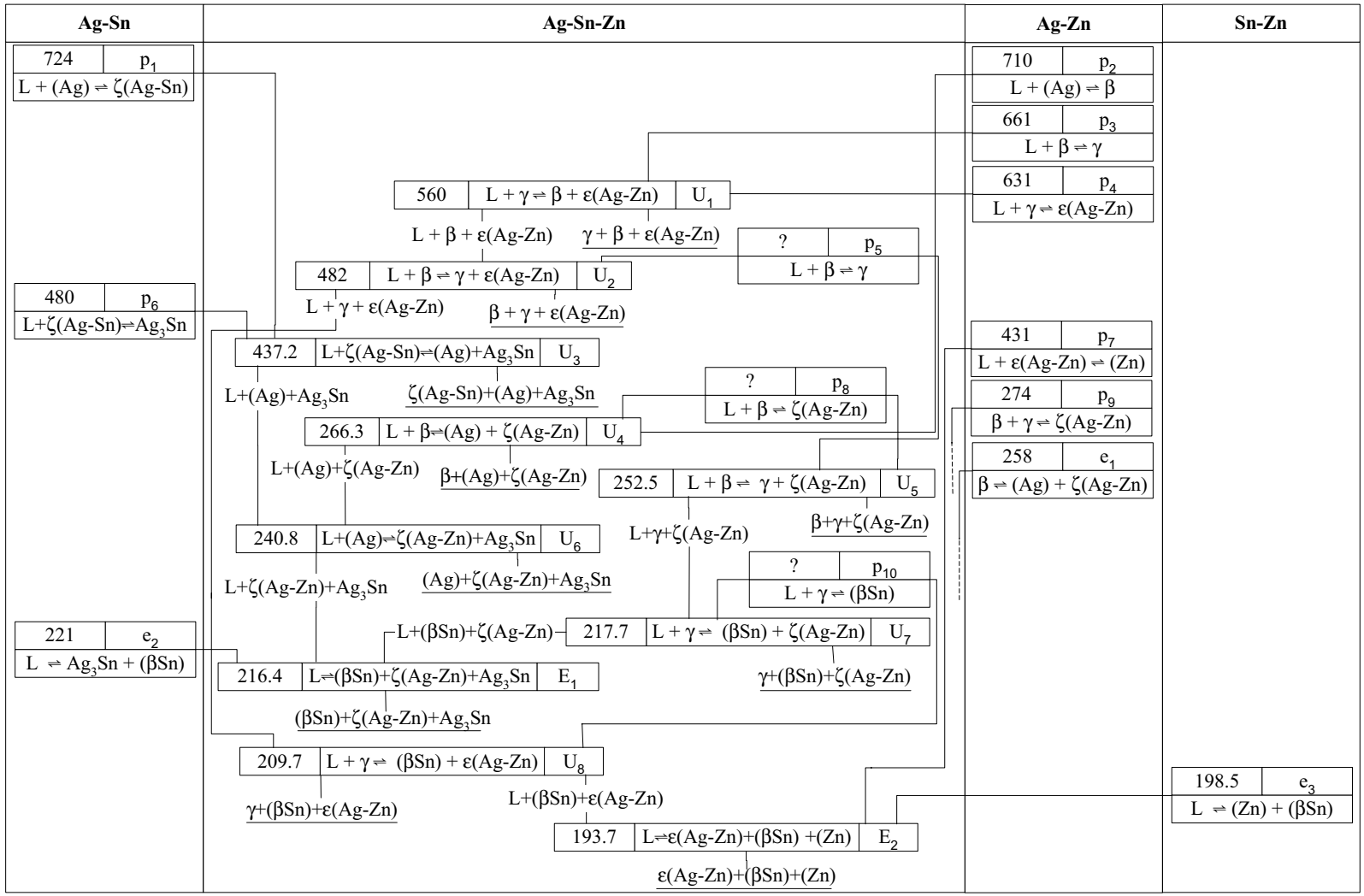

Fig. 1: Ag-Sn-Zn. Reaction scheme

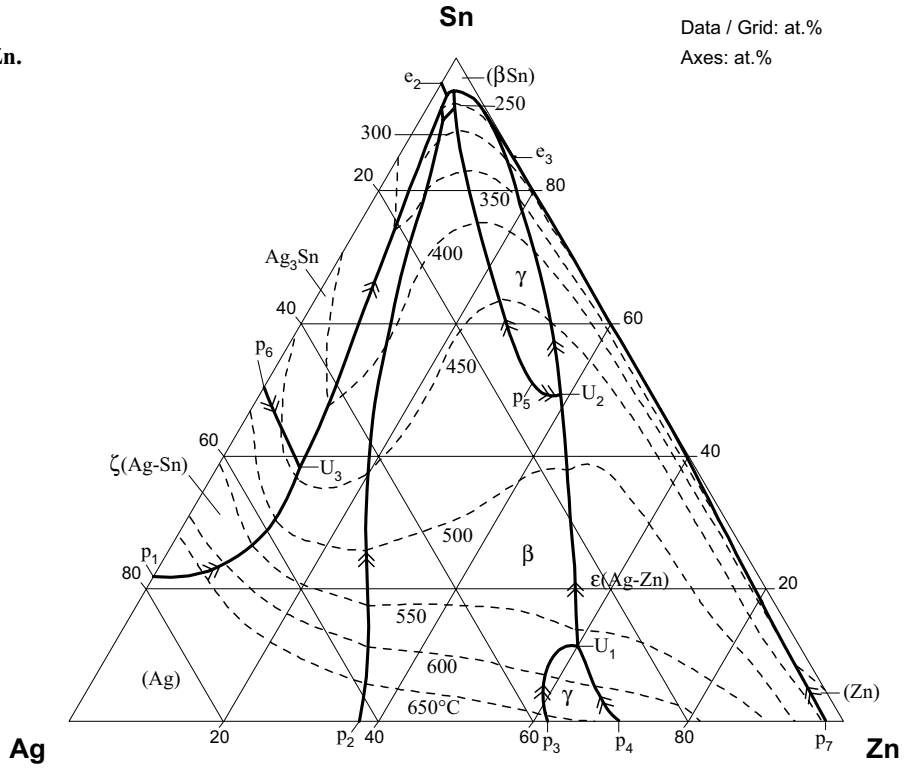

Fig. 2: Ag-Sn-Zn. Liquidus surface projection

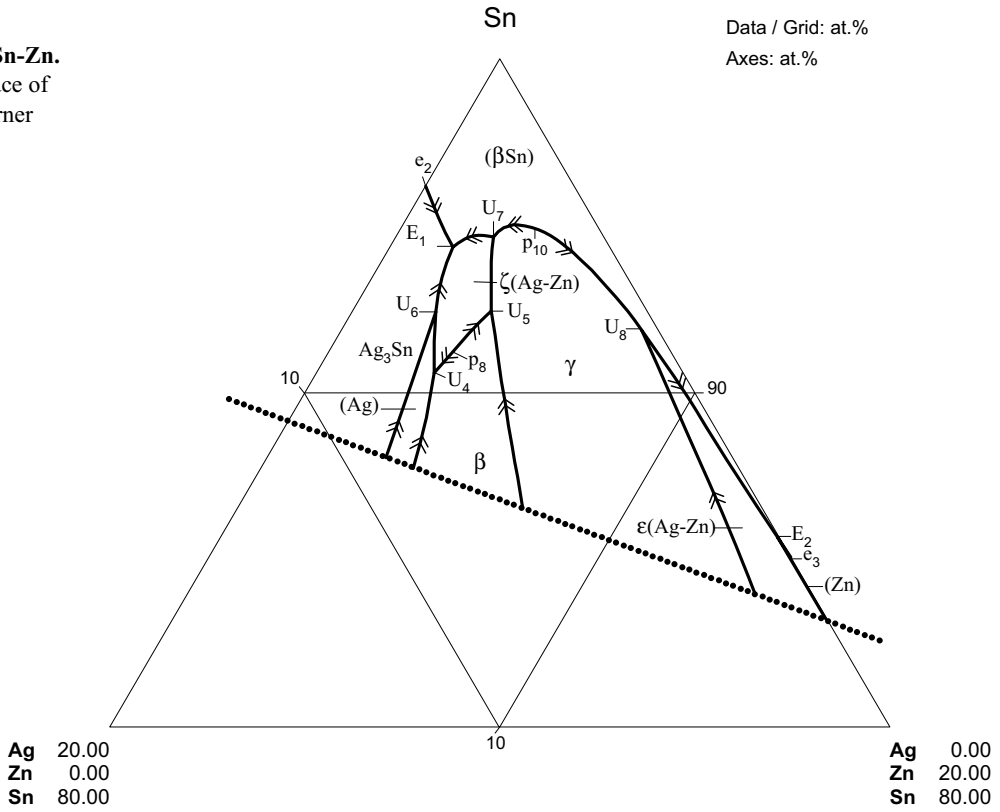

Fig. 3: Ag-Sn-Zn. Liquidus surface of the Sn rich corner

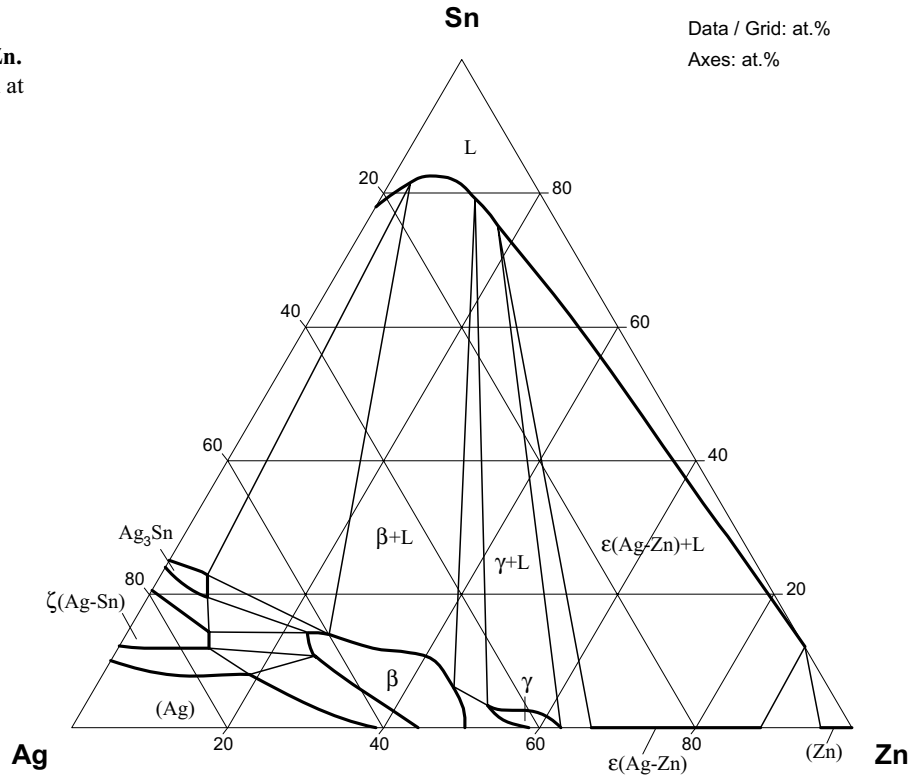

Fig. 4: Ag-Sn-Zn. Isothermal section at 380°C

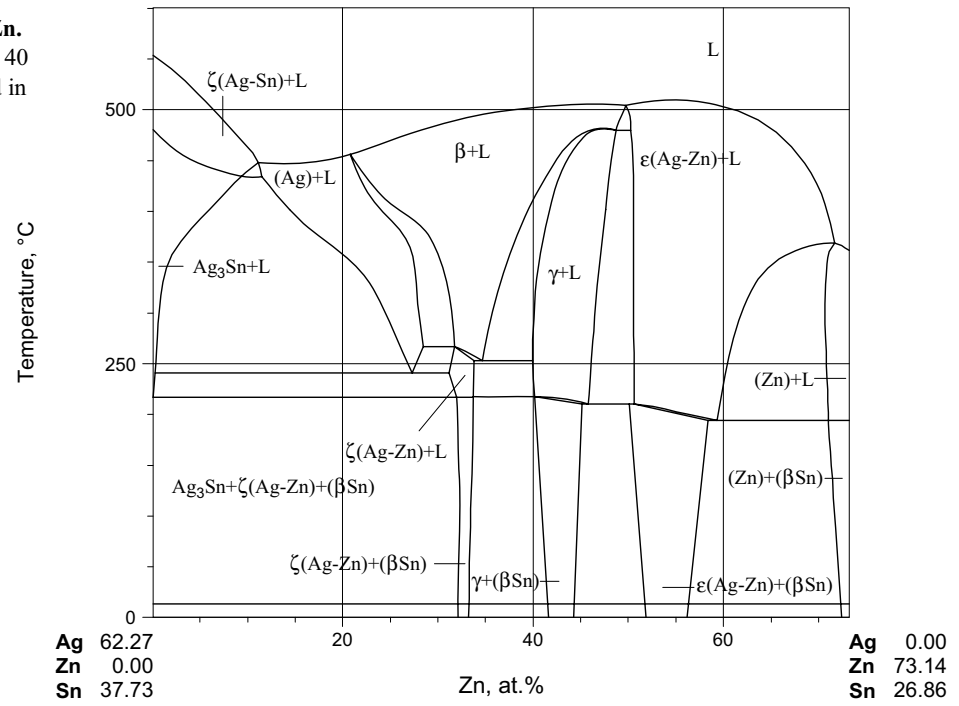

Fig. 5: Ag-Sn-Zn. Vertical section at 40 mass% Sn, plotted in at.%

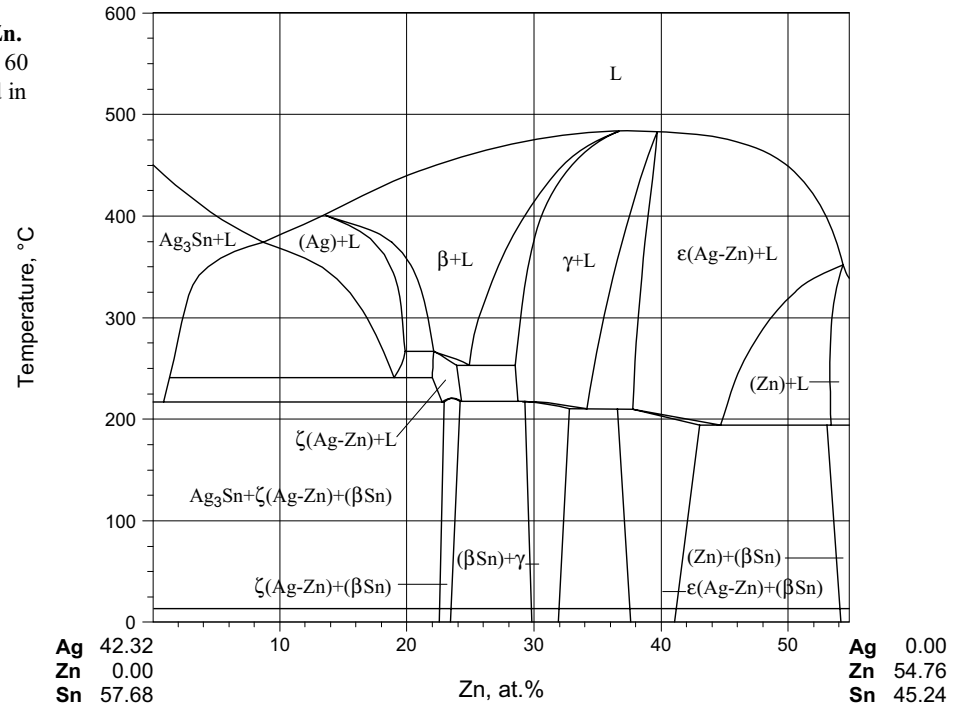

Fig. 6: Ag-Sn-Zn. Vertical section at 60 mass% Sn, plotted in at.%