Indium – Tin – Zinc

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Introduction

In the first phase diagram work a sketch of the liquidus surface was given by [1954Spe] as part of investigation of the quinary system Cd-Ge-In-Sn-Zn. He reported a ternary eutectic at 108°C and 52.2In-46Sn-1.8Zn (mass%), but did not yet distinguish between (In), (Sn) and the binary In-Sn phases. A detailed investigation of the phase diagram was presented by [1998Xie]. These authors measured liquidus temperatures and secondary arrests by DTA at 40 samples along four isopleths (Sn/Zn = 2, 1, 0.5 and constant 10 at.% In). Liquidus temperatures were also measured by [1998Yuj] using DTA along 10 sections from 0 to 50 at.% Zn and along constant 1 at.% Zn. [2001Sab1] measured liquidus temperatures as well as lower phase transitions by scanning calorimetry. The data of the three papers agree very well. Phase boundaries in completely solid state between (In) + (Zn), (In) + β + (Zn), β + (Zn), β + γ + (Zn), γ + (Zn), γ + (Sn) + (Zn) and (Sn) + (Zn) could not be exactly located, as the diffusion is too slow at these low temperatures [1998Xie].

The vapor pressure of Zn was measured by the Knudsen cell method at 9 samples at about 5, 10 and 15 at.% Zn and In/Sn ratios of 0.334, 0.920 and 3.00. The results are presented as $\log p = A + BT$ equations and activity of Zn plots at 352°C. In another paper [2003Wnu] the influence of small concentrations of In on the Zn-activity of dilute solutions of Zn in (Sn) was determined and expressed by interaction parameters. They summarized the results by the equation $\ln f_{Zn} = 1.268 - 8.621x_{Zn} - 3.19x_{In}$, valid for 750 K, where f_{Zn} is the activity coefficient of Zn.

The partial enthalpies of mixing of In, Sn and Zn in ternary In-Sn-Zn melts were measured by dropping small amounts of the solid elements into the calorimetric bath, starting with a binary liquid of equal amounts of moles of the other two elements. Preparation of the calorimetric bath in at least 10 steps was used for calibration. By summing up consecutive measurements integral enthalpies of mixing were calculated. These measurements are part of similar measurements in the quaternary system In-Pb-Sn-Zn. They were represented by tables and isoenthalpy plots smoothed by the Redlich-Kister formalism with a single ternary term and by Darken's formalism distinguishing "solvent" and "solutes" in the ternary system, and thus getting three ternary parameters. Using the same method [2000Anr] measured enthalpies of mixing of liquid at 70 samples. The results are tabulated as integral enthalpies, but can be recalculated to mean partial enthalpies of Zn or Sn in sections of different In/Sn (0.333, 1.0, 3.0) or Zn/In ratios (0.333, 1.0), respectively. The temperature was 339 to 341°C, for Zn in In/Sn = 0.333 also 634°C.

In 1997 three review papers [1997Lee, 1997Hua, 1997Yoo] collected data on In-Sn-Zn alloys and some other elements for the use as Pb-free solders. The above mentioned experimental phase diagram investigations [1998Xie, 1998Yuj, 2001Sab1] as well as measurements of surface, wetting and corrosion properties [1999Pra, 2000Yu, 2001Sab2] are also mainly dedicated to the knowledge of Pb-free solder materials.

There are three independent assessments of datasets for thermodynamic calculation of the In-Sn-Zn ternary system [2001Cui, 2001Xie, 2003Moe]. Phase diagrams calculated by the different sets do not deviate more than 5°C and agree well with the experimental data. The figures of this report are calculated from the dataset of [2003Moe].

Details of the experimental works on the In-Sn-Zn phase relations, structures and thermodynamics are given in Table 1.

Binary Systems

The binary systems are accepted as calculated from the binary datasets implemented into the ternary dataset of [2003Moe]: In-Sn modified by [2003Moe]; In-Zn [1996Lee]; Sn-Zn [1998Fri]. These systems are virtually equivalent to those of [Mas2].

Solid Phases

There are no ternary phases in the system. Except along the binary In-Sn system ((In), β, γ) solubilities in the solid phases are small. The crystallographic data of unary and binary solid phases are given in Table 2.

Invariant Equilibria

The reaction scheme is given in Fig. 1 as calculated from the dataset of [2003Moe]. Details of the invariant reactions are given in Table 3. In the other calculations [2001Cui, 2001Xie] the invariant temperatures agree within 5°C. The experimentally determined and tabulated values [1954Spe, 1998Xie, 1998Yuj, 2001Sab1] of the invariant temperature of E_1 all are within 107 and 109°C. The other tabulated experimental temperatures agree similarly well, as far as they can be clearly attributed to invariant reactions.

Liquidus Surface

The liquidus surface projection is shown in Fig. 2, calculated from the dataset of [2003Moe]. It is dominated by the area of primary crystallization of (Zn).

Isothermal Sections

The calculated isothermal section at 125°C is given in Fig. 3. The solubilities of Zn in the phases β and γ are not determined but they are known to be small. In the calculation they are ignored. However, they may be of similar magnitude as the solubilities of Zn in (In) and (Sn). Thus in Fig. 3 the part along the binary In-Sn system must be taken as tentative.

Temperature – Composition Sections

The four temperature composition sections investigated by [1998Xie] are shown in Figs. 4 to 7. The curves are calculated from the dataset of [2003Moe], they reproduce very well the experimental points of [1998Xie].

Thermodynamics

In the liquid phase enthalpies of mixing were experimentally investigated by two groups [1997Fio, 2000Anr]. In Fig. 8 the integral enthalpy as well as the partial enthalpy of Zn are shown along the section with In/Sn ratio of 1/1 *vs* x_{Zn}, calculated from the dataset of [2003Moe]. The datasets of [2001Cui, 2001Xie] give curves deviating less than 0.1 kJ·mol^{-1} from those of [2003Moe]. The curves fit the experimental data of [1997Fio, 2000Anr], except the partial enthalpies of Zn on the $x_{In} = x_{Sn}$ line, where the deviation slightly exceeds the scatter of the experimental points, the calculated partial enthalpies are about 1 kJ·mol^{-1} smaller than the measured ones.

The activity of Zn in nine alloys with less than 15 at.% Zn was determined by [1961Yok]. Calculations fit well with these data. Another activity determination was performed by [2003Wnu], who compared the Zn vapor pressure in dilute binary solutions of Zn in (Sn) with dilute ternary solutions of Zn and In in (Sn). The derived formula $\ln\gamma_{Zn} = 1.268 - 8.621x_{Zn} - 3.19x_{In}$ disagrees with the datasets [2001Cui, 2001Xie, 2003Moe], which give a much smaller dependence of the Zn activity a_{Zn} on the In content x_{In}. An argument against a strong dependence of a_{Zn} on x_{In} is the following consideration: in the two-phase field L + (Zn) the phase (Zn) is nearly pure Zn. Therefore the liquidus isotherms of the field of primary crystallisation of Zn are exactly isoactivity lines of Zn. As Fig. 2 shows, the ratio of the Zn content belonging to the same Zn activity between the In-Zn side and the Sn-Zn side is more than 0.5. This ratio is the factor, by which the activity coefficient of Zn increases by increasing the In mole fraction from zero to one. The above formula, however, predicts a decrease by the large factor $\exp(-3.19) = 0.041$ for a higher temperature, although activity coefficient usually decreases with increasing temperature.

Notes on Materials Properties and Applications

In-Sn-Zn alloys are promising candidates to replace the toxic Sn-Pb alloys for soldering. Near the invariant reaction U_1 the liquidus temperature is nearly the same as in the standard Sn-Pb solder alloy. Wetting behavior, with flux [2000Yu] and without flux [1999Pra], mechanical [1997Hua, 1999Pra] and corrosion [2001Sab2] properties were investigated. Due to the Zn content soldering preferably should be done under inert gas atmosphere to avoid formation of zincoxide.

References

[1954Spe] Spengler, H., "A Study of Two- and Multi-Component Systems of the B-Metals: The Quinary System Cadmium-Germanium-Indium-Tin-Zinc" (in German), *Metall*, **8**, 936-939 (1954) (Experimental, Phase Diagram, 19)

[1961Yok] Yokokawa, T., Doi, A., Niwa, K., "Thermodynamic Studies on Liquid Ternary Zinc Solutions", *J. Phys. Chem.*, **65**, 202-205 (1961) (Experimental, Thermodyn., 9)

[1996Lee] Lee, B.-J., "Thermodynamic Assessment of the Sn-Zn and In-Zn Binary Systems", *Calphad.*, **20**(4), 471-480 (1996) (Assessment, Calculation, Phase Diagram, Thermodyn., 51)

[1997Fio] Fiorani, J.M., Naguet, C., Hertz, J., Bourkba, A., Bouirden, L., "The Enthalpy of Mixing of the Quarternary (In,Pb,Sn,Zn) Liquid Homogeneous Phase", *Z. Metallkd.*, **88**(9), 711-716 (1997) (Experimental, Thermodyn., 8)

[1997Hua] Hua, F., Glazer, J., "Lead-Free Solders For Electronic Assembly" in *"Design and Reliability of Solders and Solder Interconnections"*, Mahidhara, M.K., Frear, D.R., Sasiry, S.M.L., Murty, K.L., Liaw, P.K., Witerbottom, W., (Eds.), The Minerals, Metals and Materials Soc., 65-73 (1997) (Mechan. Prop., Phase Diagram, Review, 63)

[1997Lee] Lee, N.C., "Getting Ready for Lead-Free Solders", *Soldering Surf. Mount Technol.*, **9**(2), 65-69 (1997) (Mechan. Prop., Review)

[1997Yoo] Yoon, S.W., Soh, J.R., Lee, H.M., Lee, B.-J., "Thermodynamic Aided Alloy Design and Evaluation of Pb-free Solder, Sn-Bi-In-Zn System", *Acta Mater.*, **45**(3), 951-960 (1997) (Calculation, Experimental, Phase Relations, 31)

[1998Fri] Fries, S., Lukas, H.L., "System Sn-Zn" in *"COST 507 Thermochemical Database for Light Metal Alloys"*, Ansara, I., Dinsdale, A.T., Rand, M.H., (Eds.), **Vol. 2**, European Community, Luxembourg, 288-289 (1998) (Assessment, Calculation, Phase Diagram, Thermodyn.)

[1998Xie] Xie, Y., Schicketanz, H., Mikula, A., "The In-Sn-Zn System", *Ber. Bunsen-Ges. Phys. Chem.*, **102**(9), 1334-1338 (1998) (Crys. Structure, Experimental, Phase Diagram, Phase Relations, 13)

[1998Yuj] Yujun, Z., Qiyun, Z., "Phase Diagram of Sn-In-Zn System and its Use for Lead-Free Solder", *Acta Phys. Sin. (Chin. J. Phys.)*, **14**(12), 1098-1103 (1998) (Experimental, Phase Diagram, 11)

[1999Pra] Prasad, L.C., Xie, Y., Mikula, A., "Lead Free Solder Materials In-Sn-Zn System", *J. Non-Cryst. Solids*, **250-252**, 316-320 (1999) (Experimental, Phase Diagram, Interface Phenomena, 16)

[2000Anr] Anres, P., Alaoui-Elbelghiti, M., Gambino, M., Bros, J.P., "Enthalpy of Formation of the (In-Sn-Zn) Liquid System", *Thermochim. Acta*, **346**, 49-56 (2000) (Experimental, Thermodyn., 17)

[2000Yu] Yu, S.-P., Liao, C.-L., Hon, M.-H., Wang, M.-C., "The Effects of Flux on the Wetting Characteristics of Near-Eutectic Sn-Zn-In Solder on Cu Substrate", *J. Mater. Sci.*, **35**, 4217-4224 (2000) (Electronic Structure, Experimental, Mechan. Prop., Interface Phenomena, 19)

[2001Cui] Cui, Y., Liu, X.J., Ohnuma, I., Kainuma, R., Ohtani, H., Ishida, K., "Thermodynamic Calculation of the In-Sn-Zn Ternary System", *J. Alloys Compd.*, **320**(2), 234-241 (2001) (Assessment, Calculation, Phase Diagram, Thermodyn., 16)

[2001Sab1] Sabbar, A., Zrineh, A., Gambino, M., Bros, J.P., "About Phase Equilibria in the Ternary System Indium-Tin-Zink" (in French), *Thermochim. Acta*, **369**, 125-136 (2001) (Experimental, Phase Diagram, Thermodyn., 28)

[2001Sab2] Sabbar, A., El Hajjaji, S., Ben Bachir, A., Alaoui-El Belghiti, M., Zrineh, A., "Evaluation of Corrosion Behaviour of a New Class of Pb-Free Solder Materials (Sn-In-Zn)", *Mater. Corr.*, **52**, 298-301 (2001) (Electrochemistry, Interface Phenomena, Phys. Prop., Experimental, 11)

[2001Xie] Xie, Y., Qiao, Z.Y., Mikula, A., "The Sn-In-Zn System. Application of CALPHAD Technique to Phase Diagram Measurement", *Calphad*, **25**(1), 3-10 (2001) (Assessment, Calculation, Phase Diagram, Thermodyn., 9)

[2003Moe] Moelans, N., Hari Kumar, K.C., Wollants, P., "Thermodynamic Optimization of the Lead-Free Solder System Bi-In-Sn-Zn", *J. Alloys Compd.*, **360**, 98-106 (2003) (Assessment, Calculation, Phase Diagram, Thermodyn., 44)

[2003Wnu] Wnuk, G., Romanowska, J., Pomianek, T., "Influence of In on the Activity of Zinc in Liquid (Tin+Zinc+Indium)", *J. Chem. Thermodyn.*, **35**(5), 717-717 (2003) (Experimental, Thermodyn., 14)

Table 1: Investigations of the In-Sn-Zn Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1954Spe]	DTA	first sketch of liquidus surface
[1961Yok]	Knudsen cell effusion	vapor pressure of Zn, 9 alloys, $x_{Zn} \leq 0.15$, 352°C
[1997Fio]	drop calorimetry	partial and integral enthalpies of mixing of liquid, 347 or 383°C, 40 measurements
[1998Xie]	DTA, X-ray, microprobe	4 isopleths, $x_{Sn}/x_{Zn} = 2$, 1, 0.5 and $x_{In} = 0.1$
[1998Yuj]	DTA	liquidus surface < 50 mass% Zn
[2000Anr]	drop calorimetry	partial and integral enthalpies of mixing of liquid, 440 and 634°C, 70 measurements
[2001Sab1]	DSC	6 isopleths, $x_{In}/x_{Sn} = 0.05$, 0.15, 0.50, 0.52, 0.67 or 0.85
[2003Wnu]	isopiestic vapor pressure with liquid Sn-Zn	477°C, a_{Zn} of dilute In + Zn in liquid Sn

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(In) < 156.634	*tI*2 *I*4/*mmm* In	 *a* = 325.20 *c* = 494.70	dissolves 16.3 at.% Sn and 1.8 at.% Zn [2003Moe] pure In [Mas]
(βSn) 231.9681 - 13	*tI*4 $I4_1/amd$ βSn	 *a* = 583.18 *c* = 318.18	dissolves 3.6 at.% In and 0.6 at.% Zn [2003Moe] pure Sn, at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αSn) < 13	*cF*8 $Fd\bar{3}m$ C (diamond)	a = 648.92	pure Sn [Mas2]
(Zn) < 419.58	*hP*2 $P6_3/mmc$ Mg	a = 266.49 c = 494.70	dissolves 0.7 at.% In and 0.2 at.% Sn [2003Moe] pure Zn [P]
β, $In_{1-x}Sn_x$ ≲ 144	*tI*2 *I*4/*mmm* In	a = 346.3 c = 440.4	$0.19 \le x \le 0.57$ 25 at.% Sn, 24°C [V-C2]
γ, In_xSn_{1-x} < 224	*hP*1 *P*6/*mmm* BiIn	a = 320.6 c = 299.7	$0.06 \le x \le 0.24$ 80 at.% Sn, −10°C [V-C2]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				In	Sn	Zn
L + (Sn) ⇌ γ + (Zn)	183.3	U_1	L	9.9	79.5	10.6
			(Sn)	3.6	95.7	0.6
			γ	6.5	93.5	0.0
			(Zn)	0.02	0.03	99.95
L + (In) ⇌ β + (Zn)	121.5	U_2	L	76.1	21.0	2.9
			(In)	81.8	16.3	1.9
			β	80.7	19.3	0.0
			(Zn)	0.06	0.01	99.93
L ⇌ β + γ + (Zn)	107.4	E_1	L	52.5	45.0	2.5
			β	57.0	43.0	0.0
			γ	23.6	76.4	0.0
			(Zn)	0.03	0.01	99.96

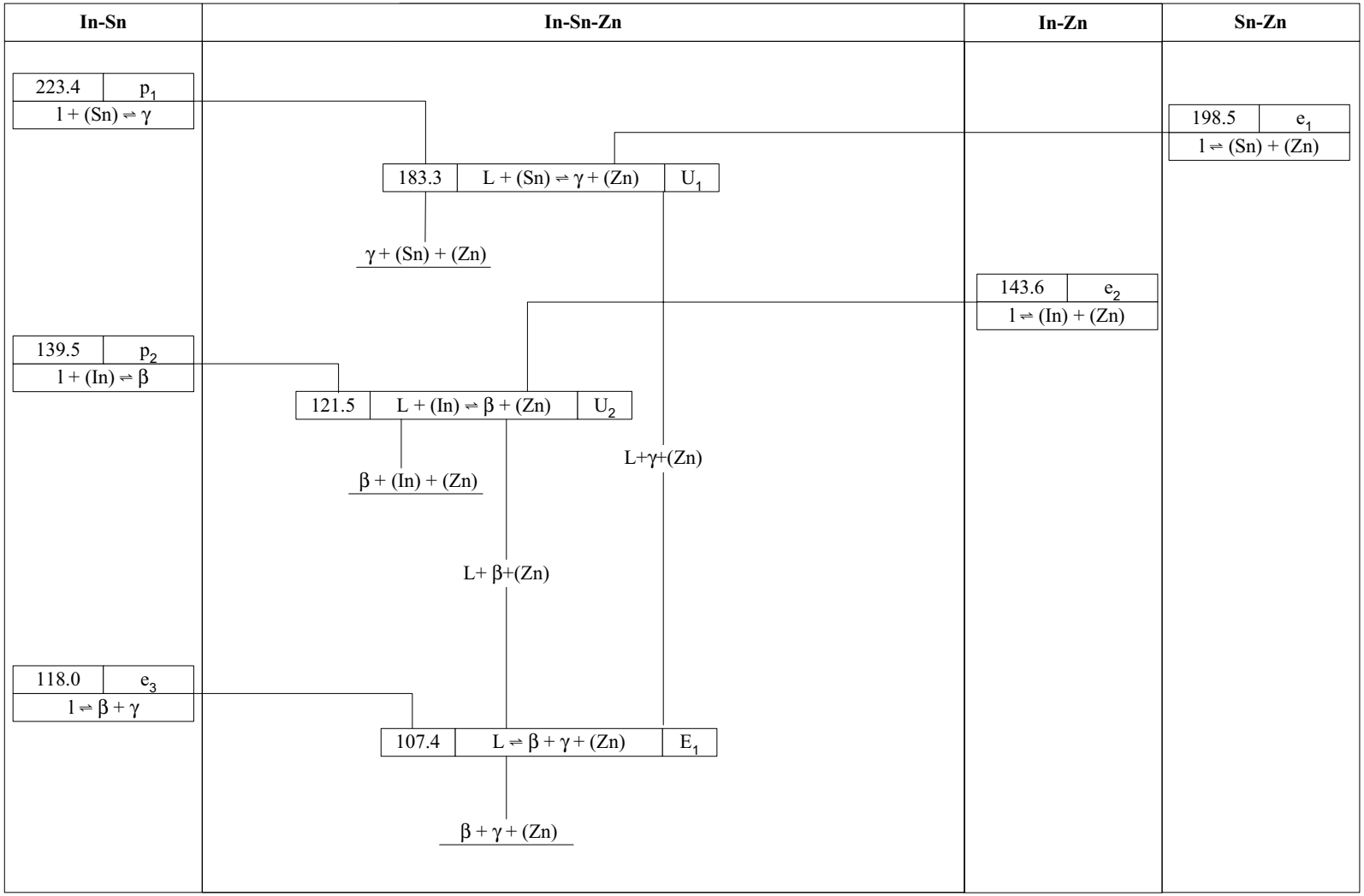

Fig. 1: In-Sn-Zn. Reaction scheme

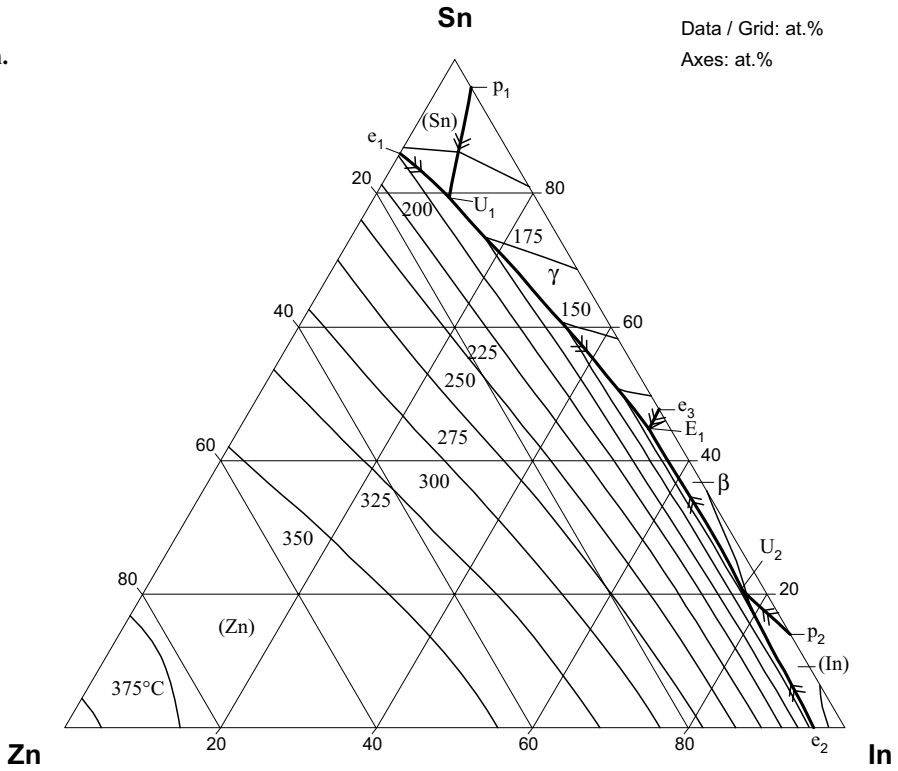

Fig. 2: In-Sn-Zn. Liquidus surface projection

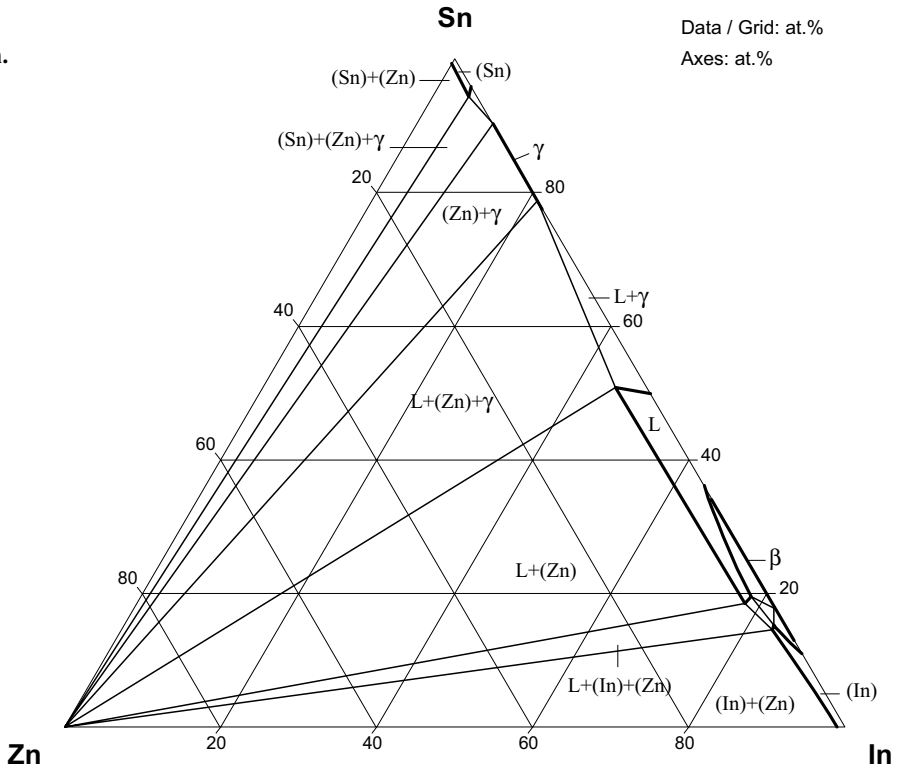

Fig. 3: In-Sn-Zn. Isothermal section at 125°C

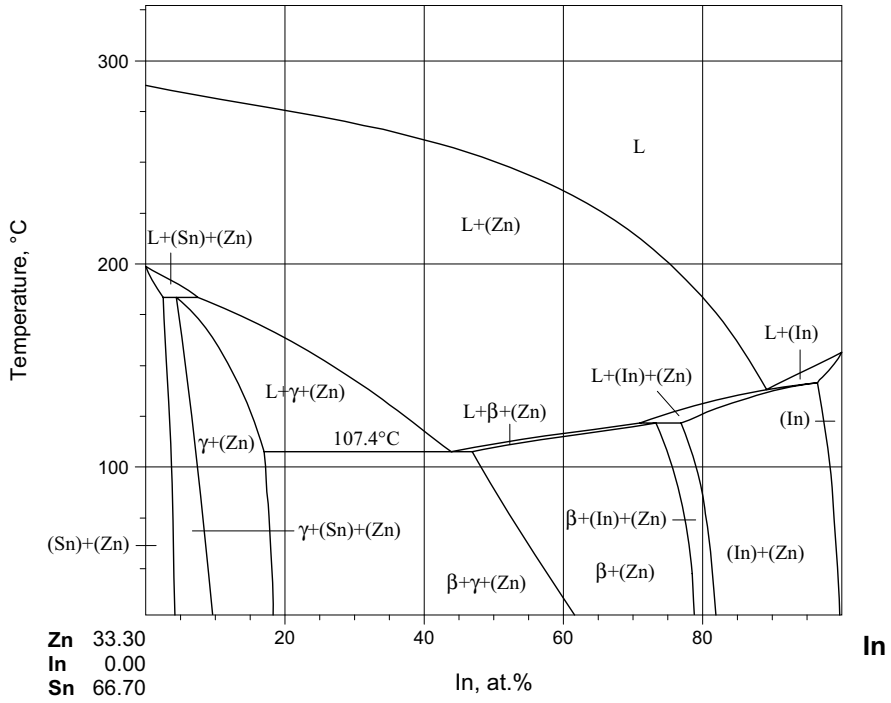

Fig. 4: In-Sn-Zn. Isopleth at Sn/Zn = 2/1

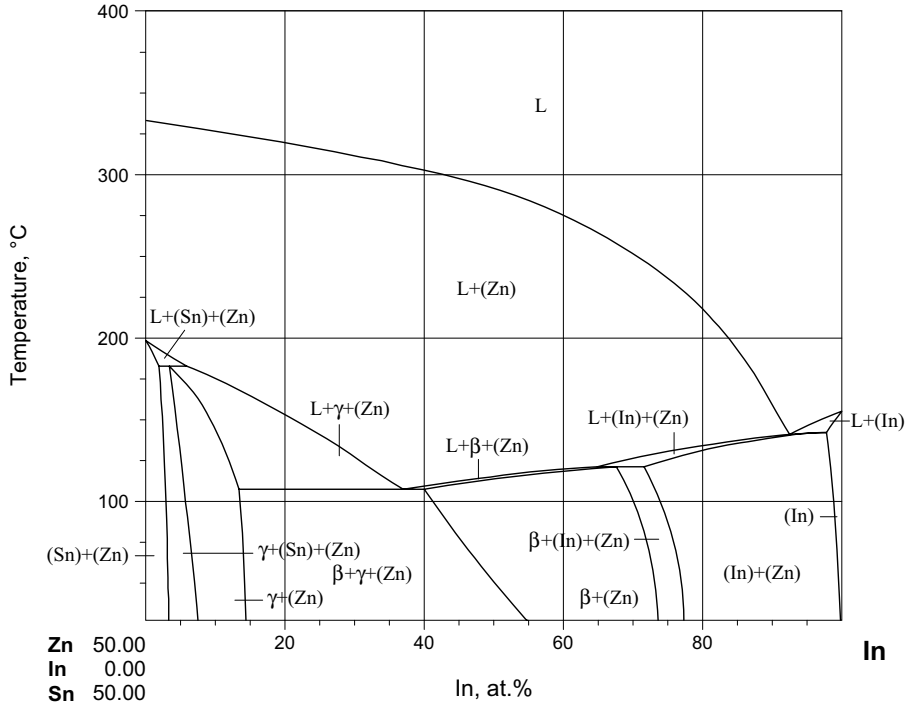

Fig. 5: In-Sn-Zn. Isopleth at Sn/Zn = 1/1

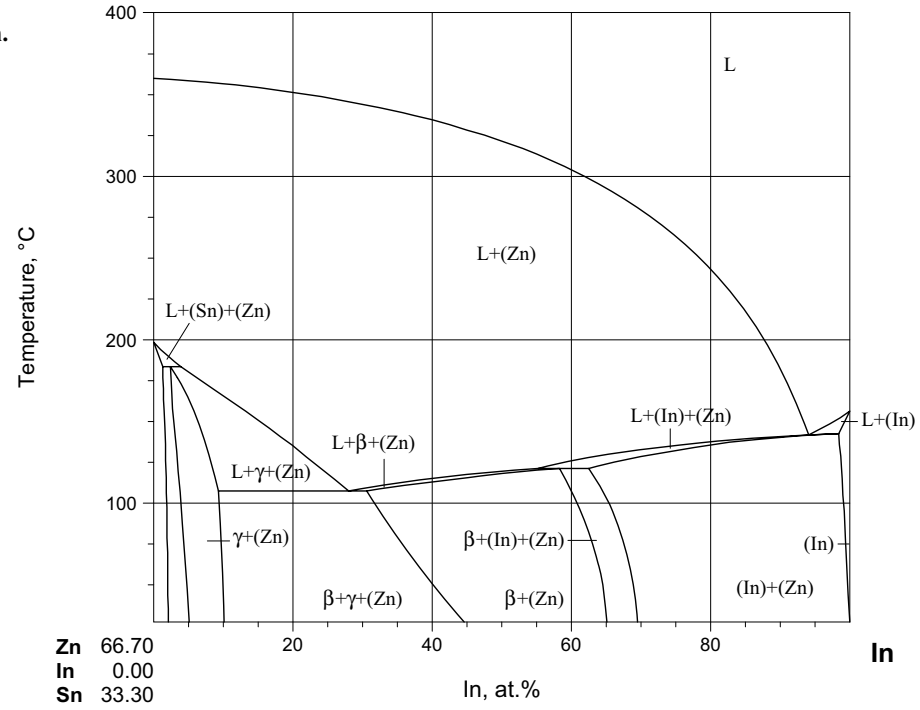

Fig. 6: In-Sn-Zn. Isopleth at Sn/Zn = 1/2

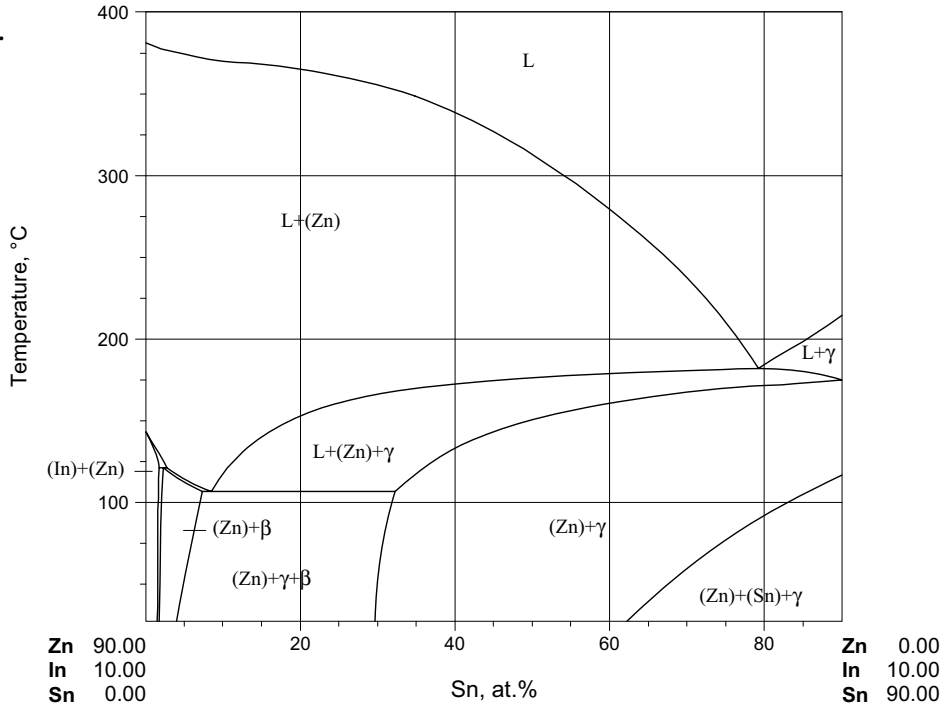

Fig. 7: In-Sn-Zn. Isopleth at constant 10 at.% In

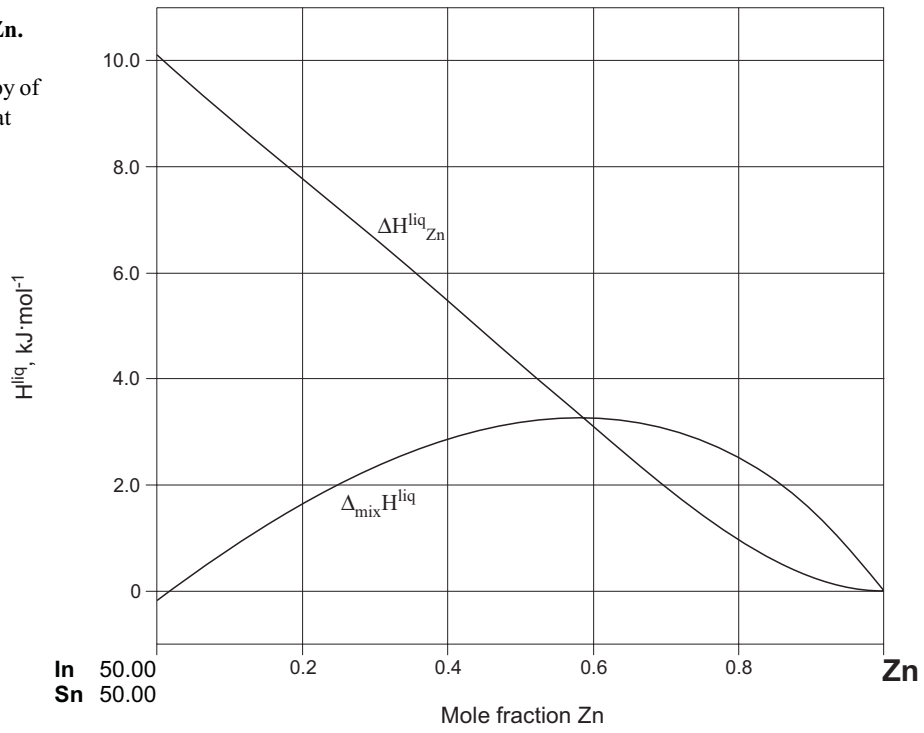

Fig. 8: In-Sn-Zn. Integral and Zn-partial enthalpy of mixing of liquid at 445°C