Silver – Lead – Tin

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Introduction

Based on thermal analysis and metallography of 102 alloys, [1911Par] reported seven vertical sections, the liquidus surface and two invariant equilibria. The results were later discussed by the same author again [1913Par]. Because the binary systems adopted are too old, the data are not very reliable.
[1946Ear] investigated the liquidus surface of the Pb corner and the ternary eutectic by thermal analysis, micrographic observation, segregation study of slowly cooled alloys and small-scale melting experiments of a total of 59 alloys. [1933Gar] reported liquidus and solidus curves along the section Pb-Ag_3Sn with up to 7 mass% Ag_3Sn and put into evidence the formation of a solid solution between Pb and Ag_3Sn; however, the points scatter markedly. [1944Rus] determined the solidification ranges of three Ag-Pb-Sn alloys by thermal analysis. A review of the ternary system was presented by [1988Ran]. [1987Tar] calculated the eutectic temperature depression in the Sn-Pb system coarsened by addition of silver as –3.3°C/mass% Ag. This value is in excellent agreement with their own experimental values, which ranged from –3.3 to –2.6°C, and with value of –3.7°C/mass% Ag derived from [1946Ear]. [1996Fri] studied the changes occurring in a eutectic Ag-Sn solder due to addition of lead. It was shown, that already at very small lead contents (< 0.5 at.%) a ternary eutectic reaction takes place at 178°C. [2001Kat] calculated isopleth (Sn-3.5 mass% Ag)-(Sn-37 mass% Pb). [2003Zen] presented calculated liquidus surface projection as well as vertical section of the Ag-Sn-Pb phase diagram from the binary Ag-Sn eutectic composition to pure Pb.
By means of emf, using the cell Sn(l), SnO_2(s)/calcia stabilized zirconia/Sn(alloy), SnO_2(s), [1973Jag] studied the partial free energy of mixing of Sn in the molten Ag-Pb-Sn system at 1073 K, along the concentration lines with x_{Ag}/x_{Pb} ratios of 3/7.1 and 7/3. On each line nine alloys were examined. Using the results of [1973Jag, 1978Cho] and [1983Lee, 1984Lee] derived thermodynamic descriptions of the liquid phase. [1992Lee] optimized the available thermodynamic values and calculated activities of Ag and Pb in the Ag-Sn-Pb system at 800°C.
The morphology of eutectic in Sn-36Pb-2Ag (mass%) alloy was discussed by [2002Nog].
[1979Zah] studied 6 alloys that were positioned near the corners and in the sides of the following composition triangle: 20Ag20Sn60Pb - 20Ag60Sn20Pb - 60Ag20Sn20Pb (at.%). The density, surface tension and their temperature coefficients were examined in the temperature interval from liquidus to 800°C.
[1992Sca] investigated the effects of accelerated fatigue tests on crack formation in 95.5Pb-2Sn-2.5Ag (mass%) solder joints. [1998Vei] presented the results of the experimental determination of the viscoelastic tensile and shear properties of the eutectic 62Sn-36Pb-2Ag (mass%) solder alloy in the temperature range between –20 and 100°C. The aims of [2001Bra, 2002Ama, 2004Isl] are concerned with the development of lead-free solders, the 62Sn-36Pb-2Ag (mass%) solder was used for comparative experiments. The characteristics of melting and wetting were studied by [2001Bra]. Strain rate as a function of steady state stress for 62Sn-36Pb-2Ag solder was presented by [2002Ama]. [2004Isl] presented the interfacial reactions of 62Sn-36Pb-2Ag solder with Ni.
The shear test of 62Sn-36Pb-2Ag balls bonding placed on copper pad and cooled at 10 $K \cdot min^{-1}$ to 200 $K \cdot min^{-1}$ has been performed by [2002Nak]. [1998Sch] presented experimental data for Cu-Sn intermetallic growth between copper and 62Sn-36Pb-2Ag solder. The morphology of eutectic in Sn-36Pb-2Ag alloy was discussed by [2002Nog].

Binary Systems

The accepted Ag-Pb phase diagram is taken from [2002Luk]. The Ag-Sn binary system is taken from [1987Kar]. The Pb-Sn phase diagram is taken from [1988Kar].

Solid Phases

Solid phases observed in this system are given in Table 1.

Quasibinary Systems

[1911Par] reported an invariant equilibrium L ⇌ (αPb) + Ag_3Sn with maximal solidus temperature of about 300°C. A ternary maximum at 310°C was reported by [1946Ear] too. These results are doubtful since the Ag-Sn system contains the Ag_4Sn phase and two U type nonvariant equilibria must be realized in the Pb corner of the phase diagram.

Invariant Equilibria

A ternary eutectic is reported by [1946Ear]. The only known values are the temperature and equilibrium composition of the liquid, which are taken from [1946Ear]. They are presented in Table 2. Two U reactions, in which Ag_4Sn is involved, are also qualitatively presented in Table 2.

Liquidus Surface

[2003Zen] calculated liquidus surface projection of the Ag-Pb-Sn phase diagram using CALPHAD technique. It is presented in Fig. 1 and the reaction scheme is shown in Fig. 2. The triangle drawn by dashed lines shows the calculated compositions of the three solid phases that are formed in the eutectic reaction L ⇌ (βSn) + (αPb) + Ag_3Sn.

Temperature – Composition Sections

The vertical sections 96.2Sn3.8Ag - 74.79Sn25.21Pb and 96.2Sn3.8Ag - Pb were calculated by [2001Kat] and [2003Zen], respectively. They are presented in Fig. 3 and Fig. 4.

Thermodynamics

The activities of Ag, Pb and Sn in the liquid alloys at 800°C are shown in Fig. 5. Activities of tin have been experimentally determined by [1973Jag], using the following cell:
Sn(l),SnO_2(s)/Calcia stabilized zirconia/Sn(alloy),SnO_2(s)
Activities of lead and silver have been then obtained by Gibbs-Duhem integration. These results have been used by [1983Lee, 1984Lee, 1992Lee] for modelling the liquid alloy. Experimental data at 800°C could be excellently represented by the Redlih-Kister Muggianu model including the ternary interaction parameters as follows:
$\Delta G^{xs}/J \cdot mol^{-1} = -2929 x_{Ag} x_{Sn} x_{Pb} + x_{Ag} x_{Sn} x_{Pb} (47680 x_{Ag} + 10137 x_{Sn} + 6296 x_{Pb})$

Notes on Materials Properties and Applications

Soldering is the most important method for joining mechanical components in electronics. The 62Sn-36Pb-2Ag (mass%) eutectic alloy is widely used as a solder and it is one of the major bonding materials in electronic devices.
[1979Zah] showed that temperature dependences of density of Ag-Pb-Sn alloys are linear. The isobaric coefficients of thermal expansion are minimal ($\beta \approx 8 \cdot 10^{-5} °C^{-1}$ and $\beta \approx 9 \cdot 10^{-5} °C^{-1}$) at Ag contents of ~ 55 and ~ 20 at.% and Pb contents of 20 and 55 at.%, respectively. The higher Ag content leads to the higher surface tension coefficient, and *vice versa*, the higher Pb content leads to the lower one. For example, the 20Sn-60Ag-20Pb (at.%) alloy coefficient of surface tension is equal to $\sigma = 527\ mJ \cdot m^{-2}$ and for the 20Sn-20Ag-60Pb (at.%) alloy the coefficient of surface tension is equal to $415\ mJ \cdot m^{-2}$ at 750°C.
The investigation of the effect of accelerated fatigue tests on crack formation in the 62Sn-36Pb-2Ag (mass%) solder joint shows that the crack occurs at a critical number of cycles when a Sn-depleted region is formed, yielding weaker inner layers with lower shear strength. The increasing of mechanical stress leads to increasing in tin depletion. This depletion is not homogeneously distributed along the surface.

The apparently spontaneous fractures take place when the crack can propagate along Sn depleted inner regions which are continuously extended from one end of alloy to another [1992Sca].
The experimental results of [1998Vei] show that the temperature dependences of the dynamic Young's modulus and shear modulus of the eutectic 62Sn-36Pb-2Ag (mass%) solder alloy in the temperature range between –2 and 100°C can be approximated by linear functions:
$E(T)/\mathrm{GPa} = -0.055T + 41.90$;
$G(T)/\mathrm{GPa}) = -0.022T + 15.16$.
The dynamic Young's and shear moduli decrease by approximately 6% and the viscous damping coefficient increases by approximately 80% for a temperature rise from room temperature to 60°C.
The eutectic 62Sn-36Pb-2Ag (mass%) solder alloy is used in a ball grid array technique, that is a bonding process which solder balls are arranged on Cu pads in a print board and heated in a reflow instrument after setting IC chips on them. This process makes semiconductor devices higher integrated, smaller, thinner and lighter than conventional ones.
It must be noted, that there is tremendous interest presently in Pb-free solder assembly in the surface mount assembly industry in response to recent Japanese and European initiatives and proposed governmental restrictions regarding Pb usage and disposal.

References

[1911Par] Parravano, N., "The Ternary Silver - Tin - Lead System" (in German), *Int. Z. Metallogr.*, **1**, 89-108 (1911) (Phase Relations, Experimental, 7)

[1913Par] Parravano, N., "The Ternary Silver - Tin - Lead System" (in German), *Int. Z. Metallogr.*, **3**, 15-22 (1913) (Phase Relations, Theory, 4)

[1933Gar] Garre, B., Vollmert, F., "Härtbare Bleilegierungen", *Z. Anorg. Allg. Chemie*, **210**, 77-80 (1933) (Phase Relations, Experimental, 1)

[1944Rus] Russell, J.B., Mack, J.O., "Substitute Solders of the 15-85 Tin - Lead Type", *Metals Technology*, October (1944) (Experimental, 25)

[1946Ear] Earle, L.G., "Some Data Concerning Lead Alloys Containing Tin (up to 63%) and Silver (up to 3%)", *J. Inst. Metals*, **72**, 403-413 (1946) (Phase Relations, Experimental, #, 9)

[1973Jag] Jagannathan, K.P., Ghosh, A., "A Thermodynamic Study of the Molten Pb-Sn-Ag System", *Metall. Trans*., **4**, 1577-1583 (1973) (Thermodyn., Experimental, 23)

[1978Cho] Chou, K.-C., "Thermodynamics for Ternary and Multicomponent Systems", *Sci. Sinica*, **11**, 73-86 (1978), translated from *Acta Metall. Sinica* **12,** 232-244 (1976) (Thermodyn., Theory, 15)

[1979Zah] Zaharova, T.V., Popel, S.I., Gavrilova, A.V., "Densities and Surface Tensions of Pb-Sn-Ag Melts" (in Russian), *Izv. Vyss. Uchebn. Zaved., Tsvetn. Metall.*, **1**, 86-90 (1979) (Experimental, Interface Phenomena, Thermodyn., 5)

[1983Lee] Lee, D.N., Lee, S.K., "Calculation of the Partial Molar Properties of Ternary Alloys from Binary Data Using the Shortest Distance Composition Path", *Scr. Metall.*, **17**(7), 861-866 (1983) (Calculation, Thermodyn., 17)

[1984Lee] Lee, H.M., Lee, S.K., Lee, D.N., "Optimization of Ternary Thermodynamic Data", *J. Korean Inst. Metals*, **22**, 398-407 (1984) (Thermodyn., Theory, 30)

[1987Kar] Karakaya, I., Thompson, W.T., "Ag-Sn (Silver-Tin)", *Bull. Alloy Phase Diagrams*, **8**(4) 340-347 (1987) (Phase Diagram, Phase Relations, Crys. Structure, Assessment, #, 51)

[1987Tar] Tarby, S.K., Notis, M.R., "Effect of Small Additions of Silver on the Eutectic Temperature in the Lead-Tin System", *Metall. Trans. B*, **17B**, 829-832 (1987) (Experimental, Thermodyn., 16)

[1988Kar] Karakaya, I., Thompson, W.T., "Pb-Sn (Lead-Tin)", *Bull. Alloy Phase Diagrams*, **9**(2), 200-202 (1988) (Phase Diagram, Crys. Structure, Assessment, #, 61)

[1988Ran] Ran, Q., Lukas, H.L., "Silver-Lead-Tin" MSIT Ternary Evaluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), MSI, Materials Science International Services GmbH,

Stuttgart; Document ID: 10.11471.1.20, (1988) (Crys. Structure, Phase Diagram, Assessment, 9)

[1992Lee] Lee, H.M., "Interaction Parameters of Lead-Base Ternary Systems", *Calphad*, **16**(1), 47-52 (1992) (Experimental, Thermodyn., 21)

[1992Sca] Scandurra, A., Licciardello, A., Torrisi, A., La Mantia, A., Puglisi, O., "Fatigue Failure in Pb-Sn-Ag Alloy During Plastic Deformation: A 3D-SIMS Imaging Study", *J. Mater. Res.*, **7**(9), 2395-2402 (1992) (Experimental, Mechan. Prop., 19)

[1996Fri] Fritz, K., Schmitt-Thomas, Kh.G., "Lead Influence on the Eutectic $SnAg_{3.5}$" (in German), *Metall*, **50**(10), 633-635 (1996) (Experimental, Phase Diagram, Phase Relations, Morphology, #, 6)

[1998Sch] Schaefer, M., Fournelle, R.A., Liang, J., "Theory for Intermetallic Phase Growth Between Cu and Liquid Sn-Pb Solder Based on Grain Boundary Diffusion Control", *J. Electron. Mater.*, **27**(11), 1167-1176 (1998) (Experimental, Morphology, Theory, Transport Phenomena, 26)

[1998Vei] Veidt, M., "Viscoelastic Tensile and Shear Properties of the 62 wt% Sn - 36 wt% Pb - 2 wt% Ag Solder Alloy", *J. Mater. Sci.*, **33**, 1607-1610 (1998) (Experimental, Mechan. Prop., 18)

[2001Bra] Bradley, E., III, Hranisavljevic, J., "Characterization of the Melting and Wetting of Sn-Ag-X Solders", *Trans. Electr. Pack. Manuf.*, **24**(4), 255-260 (2001) (Experimental, Phase Relations, 16)

[2001Kat] Kattner, U.R., Handwerker, C.A., "Calculation of Phase Equilibria in Candidate Solder Alloys", *Z. Metallkd.*, **92**(7), 740-746 (2001) (Calculation, Phase Diagram, Phase Relations, #, 6)

[2002Ama] Amagai, M., Watanabe, M., Omiya, M., Kishimoto, K., Shibuya, T., "Mechanical Characterization of Sn-Ag-Based Lead-Free Solders", *Microelectron. Reliability*, **42**, 951-966 (2002) (Mechan. Prop., Morphology, Phys. Prop., 22)

[2002Luk] Lukas, H.L., "Ag-Pb (Silver-Lead), MSI Binary Evaluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), MSI, Materials Science International Services GmbH, Stuttgart; Document ID: 20.12122.1.20 (2005) (Crys. Structure, Phase Diagram, Phase Relations, Assessment, 6)

[2002Nak] Nakamori, T., Ikeda, M., Noguchi, K., Shimizu, I., Ohno, Y., "Influence of Shear Heigh on Shear Strength of Tin-Lead Solder Ball Bonding", *Mater. Trans., JIM*, **43**(8), 2130-2136 (2002) (Experimental, Mechan. Prop., 15)

[2002Nog] Nogichi, K., Ikeda, M., Shimizu, I., Ohno, Y., Nakamori, T., "Influence of Silver Addition and Reflow Cooling Rate on Microstructure and Strength of Tin-Lead System Solder Ball Bonding" (in Japanese), *J. Jpn. Inst. Met.*, **66**(8), 799-807 (2002) (Experimental, Mechan. Prop., Morphology, 11)

[2003Zen] Zeng, X., "Thermodynamic Analysis of Influence of Pb Contamination on Pb-Free Solder Joints Reliability", *J. Alloys Compd.*, **348**, 184-188 (2003) (Calculation, Phase Relations, Thermodyn., #, 26)

[2004Isl] Islam, M.N., Chan, Y.C., Sharif, A., "Interfacial Reactions of Sn-Cu and Sn-Pb-Ag Solder with Au/Ni During Extended Time Reflow in Ball Grid Array Packages", *J. Mater. Res.*, **19**(10), 2897-2904 (2004) (Experimental, Kinetics, 25)

Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Ag) < 962	*cF*4 *Fm*$\bar{3}$*m* Cu	*a* = 408.57	pure Ag at 25°C [Mas2]
(αPb) < 327.5	*cF*4 *Fm*$\bar{3}$*m* Cu	*a* = 495.02	pure Pb at 25°C [Mas2]
(βPb)	*hP*2 $P6_3/mmc$ Mg	*a* = 326.5 *c* = 538.7	pure Pb at 25°C, > 10.3 GPa [Mas2]
(αSn) < 13	*cF*8 *Fd*$\bar{3}$*m* C (diamond)	*a* = 648.92	pure Sn, [Mas2]
(βSn) 232 - 13	*tI*4 $I4_1/amd$ βSn	*a* = 583.18 *c* = 318.18	Pure Sn at 25°C [Mas2]
(γSn)	*tI*2 ? γSn	*a* = 370.0 *c* = 337.0	pure Sn at 25°C, > 9.0 GPa [Mas2]
Ag_4Sn < 724	*hP*2 $P6_3/mmc$ Mg	*a* = 294.36 *c* = 478.45	[1987Kar]
Ag_3Sn < 480	*oP*8 *Pmmn* Cu_3Ti	*a* = 596.82 *b* = 478.02 *c* = 518.43	[1987Kar]

Table 2: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Ag	Pb	Sn
L + (Ag) ⇌ Ag_4Sn + (Pb)	182	U_1	L	4.5	94.5	1
L + Ag_4Sn ⇌ Ag_3Sn + (Pb)	~ 180	U_2	L	4	87	9
L ⇌ Ag_3Sn + (Pb) + (Sn)	176	E	L	1.75	24.45	73.80

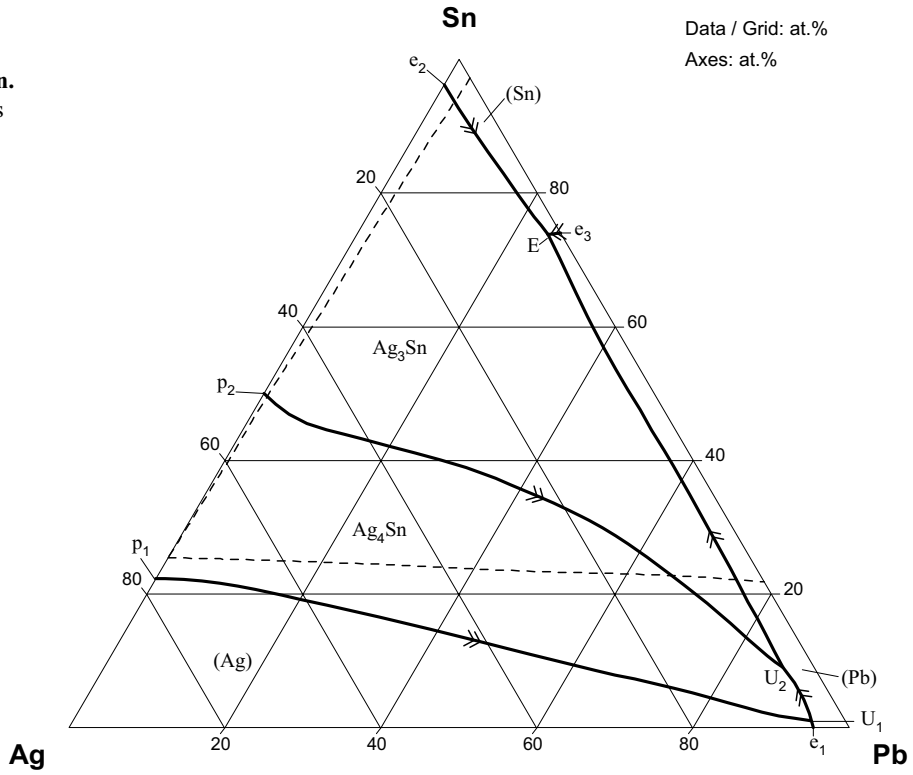

Fig. 1: Ag-Pb-Sn. Calculated liquidus surface projection

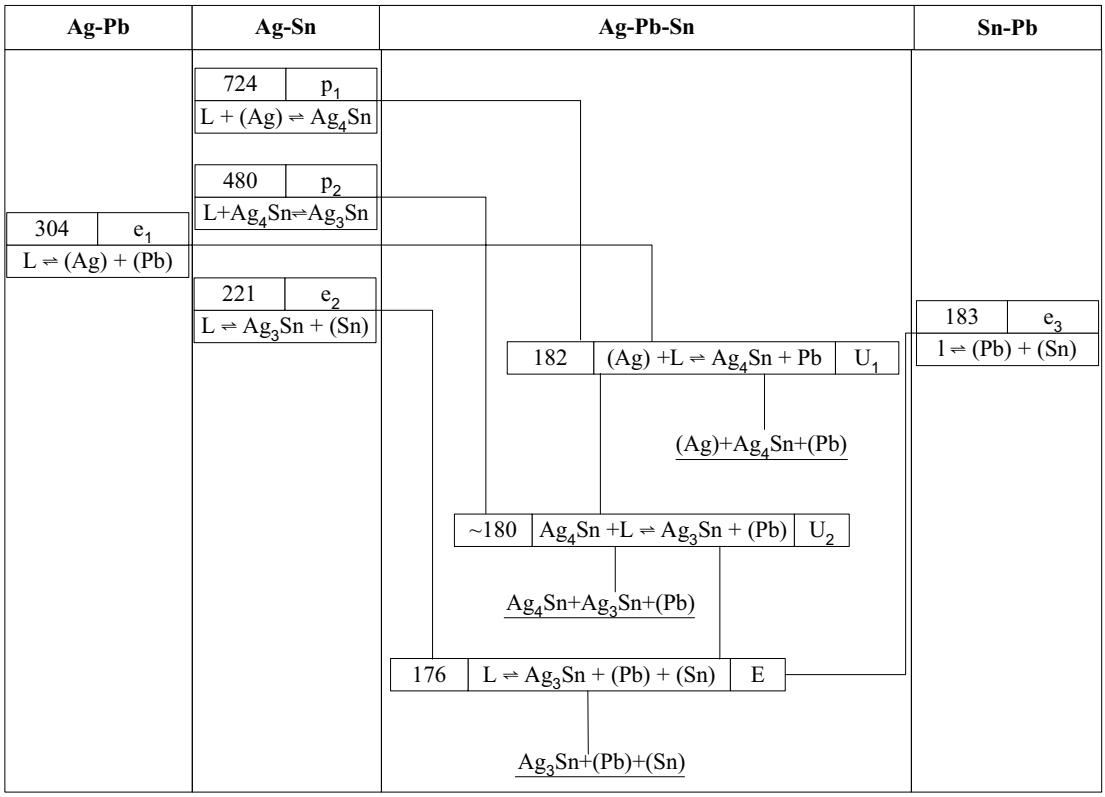

Fig. 2: Ag-Pb-Sn. Reaction scheme

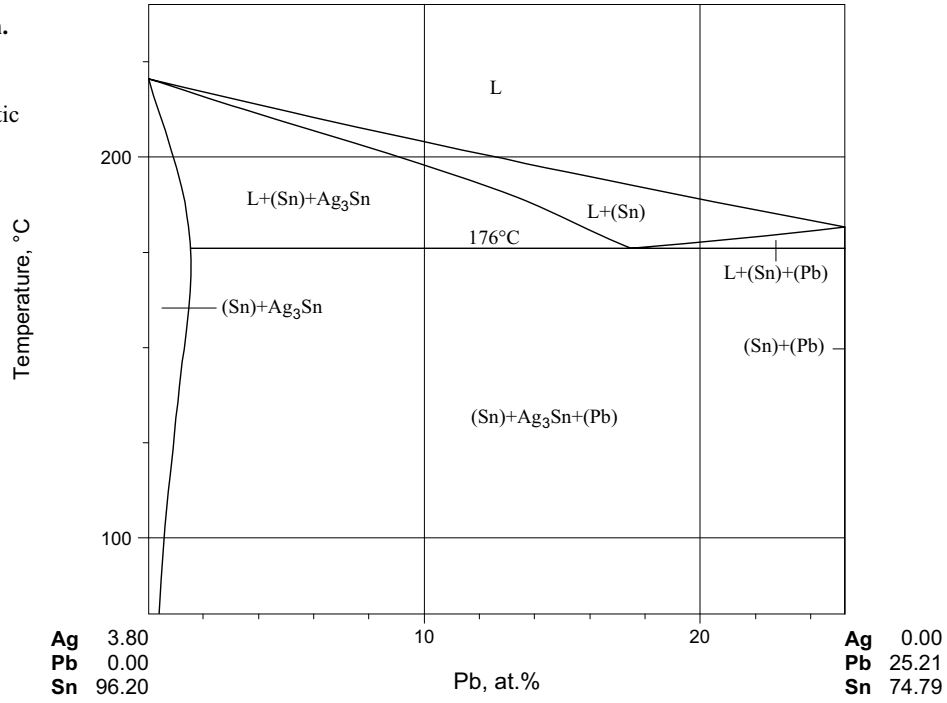

Fig. 3: Ag-Pb-Sn. Calculated vertical section from the binary Ag-Sn eutectic composition e_2 to $Sn_{25.21}Sn_{74.79}$

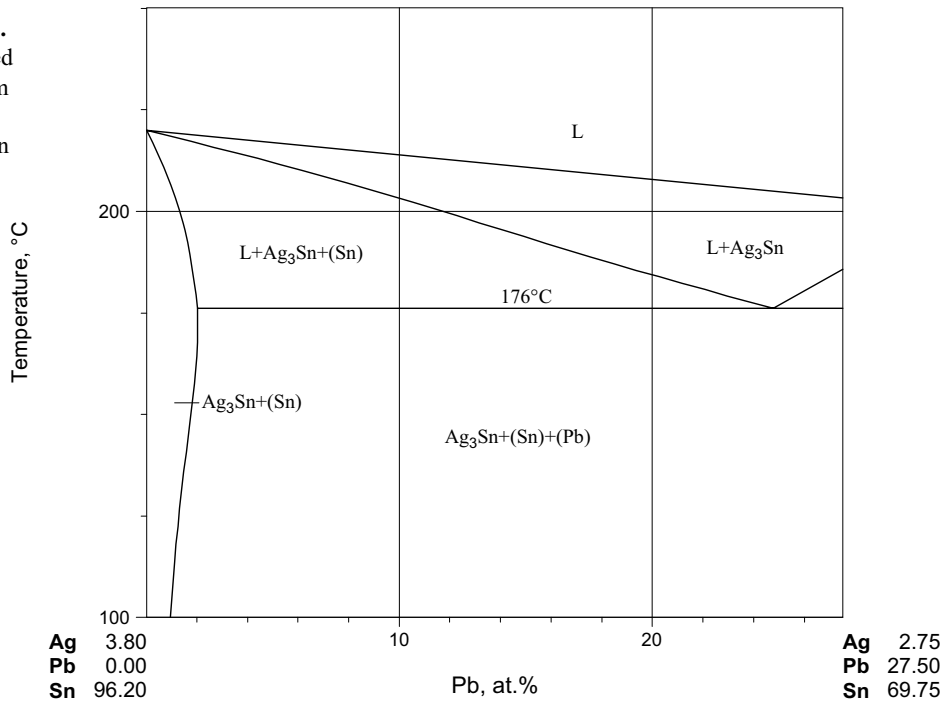

Fig. 4: Ag-Pb-Sn. Part of the calculated vertical section from the binary Ag-Sn eutectic composition e_2 to pure Pb

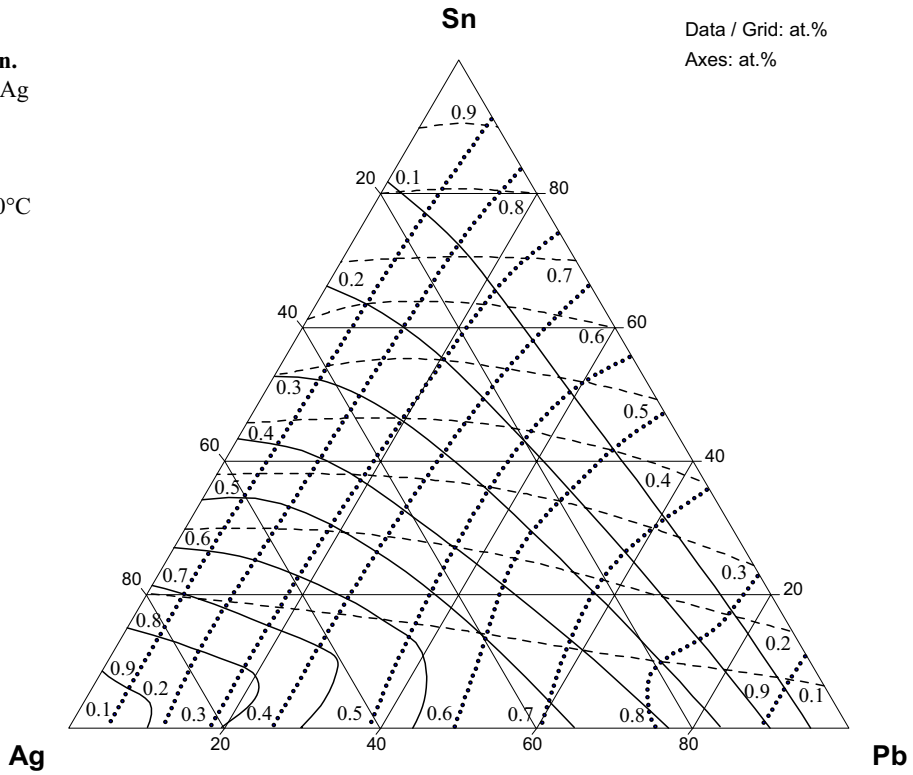

Fig. 5: Ag-Pb-Sn. Isoactivity lines of Ag (solid lines), Pb (dotted lines), Sn (dashed lines) in liquid alloys at 800°C