Silver – Bismuth – Tin

Andy Watson

Introduction

The Ag-Bi-Sn system has been the subject of intense scrutiny in recent years owing to its possible application as a lead free solder material. However, the vast majority of the interest has been with respect to physical and mechanical properties rather than phase equilibria. Numerous reviews have appeared in the literature [1997Hua, 1997Lee, 1999Ohn, 2001Kat, 2001Sug, 2003Ohn] covering mechanical and physical property studies but all refer ultimately to the same small body of work conducted on the phase equilibria. Studies of the phase equilibria in the ternary system began with a thermodynamic calculation by [1994Kat] that used thermodynamic descriptions of the associated binary systems to extrapolate into the three component system. Predicted liquidus temperatures agreed well with experimental observations using DTA studies of two alloys ($Ag_{3.32}$-$Bi_{1.14}$-$Sn_{94.55}$ and $Ag_{2.91}$-$Bi_{42.84}$-$Sn_{54.25}$). However, the first extensive study of the chemistry of the system was conducted by [1994Has]. Enthalpies of formation of the ternary liquid was measured by high temperature calorimetry at 783 and 878 K along sections Ag:Bi 1:3 and 1:1, Ag:Sn 1:4 and 1:1 and Bi:Sn 1:3, 1:1 and 3:1. High purity materials were used (Ag 99.998, Bi 99.999, Sn 99.999). The results were interpolated in order to construct isoenthalpic curves using models given in [1965Too, 1984Hoc]. By noting deviations in the enthalpy curves, it was possible to present an approximation of the liquidus surface. To complement the work on thermodynamic properties, [1998Has] made an extensive study of the phase equilibria in the ternary system using X-ray powder diffraction, DSC and DTA. Samples of Ag(4N), Bi(5N) and Sn(5N) were sealed in evacuated silica tubes before melting and cooling to an annealing temperature between 120 and 250°C, where they were held for 15 d. A variety of heating and cooling rates were used in the thermal studies (0.1-2°C·min^{-1}), the lowest of which was used for the determination of the invariant temperatures. Three isoplethal sections were characterized (10 at.% Bi, 40 at.% Ag and 70 at.% Bi) and three ternary invariant reactions were found. The locations of two of these were within approximately 2°C the extrapolations of [1994Kat], the third however, was around 23°C higher. More recently, a complete thermodynamic assessment of the ternary system has been presented by [2001Oht] (which was used subsequently in a calculation of the quaternary Ag-Bi-Sn-Zn by [2004Oht]). Firstly, they performed DSC studies along isoplethal sections with 10, 20, 30, 40, 50, 60, 70 and 80 at.% Bi. Sn(99.999%), Ag(99.99%) and Bi(99.99%) were homogenized at 1100°C in sealed quartz tubes and quenched into iced brine before the DSC studies. Peaks were recorded on heating and cooling at 3°C·min^{-1}. Isothermal sections at 200 and 400°C were produced from EDX studies of alloys which had been sealed in argon filled silica tubes and equilibrated for 14 and 7 d, respectively. Using the experimental data of [1994Has, 1998Has] and the results of their own DSC and EDX studies, they produced a thermodynamic description of the system that is in good agreement with all of the available experimental data. Interaction parameters were introduced for the liquid and the ζ phases, and Bi was allowed to substitute for Sn in the model for the Ag_3Sn compound. This latter aspect of the modeling was necessary to make the phase boundaries involving this phase in the ternary system fit the experimental data, despite the fact that little solubility of Bi in this phase has been found experimentally. A reaction scheme is also presented showing three invariant equilibria: 2 transition reactions and a ternary eutectic. However, the reaction given at 263.3°C is higher than the binary eutectic in the Ag-Bi system. In order for the ternary reaction to be a transition then there must be a maximum in the monovariant line from the binary Ag-Bi eutectic. This is suggested in [1998Has]. The assessed temperature of this reaction given by [2001Oht] is 263.6°C. [2001Lee] used thermodynamic data to predict viscosity and surface tension of the Ag-Bi-Sn liquid. However, they did not use the data of [2001Oht] but just the descriptions for the binary systems. Nevertheless, they found reasonable agreement with their experimental data.

Binary Systems

The Ag-Sn binary system is accepted from the thermodynamic assessment of [1999Oht] and is presented in Fig. 1 with an amendment to the Ag_3Sn phase showing some homogeneity which was ignored in the modeling. The Ag-Bi and Bi-Sn systems are taken from the thermodynamic assessments of [1993Kar] and [1994Oht], respectively.

Solid Phases

Solid phases in the system are listed in Table 1. There are no ternary compounds and little experimental evidence of extension of binary phases into the ternary. However, [2001Oht] found that allowing substitution of Bi for Sn in Ag_3Sn in the modeling of the system resulted in a better fit of the calculated phase boundaries to the experimental data.

Invariant Equilibria

Three invariant equilibria exist in this system. Details are given in Table 2 and the reaction scheme is given in Fig. 2. The reaction scheme is based on [2001Oht].

Liquidus, Solidus and Solvus Surfaces

The liquidus surface is shown in Fig. 3. The primary crystallization fields are given by [2001Oht] whereas the liquidus isothermal lines are experimentally determined from calorimetric (605 and 510°C) and differential thermal analysis (477, 427 ant 377°C) measurements of [1994Has]. The liquidus isothermal lines in the Sn rich corner of the system (< 60 at.% Bi, < 7 at.% Ag), taken from [2001Kat] are given in Fig. 4. The enthalpies of mixing of the liquid phase as measured by [1994Has] are exothermic in the Ag rich corner, and endothermic in the main part of the diagram suggesting, along with the shape of the liquidus curves in the Ag-Bi and Bi-Sn systems, the presence of a metastable miscibility gap. This is shown in Fig. 5, taken from the assessment of [2001Oht].

Isothermal Sections

Isothermal sections for temperatures of 400 and 200°C are given in Figs. 6 and 7, taken from [2001Oht]. Slight alterations have been made to the Ag_3Sn phase to show a degree of homogeneity in agreement with Fig. 1. The extension of the Ag_3Sn phase into the ternary system is a product of the optimization of the system without any supporting experimental evidence, but it was necessary for it to be included as discussed above.

Temperature – Composition Sections

Calculated temperature-composition sections taken from [2001Oht] are given in Figs. 8-13, and are based on experimental observations. Most of the phase boundaries in the calculations agree well with the experimental data which were used in the optimization. However, no experimental data were available for the Ag rich regions at low temperatures, and hence this part of the diagrams should be treated with a degree of caution.

Thermodynamics

[1994Has] measured by direct reaction calorimetry the enthalpies of formation of liquid (Ag,Bi) and (Ag,Bi,Sn) alloys at 510 and 605°C along different sections characterized by Ag/Bi = 1 (40 alloys) and 1/3 (38 alloys), Ag/Sn = 1 (35 alloys) and 1/4 (30 alloys), Bi/Sn = 1/3 (30 alloys), 1 (40 alloys) and 3 (29 alloys). Figure 14 shows the experimental isoenthalpic lines drawn at 605°C from [1994Has]. A general expression of the excess Gibbs energy of mixture in the liquid state has been derived by [2001Oht, 2004Oht] as a function of the temperature as part of the assessment of the ternary system. The calculated curves are in excellent agreement with the experimental data of [1994Has]:

$\Delta_{mix}G^{xs} = x_{Ag}x_{Sn}L_{Ag,Sn} + x_{Bi}x_{Sn}L_{Bi,Sn} + x_{Ag}x_{Bi}L_{Ag,Bi} + x_{Ag}x_{Bi}x_{Sn}L_{Ag,Bi,Sn}$

$L_{Ag,Sn} = -4902.5 + 4.30532T + (-16\,474 + 3.12507T)(x_{Ag} - x_{Sn}) - 7298.6\,(x_{Ag} - x_{Sn})^2$

$L_{Bi,Sn} = 487 + 0.966T - (32 + 0.235T)(x_{Bi} - x_{Sn})$

$L_{Ag,Bi} = 4589.8 + 23.73047T - 3.93814T\ln T - (5716.6 + 0.91452T)(x_{Ag} - x_{Bi}) + (-2630.2 + 0.88522T)(x_{Ag} - x_{Bi})^2$

$L_{Ag,Bi,Sn} = (1700 + 76.2T)x_{Ag} + (11\,000 + 4T)x_{Bi} + (20\,000 - 38.95T)x_{Sn}$

Notes on Materials Properties and Applications

Owing to increasing concerns over the use of lead, alloys of the Ag-Bi-Sn system have become of interest as possible replacements for the traditional Pb-Sn solder materials [1994Kat, 1997Hua, 1997Lee]. Consequently, a good deal of research has been conducted on the properties of alloys in this system focusing on Sn rich alloys and of Bi-Sn eutectic alloys with small additions of Ag [2002Kat]. With increasing Bi content, the melting temperature of Ag-Bi-Sn alloys decreases promoting wetting behavior [2002Cho]. When used in conjunction with a copper substrate, this can also be attributed to a reduction in the formation of Cu-Sn compounds owing to the presence of Ag. A small addition of Ag was found to improve significantly the ductility of Bi-Sn eutectic solder [1997McC]. The strength of a solder joint is an important issue; and this increases with increasing strain rate [2004Sho] and increasing Bi content owing to solid solution strengthening [2002Shi], with a corresponding loss in ductility. The bonding strength of Bi-Sn joints near room temperature is higher than that of the Sn-3.5Ag solder, but the ductility is lower [2001Kik]. Creep rate of the materials also increases with increasing Bi content [2002Yu], whereas [1998Kar1, 1998Kar2, 1999Kar, 2001Kar] pointed out than addition of Bi drastically degrades the thermal fatigue resistance of Sn-3.5 at.% Ag solder. The choice of substrate material also affects the strength of the solder joint. Cu increases the strength of the joint whereas Ni/Cu finishes are found to decrease it [2004Hwa]. Rare earth additions can improve the wettability of the liquid solder and increase the strength of the joint by refinement of the (βSn) phase [2002Xia1, 2004Wu]. Although Ag-Bi-Sn solders are superior to other candidates with respect to the melting properties and wettability [2001Bra], they are subject to the fillet-lifting (or lift-off) phenomenon [2001Tak]. Fillet-lifting was shown to occur in alloys (3 to 20 at.% Bi) with insufficient latent heat release near the final solidification temperature for the alleviation of the temperature gradient in the solder joint.

Miscellaneous

Solder powders can be prepared by mechanical alloying [2003Lai]. Grinding media is very important, ceramic balls providing a stronger impact force. As Ag-Bi-Sn solders have higher melting points (202-225°C) than the most popular eutectic Pb-Sn solder (183°C), [2003Shi] uses indium additions to lower the melting point of the solder alloy and to keep the good wetting performances and good mechanical properties which characterizes Ag-Bi-Sn solders [2002Xia2]. Applying ultrasonic waves to the soldering influences the microstructure [2001Kik] and increases the strength of the bonding interface in the solder joints.

The surface tension together with the density was measured for the Ag-Bi-Sn liquid alloys (0 to 80 at.% Bi and 0 to 12 at.% Sn) in the temperature range 225 - 900°C [2001Mos] and for the Ag-Sn eutectic between 230 and 950°C [2004Gas]. A linear dependency with temperature was observed. The addition of Bi to liquid Sn and to Ag-Sn eutectic alloy (3.8 at.% Ag) reduces markedly the surface tension. The wettability of Ag-Bi-Sn solders on Cu was measured by Energy Dispersive X-ray Spectrometry [2002Tan]. The wettability and mechanical properties of solders based on Bi-Sn systems are lower than that of solders based on conventional Pb-Sn systems [1998Her, 1999Via2]. However, it may be enhanced by addition of 1 to

4 mass% Ag to the solder. An investigation of the melting properties of the 91.84Sn-3.33Ag-4.83Bi solder [1999Via1] suggested the appearance of a metastable, short-range order as a result of thermal aging at low temperature. The kinetics growth of Cu-Sn layers at the interface solder/Cu was also investigated.

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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	at 25°C [Mas2] Dissolves up to 2.76 at.% Bi [1993Kar], ~11.3 at.% Sn at 722.5°C [1999Oht]
(αBi) < 271.442	*hR*6 $R\bar{3}m$ αAs	a = 454.613 c = 1186.152	at 31°C [V-C2] Dissolves up to 3.8 at.% Sn at 140.2°C [1994Oht]
(βSn) 231.9681 - 13	*tI*4 $I4_1/amd$ βSn	a = 583.18 c = 318.18	at 25°C [Mas2] Dissolves ~16 at.% Bi at 140.2°C [1994Oht]
(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, (Ag-Sn) < 722.5	*hP*2 *P*6$_3$/*mmc* Mg	*a* = 296.58 *c* = 478.24	[1999Oht], [V-C2]
Ag_3Sn < 476.5	*oP*8 *Pmmn* Cu_3Ti	*a* = 478.02 *b* = 596.8 *c* = 518.43	[1999Oht], [V-C2] 23.5-25 at.% Sn [Mas2] Dissolves ~19 mass% Bi at 200°C (predicted) [2001Oht]

Table 2: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Ag	Bi	Sn
L ⇌ (Ag) + (Bi)	264?	e_1 (max)	-	-	-	-
L + (Ag) ⇌ ζ + (Bi)	263.6	U_1	L	2.0	97.7	0.3
L + ζ ⇌ Ag_3Sn + (Bi)	262.5	U_2	L	2.6	97.3	0.1
L ⇌ (Bi) + Ag_3Sn + (βSn)	139.2	E	L	0.5	53.9	45.6

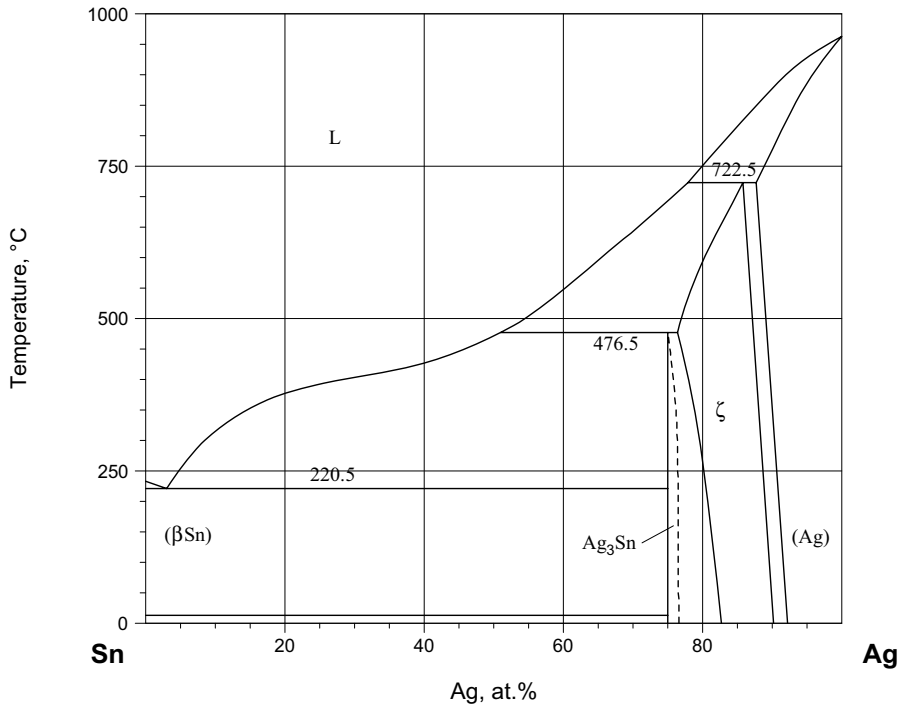


Fig. 1: Ag-Bi-Sn. The Ag-Sn binary system

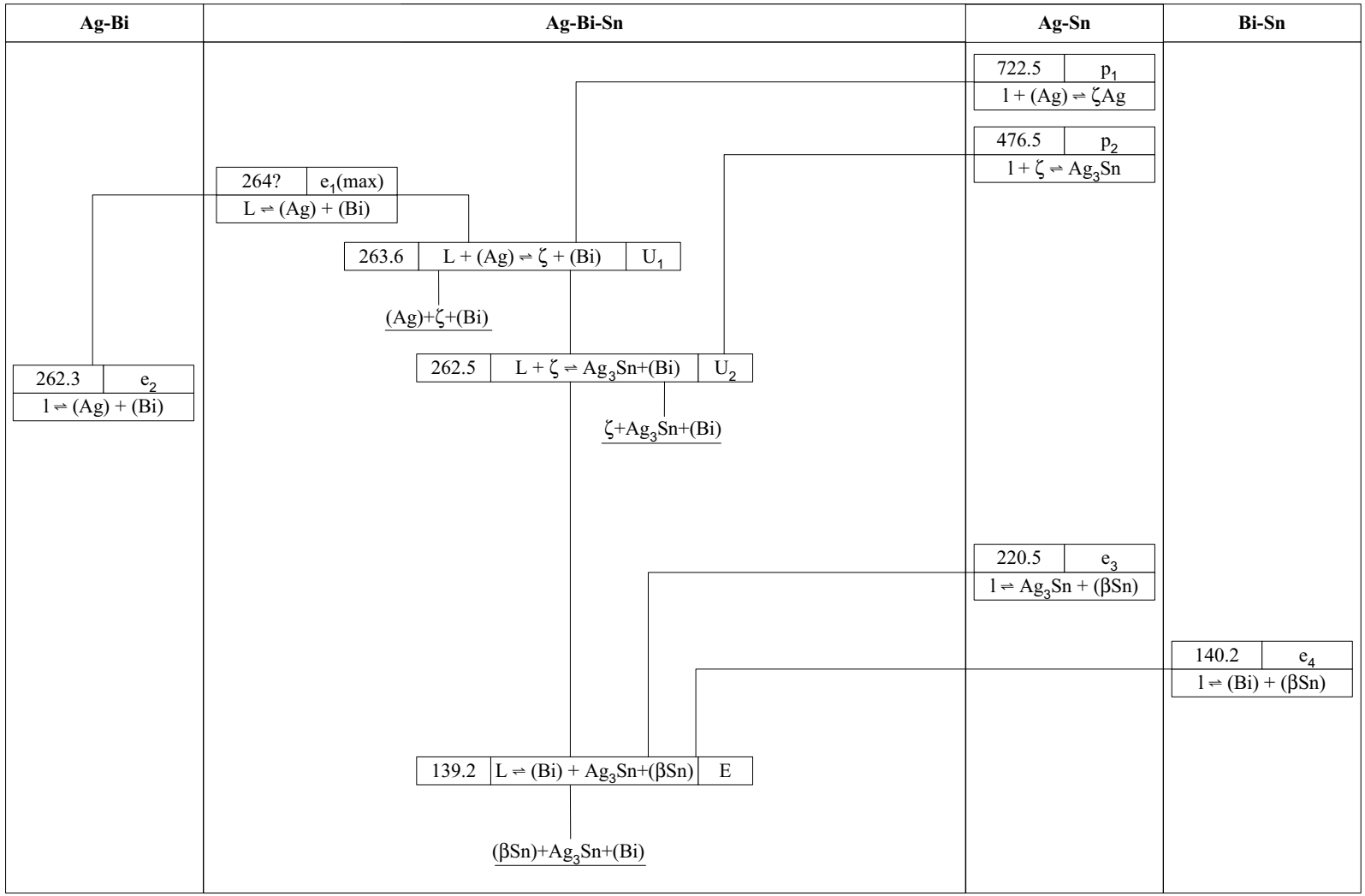


Fig. 2: Ag-Bi-Sn. Reaction scheme

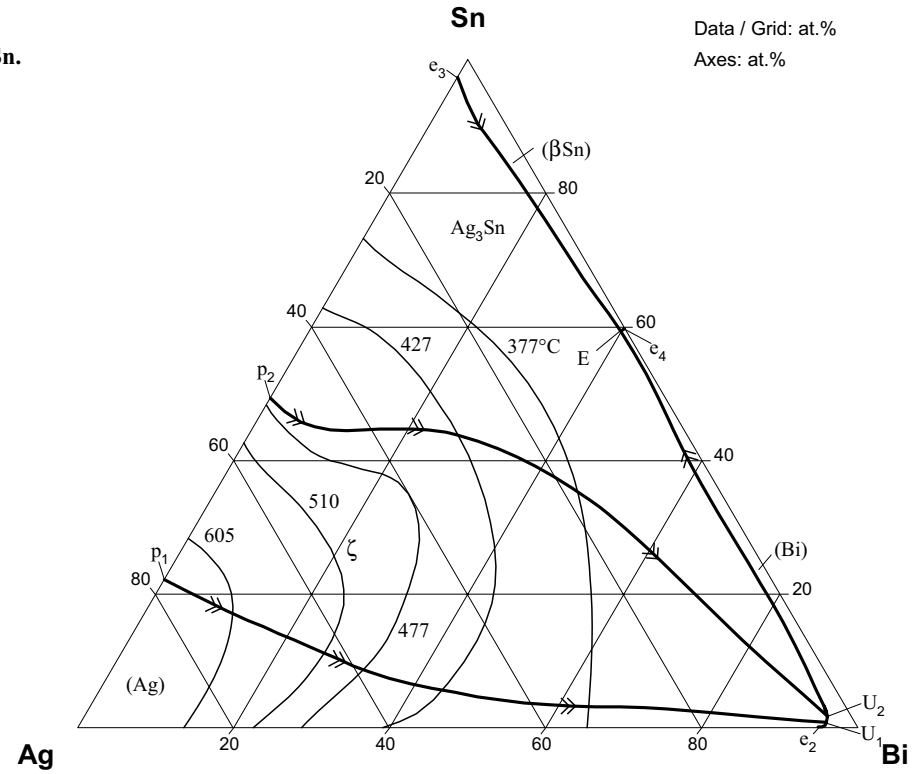


Fig. 3: Ag-Bi-Sn. Liquidus surface projection

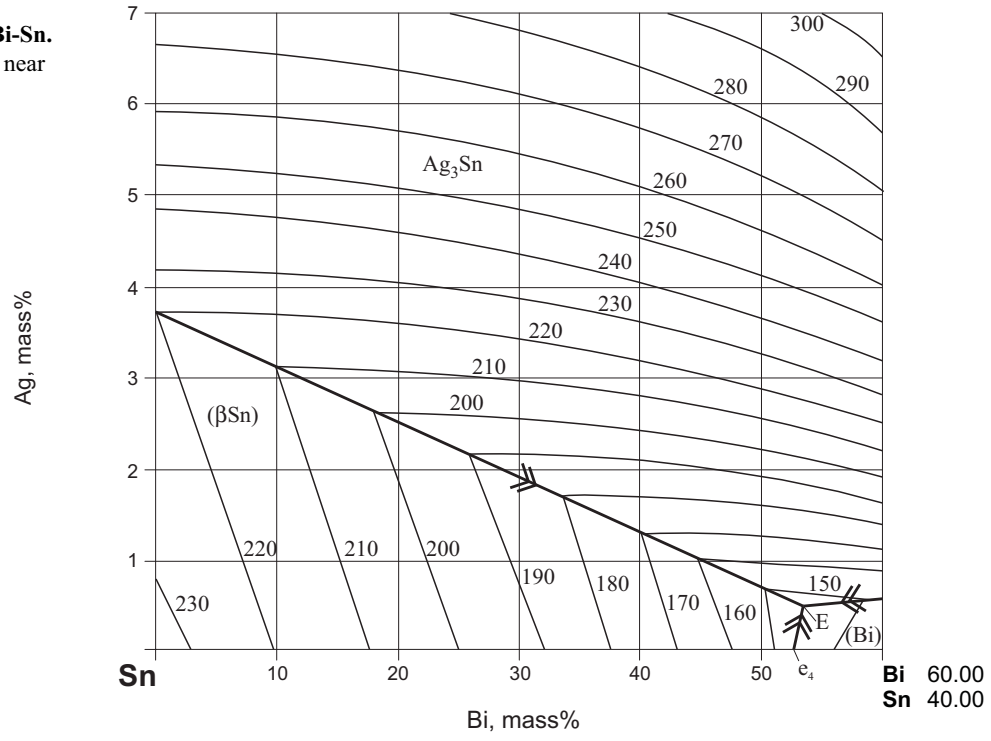


Fig. 4: Ag-Bi-Sn. Liquidus lines near the Sn corner

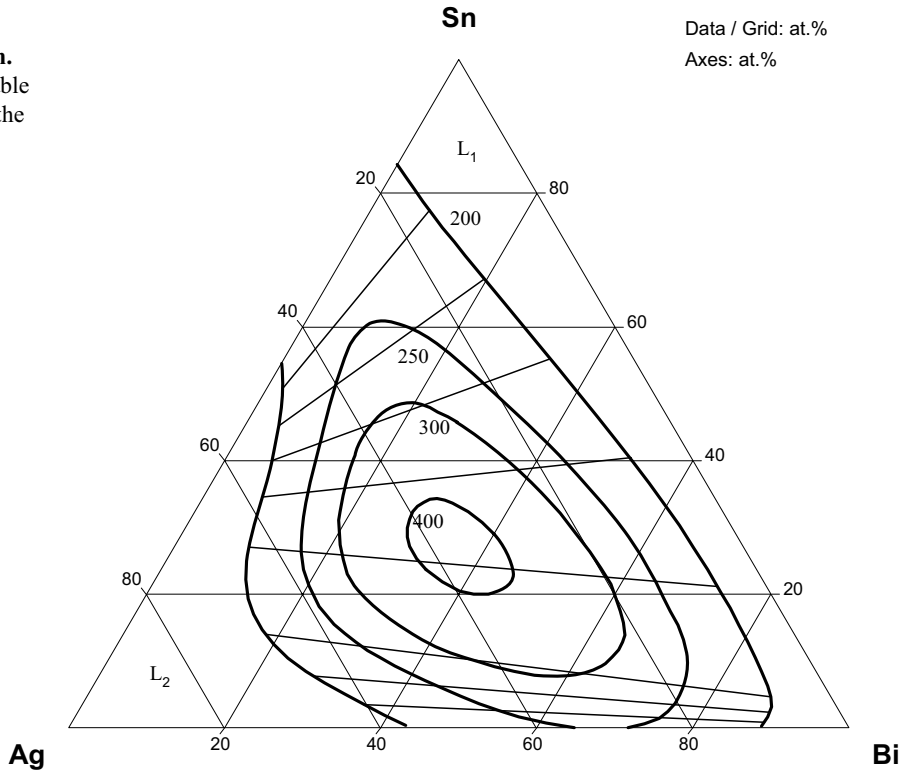


Fig. 5: Ag-Bi-Sn. Calculated metastable miscibility gap in the liquid at $200 < T < 400$°C

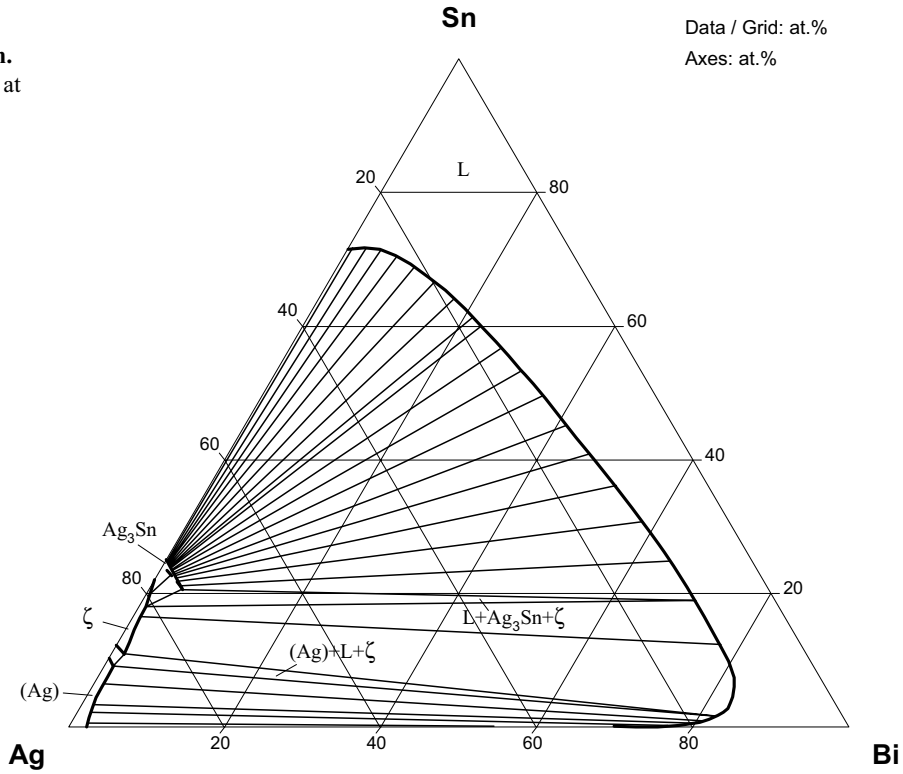


Fig. 6: Ag-Bi-Sn. Isothermal section at 400°C

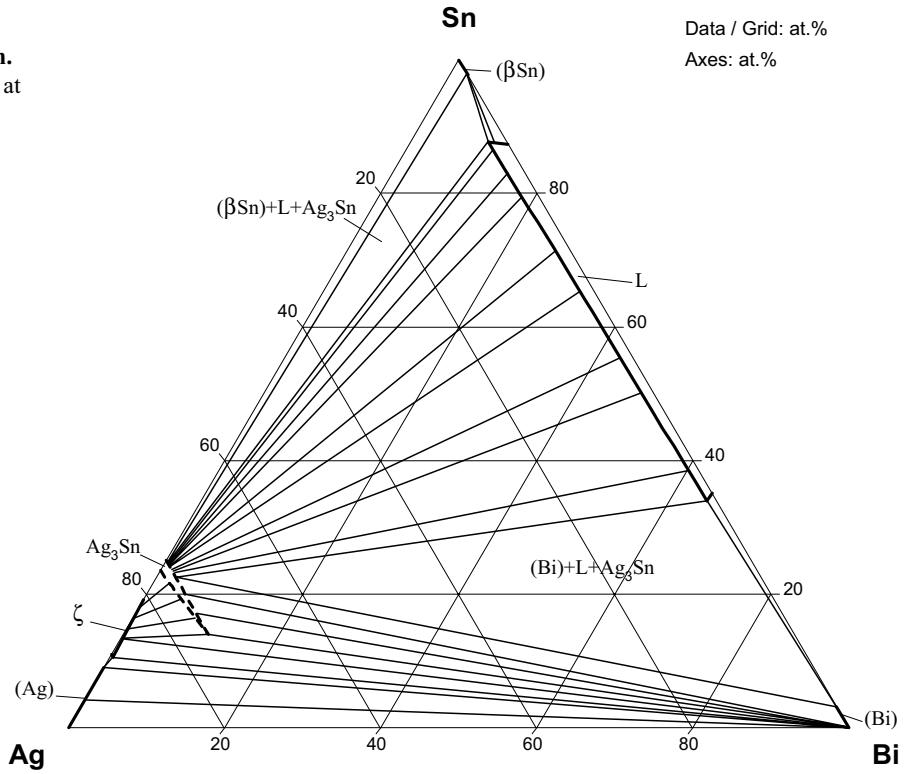


Fig. 7: Ag-Bi-Sn. Isothermal section at 200°C

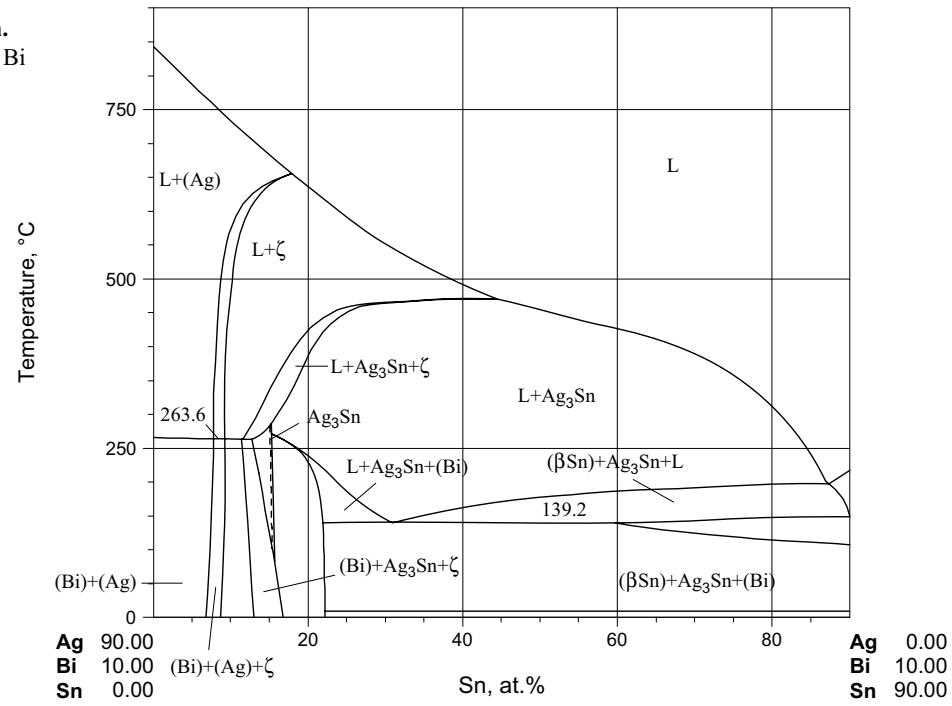


Fig. 8: Ag-Bi-Sn. Isopleth at 10 at.% Bi

Fig. 9: Ag-Bi-Sn.
Isopleth at 20 mass% Bi, plotted in at.%

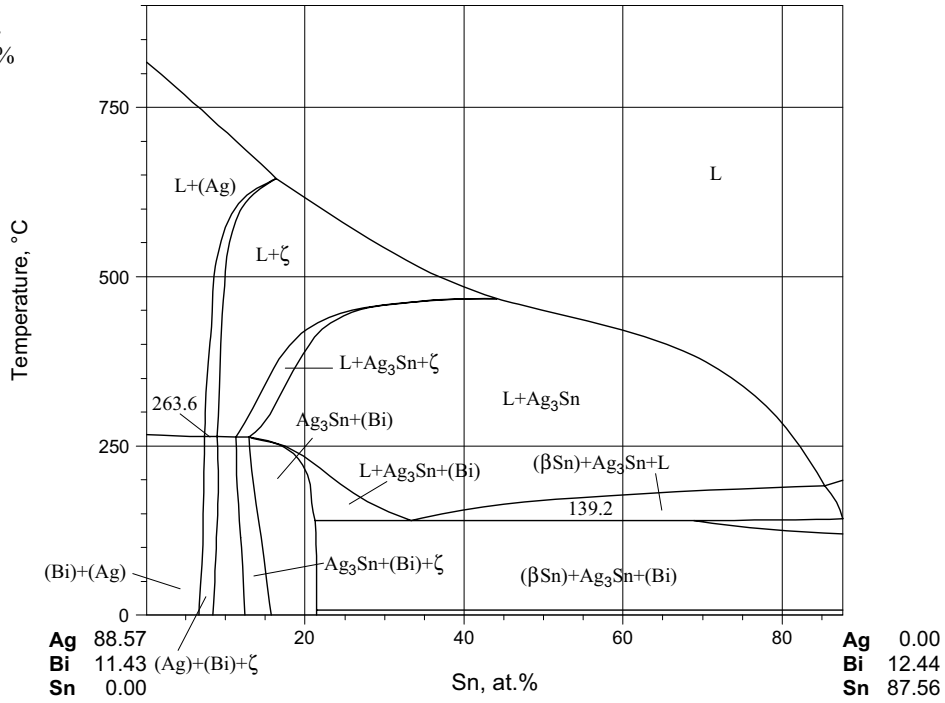
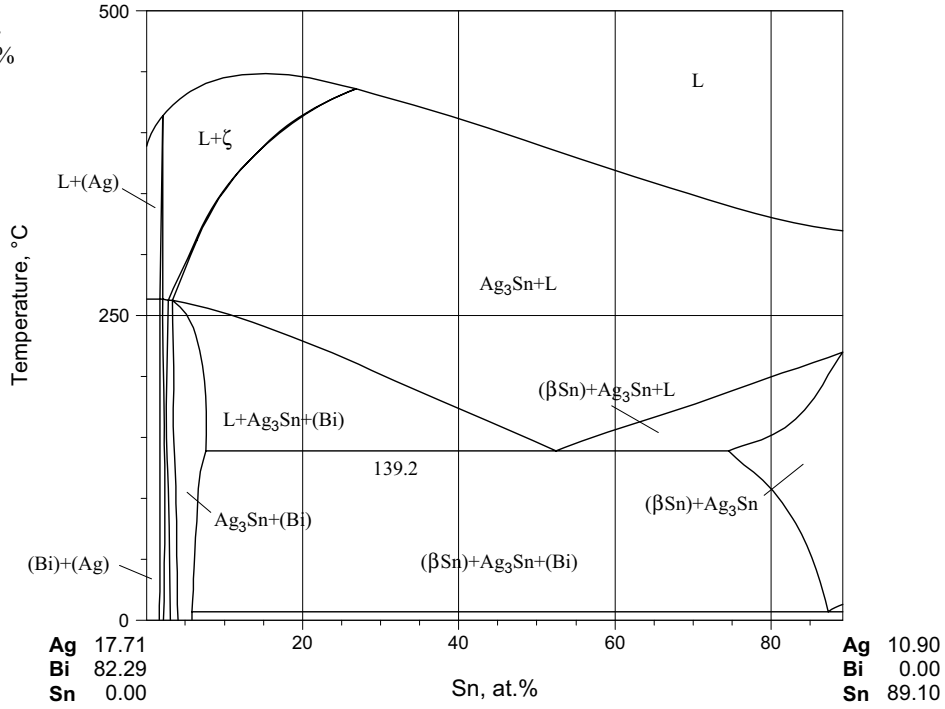


Fig. 10: Ag-Bi-Sn.
Isopleth at 10 mass% Ag, plotted in at.%



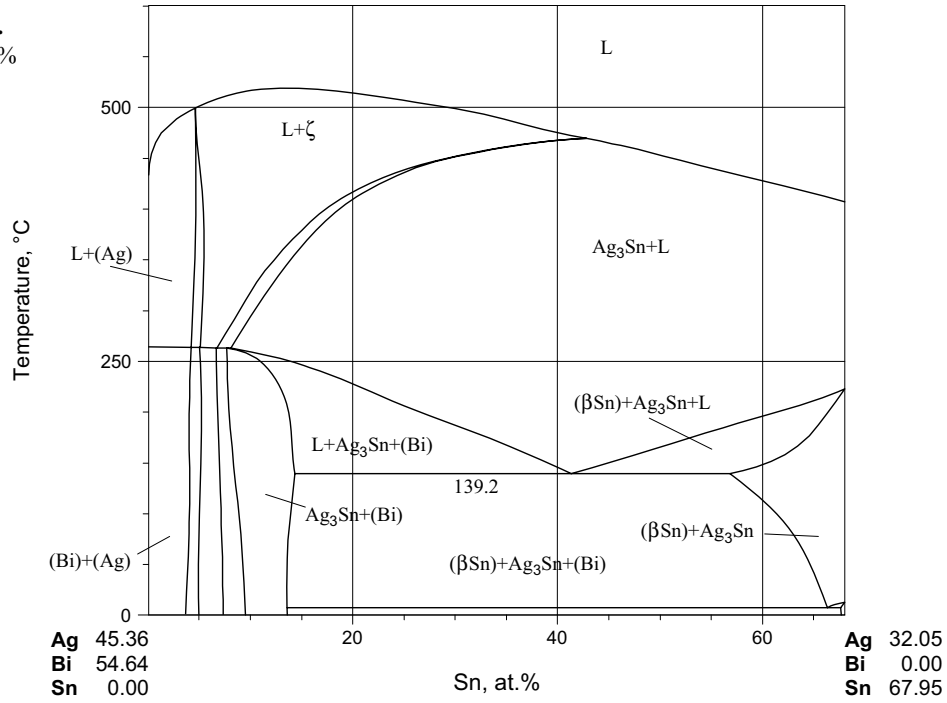


Fig. 11: Ag-Bi-Sn.
Isopleth at 30 mass% Ag, plotted in at.%

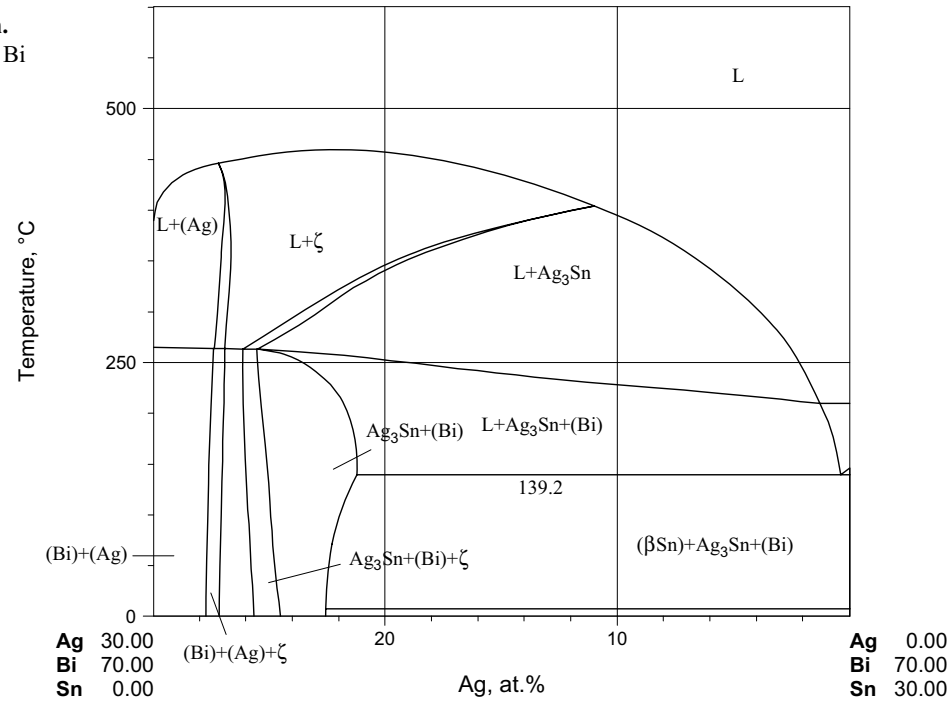


Fig. 12: Ag-Bi-Sn.
Isopleth at 70 at.% Bi

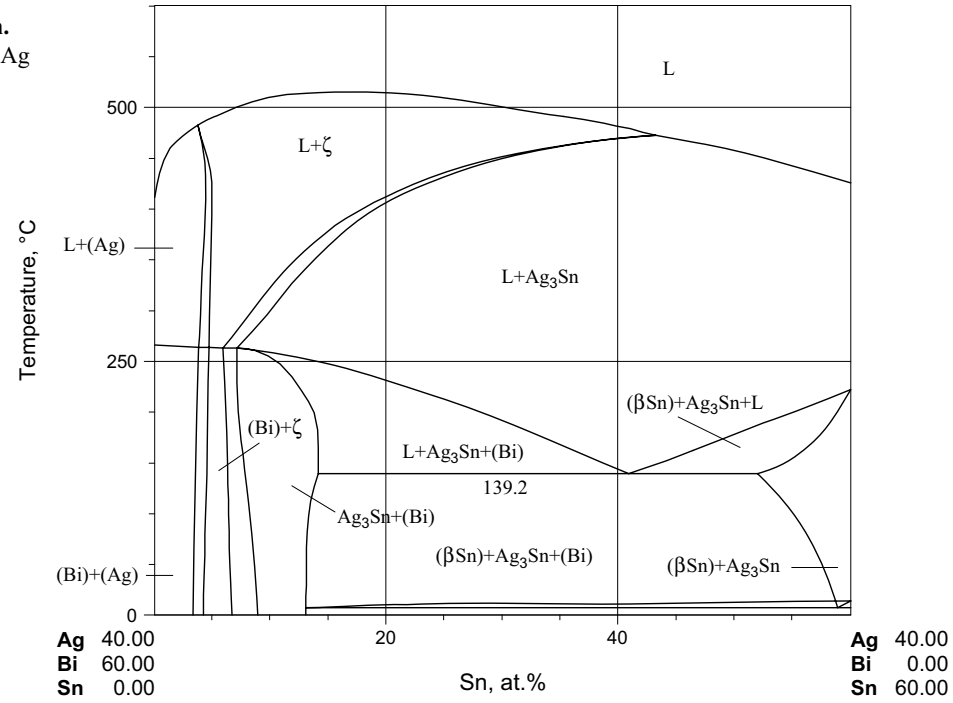


Fig. 13: Ag-Bi-Sn. Isopleth at 40 at.% Ag

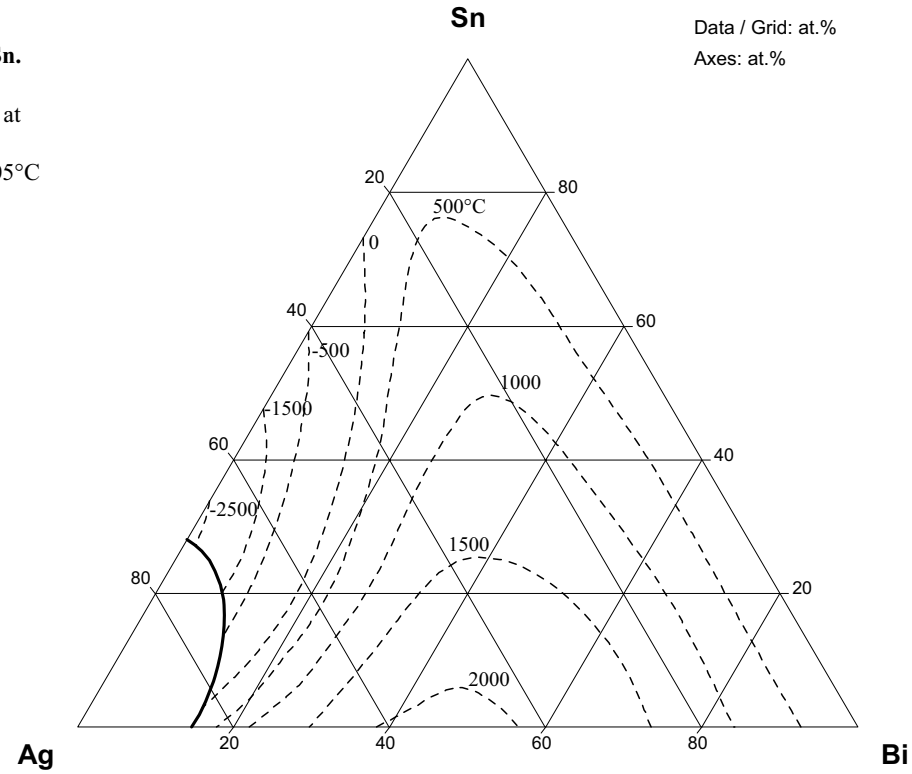


Fig. 14: Ag-Bi-Sn. Experimental isoenthalpic lines at 605°C. Full line: liquidus line at 605°C