Copper – Manganese – Tin

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Introduction

Sn based soldering alloys are good candidates for microelectronics applications and are widely used in establishing electrical contacts between metals, of which one is invariably copper.
The Cu rich part of the ternary system Cu-Mn-Sn has been extensively studied and experimental data are reported in Table 1.
Only one ternary phase $MnCu_4Sn$, called τ, has been observed and disagreements are noticed concerning its composition.
There is also disagreement in the experimental observations of solubility of Mn in the β phase of the Cu-Sn binary system. According to [1933Ver, 1955Ada], the β phase disappears at Mn contents of about 5 to 10 mass%, respectively, whereas [1942Car, 1953Fun, 1953Val, 1973Mey, 1987Leo] show a much wider β phase region, up to 30 or 40 mass% Mn. [1942Car] mentioned that β phase is stable at only elevated temperature but it can be retained above 625°C by quenching.
[1954Bla] established experimentally partial polythermal sections for 5 to 20 mass% Mn. It was shown that the higher is Mn concentration, the lower is solid solubility of Sn in (Cu), varying above 600°C from 15.8 to 5.8 mass% when Mn concentration increases up to 20 mass%. Polythermal sections at 85 and 75 mass% Cu, and at 2 mass% Mn have been constructed experimentally by [1987Leo] and [1985Dri, 1987Leo], respectively. The liquidus and solidus curves measured by [1990Boc] are in good agreement with those reported previously. From diffusion couple measurements, [2004Liu] calculated isopleths at 16.7 at.% Mn and 16.7 at.% Sn, which disagree with those reported previously. From thermodynamic description, [2004Mie] calculated isopleths which fit well with experimental data of [1942Car, 1953Fun, 1953Val, 1954Bla, 1987Leo].
Isothermal sections at 350 to 750°C have been reported by [1953Fun, 1987Leo, 2004Liu]. Very good agreement of the results of [1953Fun] and [1987Leo] has been observed, in contradiction with data [2004Liu] who observed a *A*2/*B*2 order-disorder transition. The isothermal sections of the latter work have also been calculated using a CALPHAD method and present a congruent melting of the ternary phase τ in disagreement with experimental work [1987Leo] suggesting formation of τ via a eutectoid reaction involving the β phase. Through thermodynamic considerations, [2004Mie] calculated isothermal sections which are in good agreement with those reported in the literature.
In the compilation of [1995Vil], a liquidus surface done by [1955Ada] has been reported. [2004Mie] calculated a partial liquidus surface in the Cu rich corner which is not in agreement with the one given by [1955Ada].
A complete thermodynamic description of the ternary system in the Cu rich part has been performed by [2004Mie] using ThermoCalc software.
[1961Die, 1979Cha, 1979Dri] undertook a review of the system Cu-Mn-Sn.

Binary Systems

The binary system Cu-Mn is taken from [2005Tur]. No reliable data on Cu-Sn and Mn-Sn are available in the literature after [Mas2]. Only the Cu rich part of the Cu-Sn phase diagram was re-investigated by [2004Liu] which concluded the presence of a two stage, second order reaction $A2 > B2 > D0_3$ in the bcc phase region, rather than a two-phase equilibrium between the disordered *A*2 bcc phase and the ordered $D0_3$ bcc phase as reported before. The existence of this second order transition has been detected by DSC technique at 649°C on a Cu-16.9 at.% Sn. This result has been confirmed using high temperature electron diffraction technique showing a *D*03 ordered structure at 550°C and a *B*2 ordered structure at 675°C in a Cu-16.1 at.% Sn alloy. These experimental results have been supported by a CALPHAD method in which the Gibbs energy of the bcc phase is described by the two-sublattice model in order to take into account the

*A*2/*B*2 ordering reaction. No significant modifications have been reported by this previous study. Consequently, the phase diagram proposed by [Mas2] is accepted in this assessment.
Mn-Sn phase diagram is taken from [Mas2].

Solid Phases

All crystallographic data for the unary, binary and ternary phases are reported in Table 2.
A ternary phase has been detected by several authors with different referring: δ' [1954Bla] and θ [1953Fun, 1987Leo]. Various composition have been attributed: $MnCu_5Sn_2$ [1933Ver], $MnCu_2Sn$ [1954Bla] and $MnCu_4Sn$ [1961Gla, 1968Joh, 1973Mey, 1987Leo, 2004Liu].
$MnCu_2Sn$ was investigated by [1954Bla, 1972Gel, 1981Uhl]. It was found that this alloy melts at around 657°C and its $L2_1$ structure exits down to 497°C. Two structure changes have been observed [1961Tag]. Using annealed samples, it was shown that the stable phase $MnCu_2Sn$ at room temperature is not cubic. [1942Car] suggested a hexagonal structure.
The binary β phase presents a large domain of existence inside the ternary system. This solid solution is ordered and stable at temperatures higher than 400°C. It can be retained at room temperature through quenching [1963Oxl]. In fact, its domain strongly depends on the annealing treatment of the alloys. Using quenched samples, [1942Car] stipulated that β consists of a body-centered structure with a face-centered superlattice and the lattice parameter was estimated to be $a = 616.08$ pm at a composition of $MnCu_2Sn$. This value agrees well with the one reported later in [1953Val, 1972Gel, 1977Mac]. [1973Mey] determined the lattice parameters inside the domain of the β phase and found a small variation of the lattice parameter varying from $a = 606.6 \pm 0.3$ to 617.6 ± 0.9 pm). The same author detected a lower temperature $MnCu_4Sn$ type structure in all the alloys, the lattice parameter was estimated to be $a = 698.2 \pm 0.3$ pm in agreement with the value of $a = 698.8 \pm 0.3$ given by [1961Gla].
The most reliable composition of the ternary compound τ seems to be $MnCu_4Sn$ which has been retained in this assessment.
[2004Liu] suggested that τ presents a small solubility range.

Invariant Equilibria

Invariant equilibria and reaction scheme are presented in Table 3 and Fig. 1. The values of the U_6, U_7, U_8 and E_1 given in the table are estimated from the diagram given by [1955Ada] and should be considered as tentative. For the ternary reactions U_4 and U_5, their positions have been deduced from the calculated partial liquidus surface presented by [2004Mie]. The phase compositions in other ternary reactions were directly deduced from Fig. 2 and should be also considered as tentative.

Liquidus, Solidus and Solvus Surfaces

[1995Vil] mentioned the liquidus surface constructed by [1955Ada] who found a narrow region of the primary β phase. Recently [2004Mie] undertook a thermodynamic description of the ternary system and reported a partial calculated liquidus surface in the Cu rich corner. There is a clear disagreement concerning the stability of the β phase. According to [1955Ada], the β phase disappears at Mn content of about 10 mass% whereas other studies [1942Car, 1953Fun, 1953Val, 1972Mey, 1987Leo] show a much wider β phase region reaching up to 30 or 40 mass% Mn. These last experimental results were confirmed by the thermodynamic calculation done by [2004Mie]. However, the β phase region is not allowed to extend to such high tin content [1942Car]. Consequently, the phase region has been estimated in this assessment on the base of the partial liquidus surface proposed by [2004Mie]. The sequence of the ternary reactions proposed in the Cu rich corner by [1955Ada] have not been retained in this assessment since recent thermodynamic evaluation suggested different four-phase equilibria which are more reliable. The monovariant curve proposed by [1955Ada] in the Mn rich corner is not acceptable as different solid phases participate in the equilibria. The equilibria have been changed and a sequence of two ternary reactions has been proposed. Moreover, the equilibrium L + $MnSn_2$ + η + (βSn) is more likely of eutectic type since the

solubilities of Mn and Cu in (βSn) are negligible. Then instead of the U_7 reaction proposed by [1955Ada], it was replaced by a E reaction.
The accepted liquidus surface, in accordance with the binary systems, is presented in Fig. 2 with the accepted data of [2004Mie] in the Cu rich corner and the schematic liquidus projection of [1955Ada] in the Sn corner. Tentative liquidus and isothermal curves have been indicated by dashed lines on the drawing. The calculated isothermal curves from [2004Mie] at 1000 and 900°C reproduce well those of [1955Ada]. Taking into account Alkemade's rule, position of some invariant points have been modified in Fig. 2.

Isothermal Sections

Several isothermal sections have been constructed in the Cu rich corner [1953Fun, 1987Leo, 2004Liu]. All the experimental works are in good agreement. However the isothermal sections suggested by [2004Liu] have not been retained in this assessment since some inconsistencies have been observed with the polythermal sections proposed by [1954Bla, 1987Leo]. Indeed, the latter works detected a maximum temperature of 610°C for decomposition of the τ phase, whereas [2004Liu] suggested its congruent melting at about 680°C using CALPHAD calculation. [2004Mie] calculated few isothermal sections in the Cu rich corner which are in quite good agreement with the experimental ones. Some of them are reported in Figs. 3 to 7. The diagrams have been slightly changed in accordance with the accepted binary diagrams.

Temperature – Composition Sections

Partial polythermal sections have been reported in the literature [1954Bla, 1987Leo, 1990Boc], the experimental data are in good agreement. The β phase decomposes eutectoidally into (γMn,Cu) and the ternary phase τ [1987Leo, 1954Bla]. The temperature of the eutectoid reaction varies considerably with the Mn content, and has a maximum at 610°C and 13 mass% Mn [1954Bla]. These results are in contradiction with the calculated partial isopleths [2004Liu] who proposed a congruent melting of τ at around 680°C. Since no experimental data supported the calculations, this latter work has not been accepted in this assessment. [2004Mie] also calculated isopleths which agree reasonably well with the experimental data [1953Fun, 1985Dri, 1987Leo, 1990Boc]. Some inconsistencies were observed with the polythermal sections proposed by [1955Ada] who did not detect the ternary phase τ.
Some examples of isopleths are reported in Figs. 8 to 13, in accordance with the binary edges. In order to be in agreement with the isothermal sections at 450 and 550°C, slight modifications have been done in the isopleth at 15 mass% Mn (Fig. 11) since the equilibrium τ + (βMn) + Mn_3Sn exists. The modifications are indicated as dashed lines.

Thermodynamics

The enthalpies of formation in the β region have been measured by [1972Mey] ranging from 383 to 933 $J \cdot mol^{-1}$ closely the composition $MnCu_2Sn$.

Notes on Materials Properties and Applications

Brief details of some experimental works on materials properties are reported in Table 4.
Certain Cu-Mn-Sn alloys were ferromagnetic especially when the binary β phase was present. The estimated value of the magnetization σ to be about 60.8 $Am^2 \cdot kg^{-1}$ [1983Bus] and 68.7 $Am^2 \cdot kg^{-1}$ [1975Wac] at 530°C for a $MnCu_2Sn$ alloy. These values are in the same range order as those reported previously by [1953Val]. For the same composition, [1942Car] observed a maximum value of $\sigma = 76.65\ Am^2 \cdot kg^{-1}$ at 660°C. [1914Heu] also measured the magnetic saturation which is found to be maximal (107 $Am^2 \cdot kg^{-1}$) for a composition of Mn_2Cu_9Sn. The Curie temperature of $MnCu_2Sn$ alloy has been extrapolated at 357°C [1981Uhl, 1982Uhl] where a decreasing of the magnetization occurs. This extrapolated value of the Curie temperature is far from the one calculated by [1975Wac] who found a value of 240°C. The ferromagnetic moment has been estimated to be $\mu_{OO} = 4.00\ \mu_B$ for a quenching temperature of 645°C. This value is in agreement with those of [1942Car, 1963Oxl]. On molten Cu-Sn alloys with Mn

impurities (25 at.%), [1975Gue] found a linear variation of the reciprocal magnetic susceptibility with temperature, varying from 350 to 900 g-atom·cm^{-3} in the temperature range 400 to 1400°C. These values are lower than those reported by [1975Wac] for the same composition range.
Tempering quenched Cu alloys with 5-20 mass% Mn and 4-14 mass% Sn, results in extreme brittleness, owing to unfavorable distribution of the τ phase [1954Bla]. Cold working the alloys before tempering leads to more homogeneous texture, *i.e.* dispersed particles τ in a (Cu) matrix. Thus tensile strengths of 35-38 tons/in^2 with elongations of 10-20% can be obtained.
The electrical properties of some Cu based alloys and thin evaporated films containing additions of Mn and Sn have been measured by [1990Boc]. The electrical resistivity has been found for the alloys greater than values for the films. The electrical resistivity increases regularly from about $40 \cdot 10^8$ Ohm m at Cu-25%Mn to $83 \cdot 10^8$ Ohm m at Cu-25%Sn [1984Boc].

Miscellaneous

In the case of amorphous $MnCu_2Sn$, the only annealing temperature which produced ferromagnetism was 200°C [1982Tay]. At all temperatures this phase was mixed with a major second phase Mn_2Cu_3Sn.
The magnitude and sign of the hyperfine field in $MnCu_2Sn$ has been measured at –196°C by means of Mössbauer spectroscopy and found to be +200 ± 10 kOe [1972Gel].
Low temperature specific heat measurements were performed on $MnCu_2Sn$ and show a soft phonon distribution leading to an Einstein temperature of about –220°C [1991Fra].

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Table 1: Investigations of the Cu-Mn-Sn Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1933Ver]	Thermal and microscopic methods	400-1100°C / Cu_3Sn-Mn with 5 to 15 mass% Mn
[1942Car]	X-ray diffraction	640 to 715°C / Cu-based alloys with 0-40 mass% Mn and 0-30 mass% Sn
[1953Fun]	Metallographic analysis	350 to 750°C / Cu rich corner with 0 to 20 mass% Mn and 0 to 25 mass% Sn
[1953Val]	X-ray diffraction	$MnCu_2Sn$
[1954Bla]	Metallographic analysis, DTA	400 - 700°C / Cu alloys with 5-20 mass% Mn and 4-14 mass% Sn
[1961Tag]	X ray diffraction	$MnCu_2Sn$
[1968Joh]	X-ray and neutron diffraction	$MnCu_2Sn$
[1972Gel]	X ray diffraction	Annealed at 640°C / $MnCu_2Sn$
[1972Mey]	Liquid-metal solution calorimetry	25°C / ~ $MnCu_2Sn$
[1973Mey]	X-ray analysis	25°C after annealing at 600°C for 3 h / $MnCu_2Sn$ and 50.1-64.8 at.% Cu with 24.8-32.3 at.% Mn and 8.7-25.1 at.% Sn
[1977Mac]	X ray diffraction	$MnCu_2Sn$

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1985Dri]	Metallography	400 - 1200°C / Cu rich based alloys with 2 mass% Mn and 2-10 mass% Sn
[1987Leo]	microhardness measurements, DTA, metallographic analysis,	300 to 1000°C / Cu-Mn-Sn up to 30 mass% Sn and 30 mass% Mn
[1990Boc]	DTA, microscopic and X-ray analysis	700 - 1100°C / 2 mass% Mn and 0-25 mass% Cu
[2004Liu]	Diffusion couple method, DSC, electron diffraction and high temperature X-ray diffraction techniques	550 - 700°C / Cu based alloys with 0-30 at.% Mn and 0-30 at.% Sn

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(γMn,Cu)	*cF*4 $Fm\bar{3}m$ Cu		[Mas2] Melting point [1993Gok]
		a = 362.63	at *x* = 0.04 [V-C2]
		a = 375	at *x* = 0.80 [V-C2]
(γMn) 1138 - 707		*a* = 386	at *x* = 1 [Mas2]
(Cu) < 1084.62		*a* = 361.46	at *x* = 0 [Mas2]
(δMn) 1246 - 1138	*cI*2 $Im\bar{3}m$ W	*a* = 308.0	[Mas2]
(βMn) 1087 - 707	*cP*20 $P4_132$ βMn	*a* = 631.52	[Mas2]
(αMn) < 707	*cI*58 $I\bar{4}3m$ αMn	*a* = 891.26	at 25°C [Mas2]
(γSn)	*tI*2 ? γSn	*a* = 370 *c* = 337	at 25°C, 9.0 GPa [Mas2]
(βSn) 231.9681 - 13	*tI*4 $I4_1/amd$ βSn	*a* = 583.18 *c* = 318.18	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	[Mas2]
β, $Cu_{17}Sn_3$ 798 - 586	*cI*2 *Im*$\bar{3}$*m* W	*a* = 302.61	from 13.1 to 16.5 at.% Sn and *A*2 type structure [Mas2, 2004Liu]
γ, Cu_3Sn(h) ~755 - 520	*cF*16 *Fm*$\bar{3}$*m* or *F*$\bar{4}$3*m* BiF_3 or $CuHg_2Ti$	*a* = 611.76 ± 0.10	from 15.5 to 27.5 at.% Sn [2004Liu] from 16.5 to 27.9 [Mas2, V-C2] $D0_3$ type structure [2004Liu]
γ' phase ~755 - 574	*hP*8 ? Na_3As	*a* = 428.1 *c* = 784.2	from 15.5 to 23 at.% Sn [2004Liu] *B*2 type structure [2004Liu] metastable, martensitic form of quenched γ
ε, Cu_3Sn(r) < 676	*oC*80 *Cmcm* Cu_3Sn	*a* =552.9 ± 0.8 *b* = 477.5 ± 0.6 *c* = 432.3 ± 0.5	24.5 to 25.9 at.% Sn and Cu_3Sn [Mas2, V-C2]
ζ, $Cu_{10}Sn_3$ 640 - 582	*hP*26 *P*6_3 $Cu_{10}Sn_3$	*a* = 733.0 ± 0.4 *c* = 786.4 ± 0.5	20.3 to 22.5 at.% Sn and $Cu_{10}Sn_3$ at 603°C [Mas2, V-C2]
δ, $Cu_{41}Sn_{11}$ 582 - ~350	*cF*416 *F*$\bar{4}$3*m* $Cu_{41}Sn_{11}$	*a* = 1796.46 ± 0.06	20 to 21 at.% Sn and $Cu_{41}Sn_{11}$ [Mas2, V-C2]
η, Cu_6Sn_5(h) 415 - 186	*hP*4 *P*6_3/*mmc* NiAs	*a* = 419.2 ± 0.2 *c* = 503.7 ± 0.2	43.5 to 44.5 at.% Sn and [Mas2, V-C2]
η', Cu_6Sn_5(r) < 189	*h***		44.8 to 45.5 at.% Sn, ordered form with superlattice based on η [Mas2]
γ_1, $MnCu_5$ ≤ 410	*c***	-	[1990Goe]
ε_2, $MnCu_3$ ≤ 450	*c***	-	[1990Goe]
γ_3 (Cu-Mn phase) ≤ 700	*c***	-	[1990Goe]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Mn_3Sn < 984	*hP*8 $P6_3/mmc$ Ni_3Sn	*a* = 567 *c* = 453	[V-C2] $Mn_{19}Sn_6$ in [2004Mie]
Mn_2Sn < 884	*hP*6 $P6_3/mmc$ $InNi_2$	*a* = 437.7 ± 0.1 *c* = 550.7 ± 0.1	[V-C2]
$MnSn_2$ < 549	*tI*12 *I*4/*mcm* Al_2Cu	*a* = 665.9 ± 0.3 *c* = 544.7 ± 0.3	[V-C2]
* τ, $MnCu_4Sn$	*cF*24 $F\bar{4}3m$ $AuBe_5$	*a* = 698.8 ± 0.3	[1961Gla]
* $MnCu_2Sn$(h) 657 - 497	*cF*16 $Fm\bar{3}m$ BiF_3	*a* = 617.6 ± 0.9	[1973Mey]
* $MnCu_2Sn$(r) < 497	*hP*2 *P6/mmc* Mg	*a* = 285.2 *c* = 401.4	[1954Bla]

Table 3: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Cu	Mn	Sn
L + (δMn) ⇌ (βMn) + (γMn,Cu)	1029-1000	U_1	L	3.80	79.80	16.40
L + (βMn) ⇌ Mn_3Sn + (γMn,Cu)	984-900	U_2	L	4.10	76.50	19.4
L + (γMn,Cu) ⇌ β + Mn_3Sn	798-750	U_3	L	62.94	28.90	8.16
L + Mn_3Sn ⇌ β + Mn_2Sn	700-650	U_4	L	49.89	28.90	21.21
L + β ⇌ Mn_2Sn + γ	650-600	U_5	L	50.91	22.31	26.78
L + γ ⇌ Mn_2Sn + ε	~ 510	U_6	L	39.84	17.44	42.72
L + ε ⇌ Mn_2Sn + η	415-400	U_7	L	12.22	6.02	81.76
L + Mn_2Sn ⇌ η + $MnSn_2$	400-231	U_8	L	9.22	4.42	86.36
L ⇌ η + (βSn) + $MnSn_2$	< 227	E_1	L	0.46	0.46	99.08

Table 4: Investigations of the Cu-Mn-Sn Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1914Heu]	Magnetometer	Magnetic properties
[1942Car]	Magnetometer	Magnetic properties
[1953Val]	Magnetometer	Magnetic properties
[1954Bla]	Hardness measurements	Tensile properties
[1963Oxl]	Standard Sucksmith technique	Magnetic properties
[1975Gue]	Susceptibility measurements	Magnetic properties
[1975Wac]	Susceptibility measurements	Magnetic properties
[1981Uhl]	Faraday magnetometer	Magnetic properties
[1982Uhl]	Faraday pendulum magnetometer	Magnetization and susceptibility coefficients
[1983Bus]	Spectroscopic technique, PAR vibrating sample magnetometer	Magnetization coefficient, magneto-optical Kerr rotation
[1984Boc]	Resistivity measurements	Electrical properties
[1990Boc]	Auger spectroscopy and electrical resistivity measurements	Electrical resistivity and electrical resistivity temperature coefficient

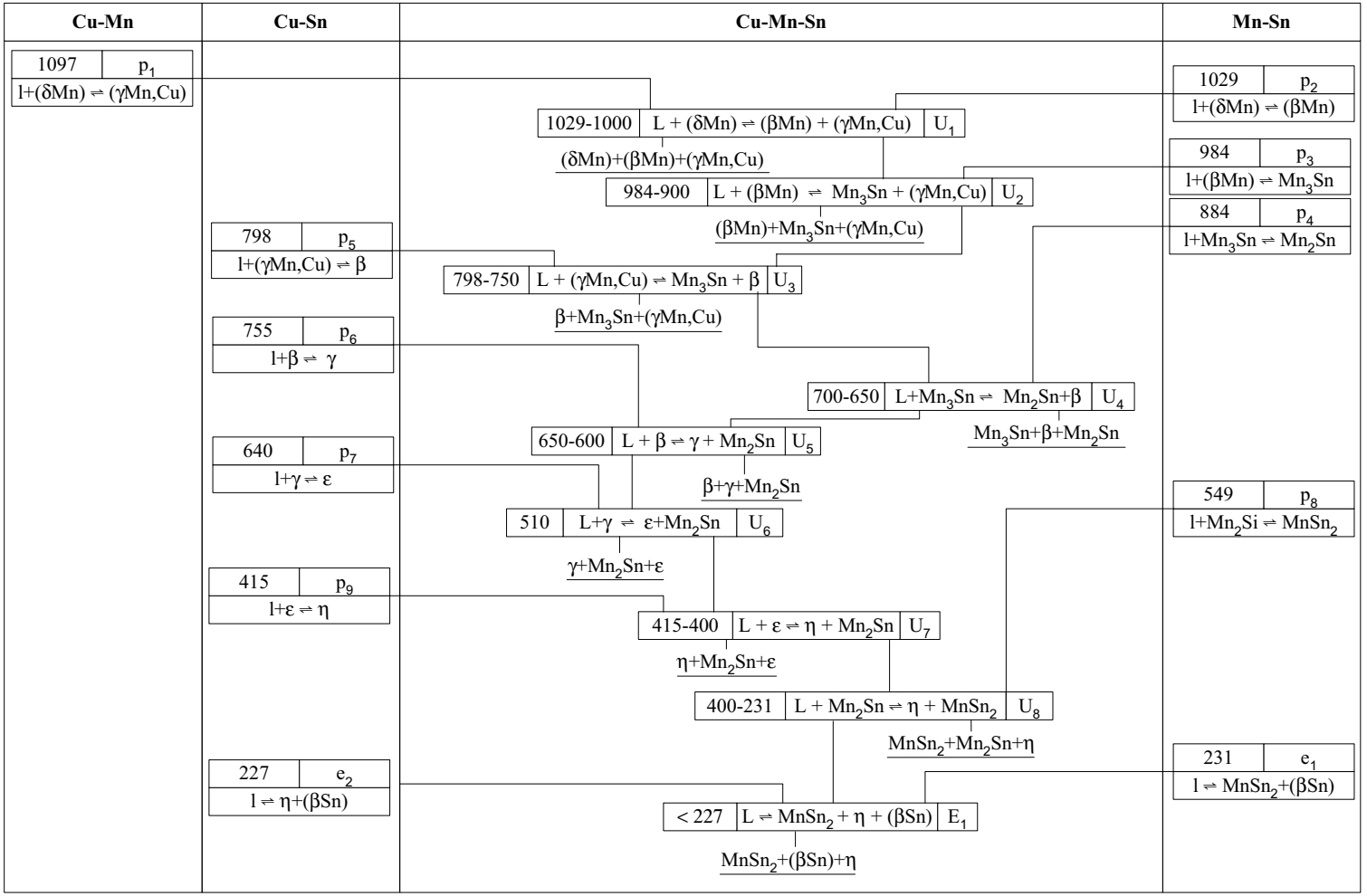

Fig. 1: Cu-Mn-Sn. Reaction scheme

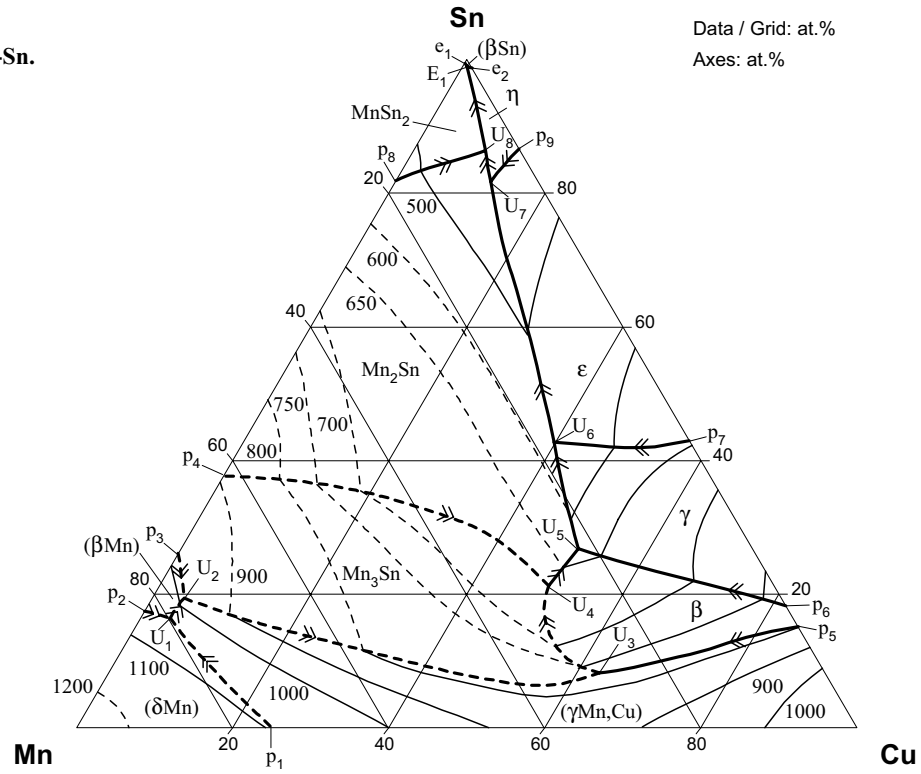

Fig. 2: Cu-Mn-Sn. Liquidus surface projection

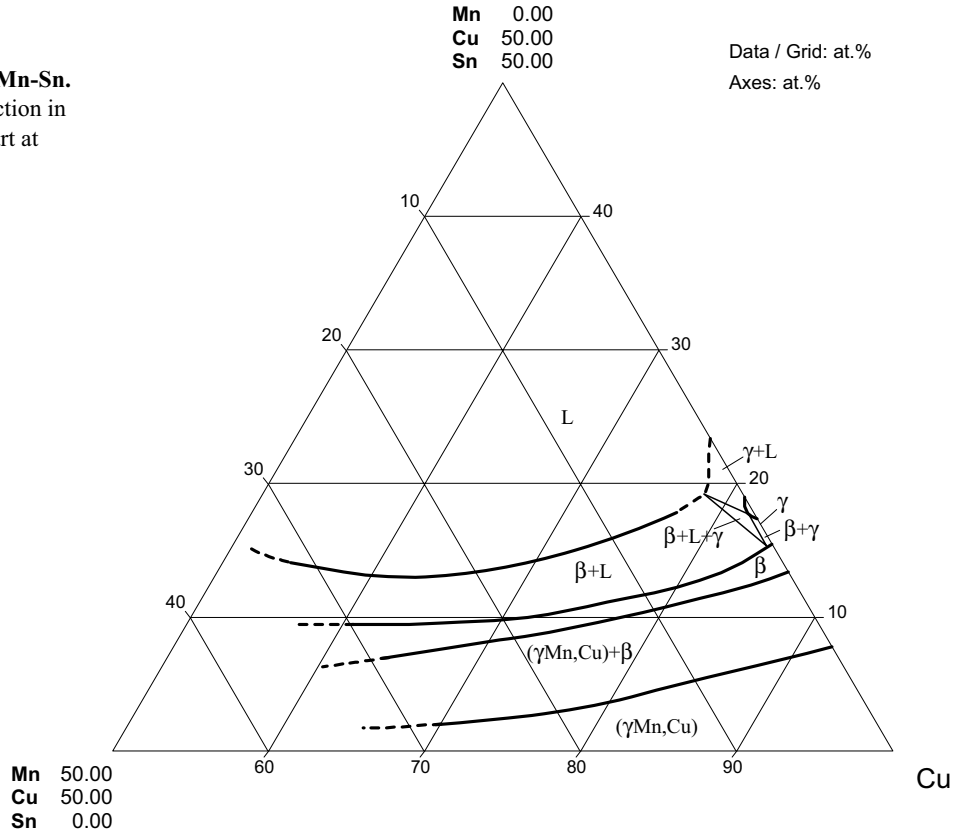

Fig. 3: Cu-Mn-Sn. Isothermal section in the Cu rich part at 750°C

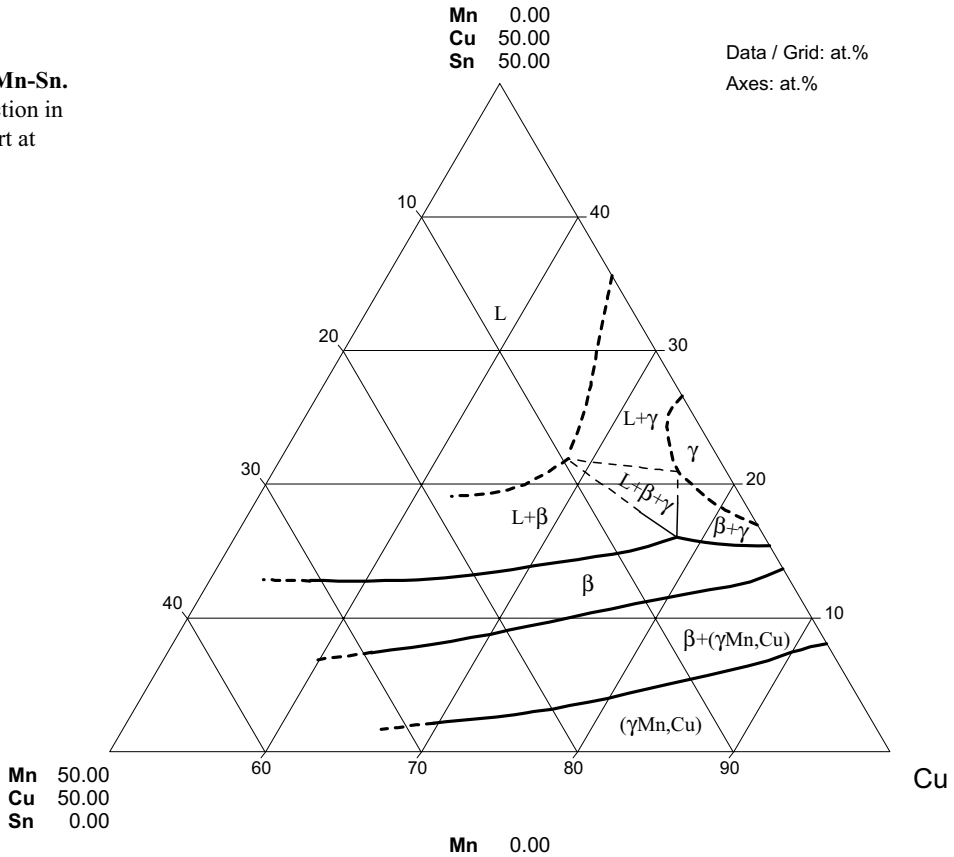

Fig. 4: Cu-Mn-Sn. Isothermal section in the Cu rich part at 700°C

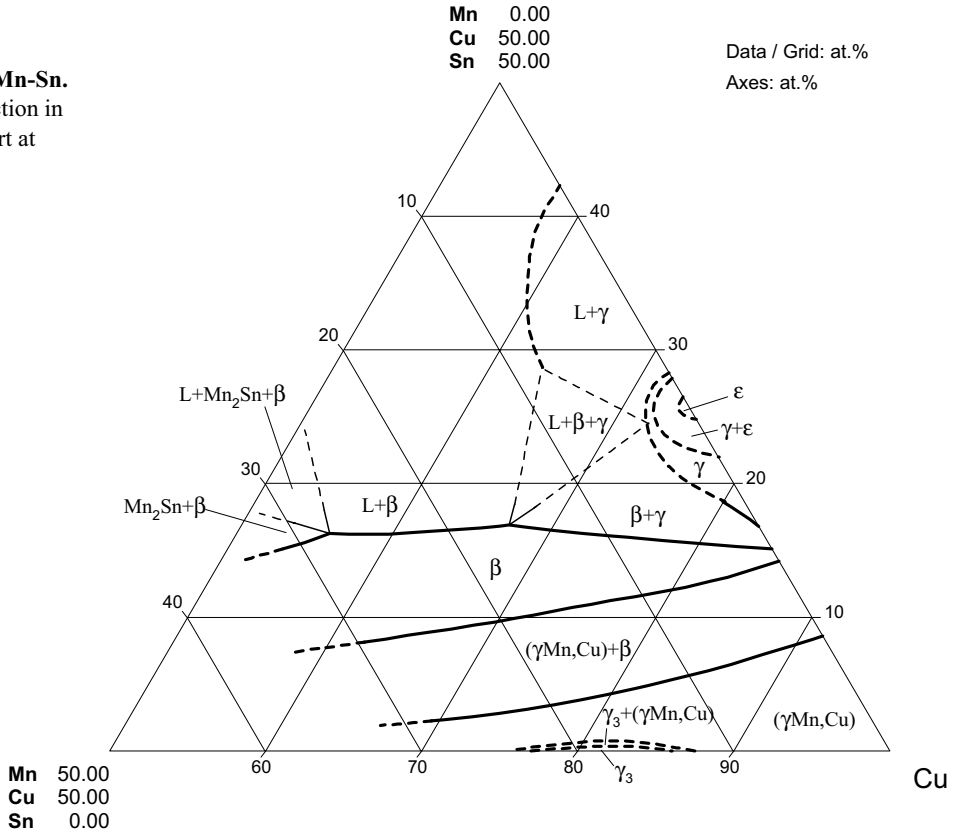

Fig. 5: Cu-Mn-Sn. Isothermal section in the Cu rich part at 650°C

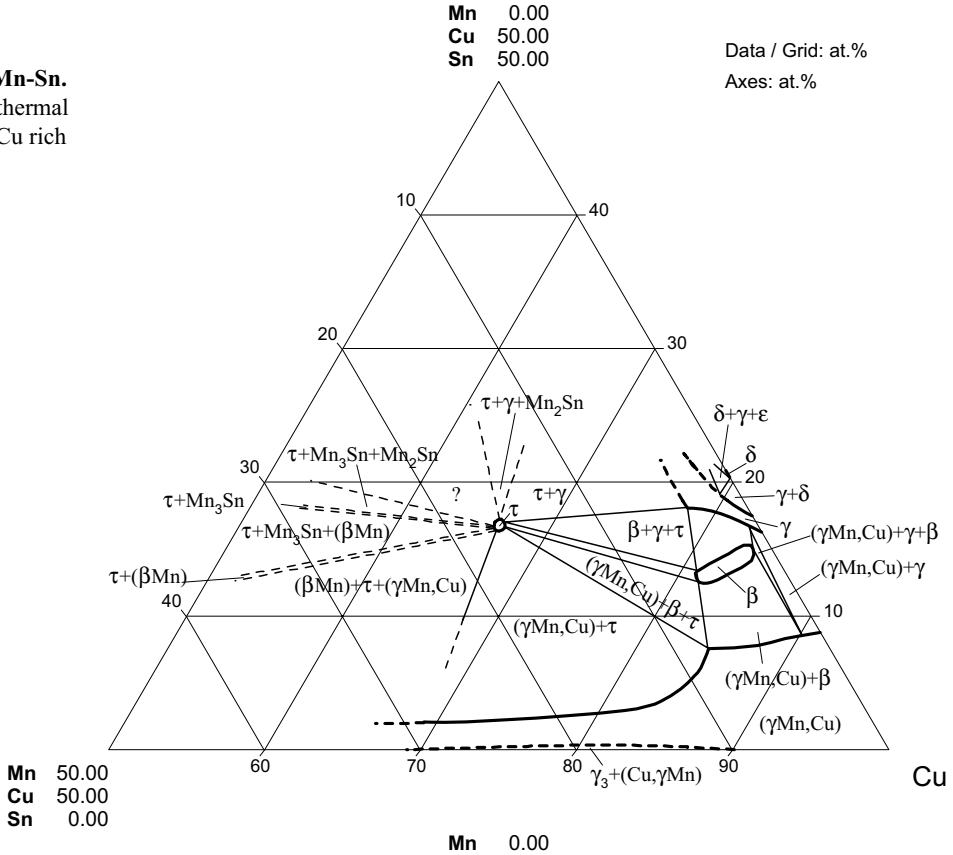

Fig. 6: Cu-Mn-Sn. Calculated isothermal section in the Cu rich part at 550°C

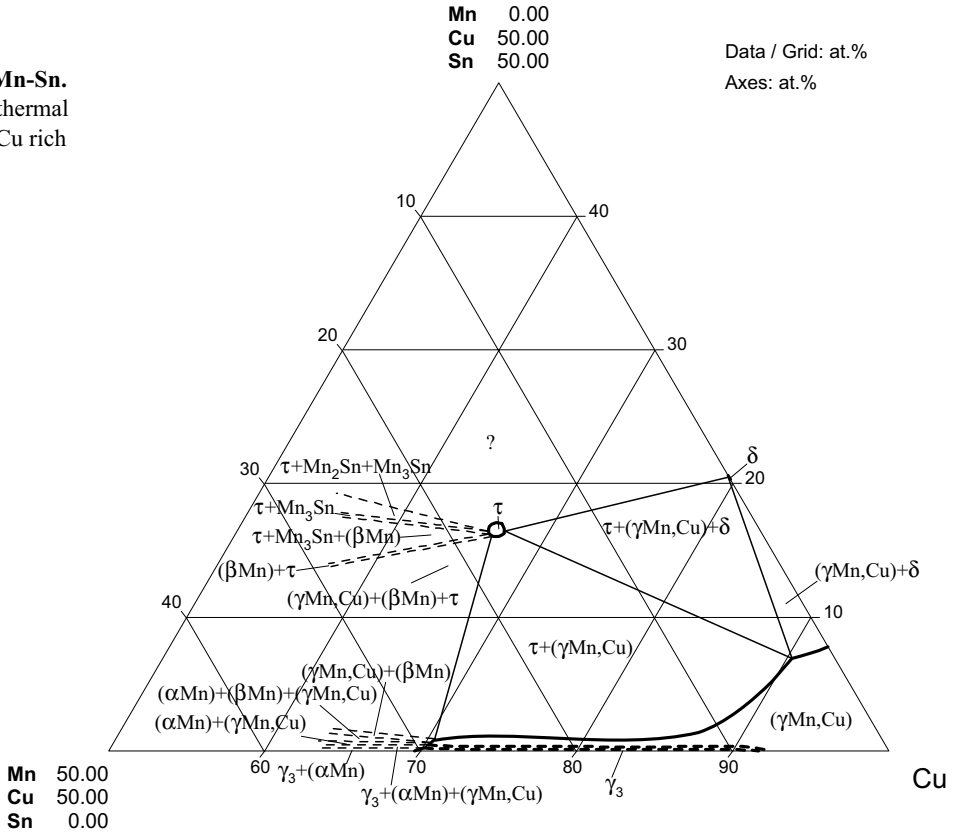

Fig. 7: Cu-Mn-Sn. Calculated isothermal section in the Cu rich part at 450°C

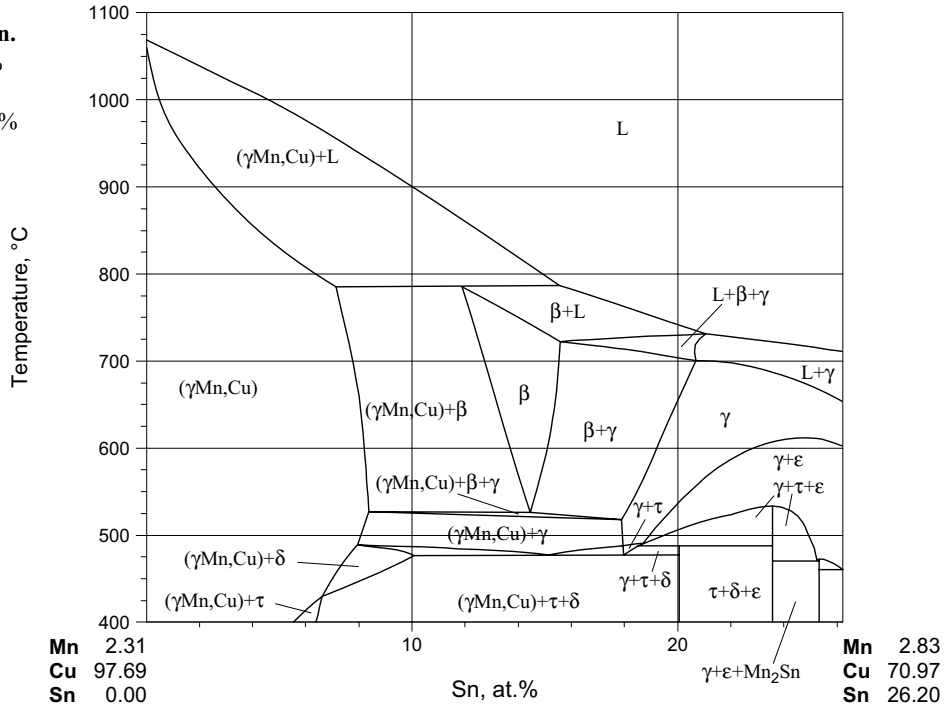

Fig. 8: Cu-Mn-Sn. Isopleth at 2 mass% Mn in the Cu rich corner, plotted in at.%

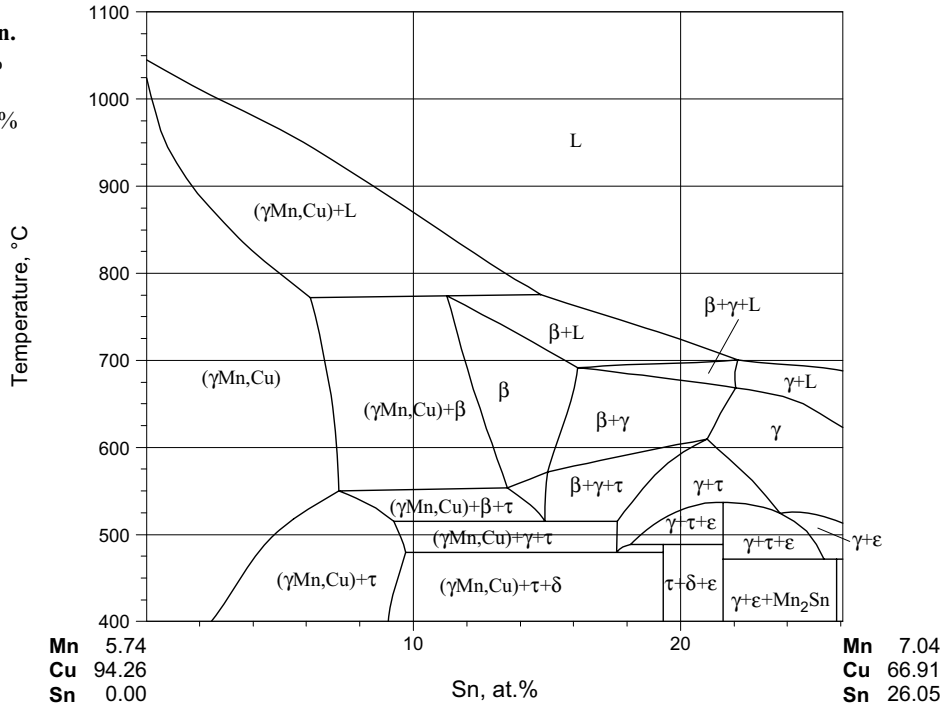

Fig. 9: Cu-Mn-Sn. Isopleth at 5 mass% Mn in the Cu rich corner, plotted in at.%

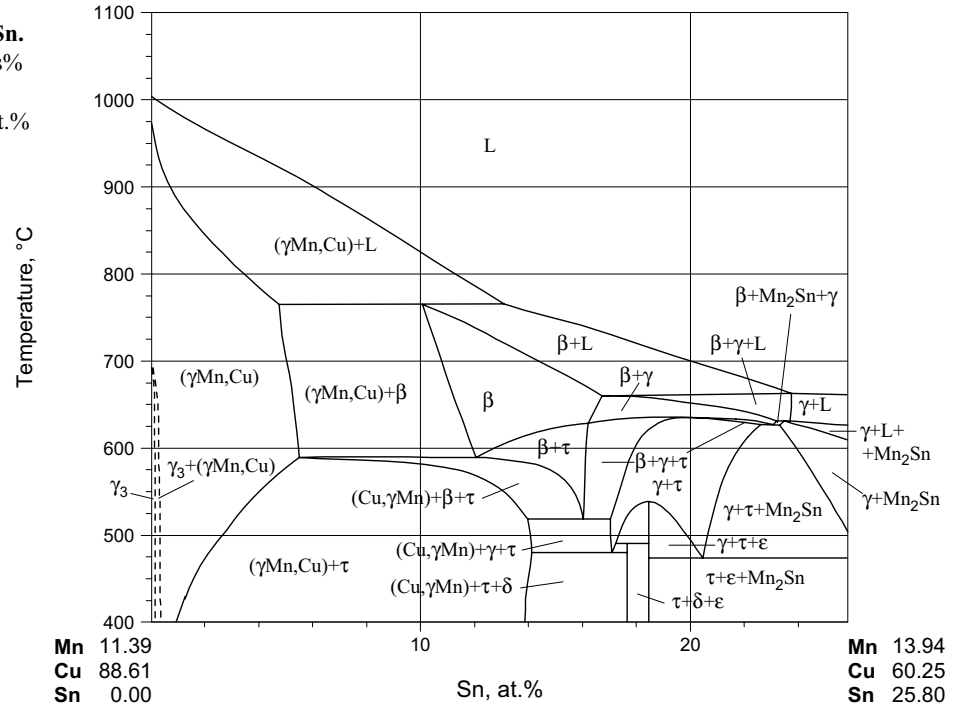

Fig. 10: Cu-Mn-Sn. Isopleth at 10 mass% Mn in the Cu rich corner, plotted in at.%

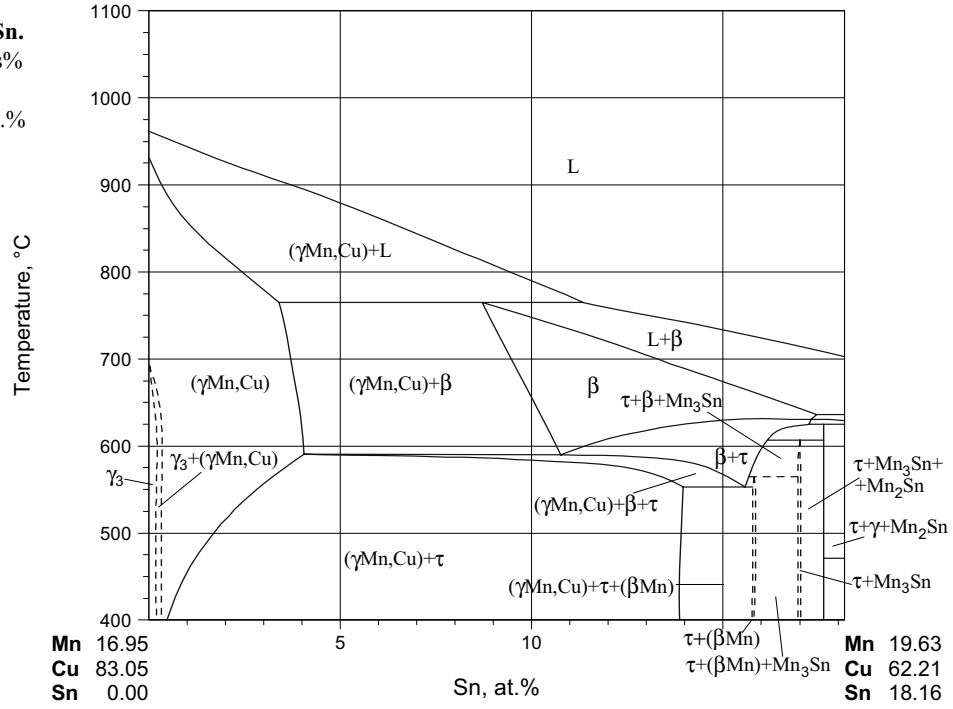

Fig. 11: Cu-Mn-Sn. Isopleth at 15 mass% Mn in the Cu rich corner, plotted in at.%

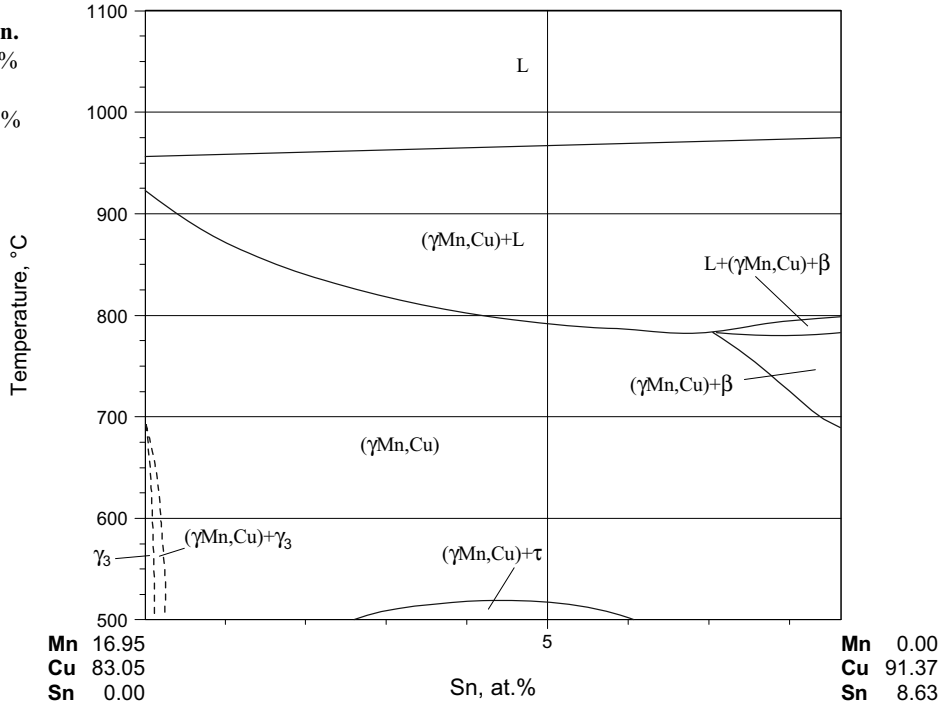

Fig. 12: Cu-Mn-Sn. Isopleth at 85 mass% Cu in the Cu rich corner, plotted in at.%

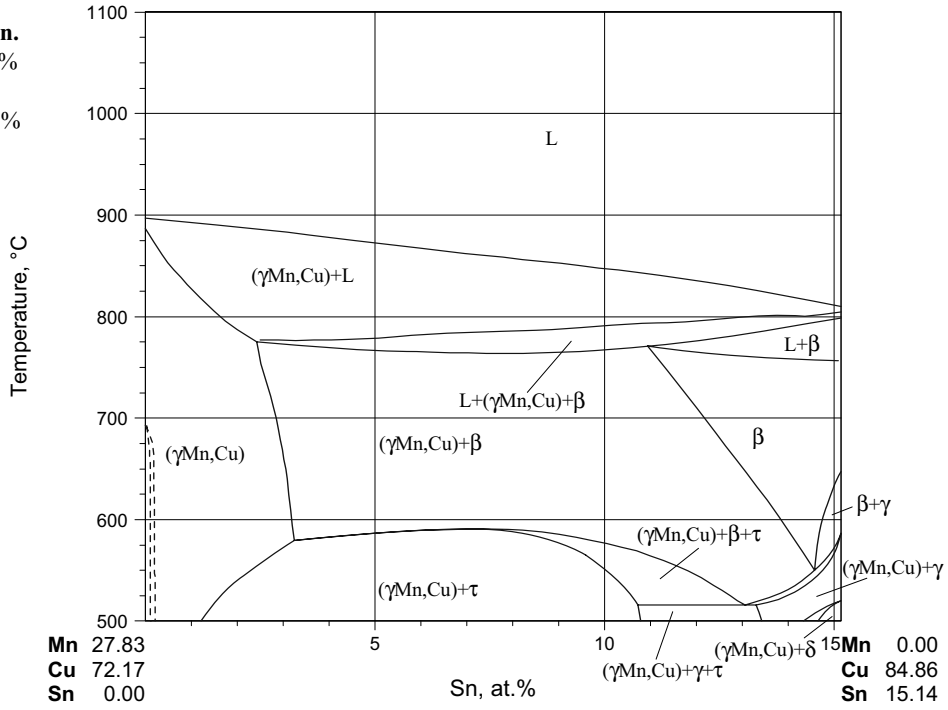

Fig. 13: Cu-Mn-Sn. Isopleth at 75 mass% Cu in the Cu rich corner, plotted in at.%