Copper – Tin – Zinc

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Introduction

Despite the fact that for the ternary Cu-Sn-Zn system plentiful experimental data are available, no complete phase diagram has been reported. One may mark the following milestones: the first systematic research of microstructures and mechanical properties of brasses alloyed by Sn with the structure (Cu) and (Cu) + β [1905Gui]; the first measurements of mutual solubility between Sn and Zn in solid Cu [1905Gui, 1912Car, 1912Joh]; the determination of liquidus surface and limit of saturation of the ternary (Cu) phase by means of differential thermal analysis (DTA) and microscopic examinations of the ternary (Cu) phase up to 30 mass% Sn and 50 mass% Zn [1913Hoy1, 1913Hoy2, 1924Tam]. [1915Hud, 1915Hoy, 1919Hoy, 1920Cam, 1921Gui, 1930Bau1, 1930Bau2, 1931Bau, 1933Yam, 2004Vil] were successful in attempts to show the phase constitution under equilibrium conditions in wide temperature ranges within 50 to 70 mass% Cu and up to 7 mass% Sn region that includes practically all the useful Sn brasses. According to these researchers the solubilities of Sn in (Cu) and β phases are functions of Zn content. High Sn contents are responsible for an eutectoid structure with the formation of a hard phase γ_1, as a consequence of reaction $\beta \rightleftharpoons$ (Cu) + γ_1. [1915Hud] has established the isothermal section at 425°C, and [1920Cam] constructed the section basing on the alloys annealed at 650°C and then cooled slowly. However, these isothermal sections contradicted in some details with the phase rule. [1930Bau1, 1930Bau2] determined seven isothermal sections from 800 to 400°C and established the phase equilibria between (Cu), β and γ_1 phases. [1933Yam] presented the isothermal sections at 650, 600 and 550°C, the results being in accordance with [1930Bau1, 1930Bau2]. In [2004Vil] the equilibrium phases and their compositions at 550, 450, and 350°C have been determined for Cu contents between 55.4 and 67.5 mass% and Sn contents up to 5.3 mass% by electron probe microanalysis (EPMA).

The liquidus surface of the Cu rich part of the Cu-Sn-Zn system was investigated by [1933Yam]. In addition, several vertical sections in Cu rich part were constructed by [1913Hoy1, 1913Hoy2, 1924Tam, 1930Bau2, 1933Yam]. Phase equilibria in the Sn rich part of the system were only focused on by [1987Zhe]. [1997Pen] reported the liquidus temperatures for 40 alloys along four vertical sections with constant Cu:Sn ratios of 1:3, 1:2, 1:1 and 2:1 (in atomic fraction). The published liquidus temperatures were taken from the distinct break in the emf values *versus* temperature curves at the liquidus. The accuracy was estimated to be ± 7 K.

[1937Kon] studied the homogeneity range of (Cu) solid solution at 500, 350 and 310°C by means of lattice parameters and compared the results with previous investigations. Beginning from early works to nowadays, the Cu-Sn-Zn alloys were melted in air using a gas-fired furnace with blast [1913Hoy1] to an induction furnace [1976Mac, 2004Vil]. Covered clay crucibles were used in the work due to [1920Cam]. As a guard against oxidation a cover of borax or charcoal gave very good results.

[1926Han, 1930Bau1] reviewed some of the earlier investigations, whilst the later reviews of the system have been made by [1936Hum, 1949Jae, 1973Smi, 1979Cha, 1979Dri].

The thermodynamic descriptions of the Cu-Sn-Zn system have been presented by [1998Jan, 2002Mie]. The isothermal section at 250°C was calculated by [2003Jeo], and the liquid phase was modelled by [2001Her], whose assessment can reproduce the measured partial Gibbs energies of Zn and the liquidus temperatures published by [1997Pen].

Binary Systems

The binary systems Cu-Sn, Sn-Zn and Cu-Zn are accepted from [1994Sau, Mas2], [2002Per] and [2006Leb], respectively.

Solid Phases

Table 1 summarizes the crystal structure data for the unary and binary phases. No ternary compounds were observed. The system shows a complete solid solution between isostructural binary β phases of the Cu-Sn and Cu-Zn systems at high temperatures. The phase γ_1 dissolves up to 28 mass% Sn and the phase γ dissolves up to 9 mass% Zn at 600°C [1933Yam]. The phase δ shows the quite small homogeneity range and dissolves up to 5 mass% Zn at 550°C [1933Yam].

Invariant Equilibria

Eight invariant four-phase reactions, five in the Cu rich part [1933Yam] and three in Sn rich one [1987Zhe], have been established experimentally. They are given in Table 2. The compositions of the equilibrium phases in Cu rich part of system are estimated from the established diagrams of [1933Yam]. According to [1933Yam], also three three-phase invariant equilibria exist in the Cu rich part of the Cu-Sn-Zn system. The reaction scheme in the Cu-Sn-Zn system is proposed in Fig. 1. In addition to the experimentally established invariant reactions, five speculative invariant four-phase reactions (U_2, U_4, U_6, U_8, E_3) are also presented and shown in the diagram by dashed lines. The derived five invariant reactions correlate with experimental data [1933Yam, 1987Zhe] and also with isothermal section at 250°C [2003Jeo].

Liquidus Surface

The liquidus surface in Cu rich part of the Cu-Sn-Zn system is shown in Fig. 2. The presented liquidus surface and liquidus isotherms are taken from the evaluation of [1979Cha], which is based on the investigations of [1913Hoy1, 1913Hoy2, 1924Tam, 1930Bau1, 1933Yam]. These investigations are in good agreement with each other. The liquidus surface and liquidus isotherms in Sn rich part of the system are according to [1987Zhe]. The liquidus isotherms in the central part of the Cu-Sn-Zn system are given by [1997Pen]. The calculated liquidus temperatures for the two vertical sections with ratio of Cu:Sn = 1:1 and 2:1 [2001Her] are in agreement with the experimental data from [1997Pen]. The calculated liquidus surfaces in the whole system presented by [1998Jan] agree well with the experimental data [1913Hoy1, 1924Tam, 1930Bau2] only in region of (Cu)-liquidus surface. The β and ε_1 liquidus surfaces calculated by [1998Jan] differ significantly from the experimental data [1930Bau2, 1933Yam, 1987Zhe]. The calculation for the Cu rich part of the Cu-Sn-Zn system presented by [2002Mie] is in reasonable agreement with the experimental data critically reviewed by [1979Cha].

Isothermal Sections

The partial isothermal section at 600°C shown in Fig. 3 is from the works [1933Yam, 1979Cha]. The partial isothermal sections at 450 and 350°C [2004Vil] are presented in Figs. 4 and 5, respectively. The compositions of the (Cu), β' and γ_1 phases in the three-phase region given by [2004Vil] differ from those obtained by [1930Bau2, 1933Yam]. According to [2004Vil], the compositions of both (Cu) and γ_1 are almost constant at 450 and 350°C. Furthermore, [2004Vil] did not observe the three-phase region (Cu) + β' + γ_1 at 550°C, whereas this region was reported by [1930Bau2] to extend up to 550°C. The results of [2004Vil] are preferable because [2004Vil] used a more accurate technique (EPMA) to determine the phase compositions. The isothermal section at 250°C calculated by [2003Jeo] is presented in Fig. 6. Figure 7 shows the homogeneity range of (Cu) at 500 and 300°C presented by [1979Cha], who used the data from [1937Kon, 1933Yam] as the base for the assessment.

Temperature – Composition Sections

Figure 8 shows the vertical section between the binary Cu-60Zn (mass%) to binary Cu-31Sn (mass%) alloys. It is drawn actually after [1933Yam] and agrees with the accepted binaries Cu-Sn and Cu-Zn. The temperature of the E_2 reaction was shown in [1933Yam] as 511 instead of 528°C; this was corrected in Fig. 8. Meanwhile, intersection of four lines into one point on the Cu-Zn side is only an approximation. According to the accepted Cu-Zn phase diagram such a case could have been only at 59.8 mass% Zn as

compared with 60 mass% Zn of the presented vertical section. As far as this difference between concentrations is very small, the indicated intersection of four lines into one point is quite justified. Figure 9 presents the part of the vertical section between binary Cu-60Zn (mass%) and binary Cu-33.6Sn (mass%) alloy within 0 to 20 mass% Zn [1933Yam]. Both sections were somewhat corrected to be consistent with the established isothermal sections.

Thermodynamics

The influence of small addition of Cu on the thermodynamic properties of a dilute solution of Zn in molten Sn has been studied using an electrochemical method in the temperature range of 450 to 650°C [1974Ngu]. The thermodynamic activities of Zn in Cu-Sn-Zn melts with compositions up to 6 at.% for both Cu and Zn between 430 and 600°C were measured by [1978Hag] employing emf technique. Using the torsion-effusion technique, the effect of small additions of Cu on the activity coefficient of Zn in dilute Sn-Zn melts at 530°C was investigated by [1974Tef]. Results of [1974Ngu, 1974Tef, 1978Hag] are very close to each other. And the Wagner interaction parameter ε_{Zn}^{Cu} was estimated to be $2.90 \pm 1.20 - (3245 \pm 900)/T$ [1974Ngu]. [1987Ryc] using the isopiestic method has determined the Wagner interaction parameters ε_{Zn}^{Sn} in the dilute solution based on Cu at 1200°C. Following the same technique, [1986Sug] measured the activity of Zn in Cu-Sn-Zn melts at 1150 and 1100°C and in the composition range up to 8 at.% for both Zn and Sn. The activity of Zn in the ternary liquid phase has been measured at 700 [1996Kar] and 750°C [1997Pen] for four vertical sections with Cu:Sn ratio of 1:3, 1:2, 1:1 and 2:1. Both groups of authors utilized the emf method. From the measured emf values, the thermodynamics properties, such as activities of Zn, the partial Gibbs energy, partial enthalpy and partial entropy of the components, were derived. [1998Pen] performed a comparison between the calculated and measured thermodynamic properties reported in [1996Kar, 1997Pen]. The summaries for the work from [1998Pen] and [1998Jan] are given in [1997Din] and [1999Kau], respectively.

Notes on Materials Properties and Applications

[1930Bau2] measured the Brinell hardness of alloys containing 35 to 45 mass% Zn and up to 5 mass% Sn. A Cu based alloy containing 38.2 mass% Zn and 3.1 mass% Sn was subjected to severe plastic deformation at 400°C using the procedure of equal-channel angular pressing (ECAP) [2001Nei, 2004Nei]. The elongation achieved in this alloy amounted up to 900% at the slowest strain rate of $1.0 \cdot 10^{-4}$ s^{-1} at 400°C. This elongation value was significantly higher than the value of 200% achieved in similar quasi-superplastic Cu-Sn-Zn alloys with about 2 mass% Pb in the temperature range of 500 to 600°C [1999Mat]. [2002Sho] investigated the interfacial reaction and mechanical properties of Sn-Zn alloy / Cu joints under the thermal exposure conditions. According to [2002Sho] the Vickers hardness decreased as a result of the transformation from Zn into Cu-Zn compounds.

Miscellaneous

The term “kalhoid” was used by early investigators [1913Hoy1, 1913Hoy2, 1919Hoy] to designate the ternary Cu-Sn-Zn alloys in order to avoid confusion with the names related to binary brass and bronze. Currently, this term is not in use.

When Sn bearing brasses are compared with bronzes, it is shown that the chief difference from the view point of structure lies in the fact that in the brasses the β phase remains stable down to room temperature, whereas in the bronzes it breaks down in the neighbourhood of 500°C into a mechanical mixture of (Cu) and γ or the eutectoid as has been proposed by [1969Rao].

[1956Fre] discussed the effects of composition and structure on properties of industrial brasses and bronzes used for making castings. Some problems associated with freezing brasses and bronzes have been discussed by [1971She]. Formations of interface phases under different conditions of interdiffusion have been examined by [1940Glu, 1976Urq, 1987Tak, 1998Lee]. The morphology and morphological stability of large precipitates formed in Cu-Sn-Zn alloys were investigated by [1967Mal] using EPMA technique.

[1987Tak] determined the interdiffusion coefficients for (Cu) phase of the Cu-Sn-Zn system at 800°C by measuring the composition profiles of the solid-solid diffusion couples using the EPMA technique.
[1997Lee, 1998Lee, 2000Kat, 2002Sho, 2003Jeo] studied the interface reactions between Cu substrate and Sn-Zn binary eutectic in lead-free solder alloys. Basing on the calculation of metastable equilibria among initial phases a new approach has been suggested for predicting the occurrence of the compound, which forms first on the substrate/solder interface during the soldering process.
[1984Mur, 1995Fra, 1995Mor, 2002Miu] investigated martensite transformation in aged Cu-Sn-Zn shape memory alloys. For the Cu-Sn-Zn parent phase, two stages of transformation during ageing at 200°C were observed [1995Fra]. The stages were established to be connected with redistribution of Sn atoms. [2002Miu] found the shape memory effect below 268 K, the superelasticity above 278 K and about 4% maximum pseudoelastic strain in Cu-4.3 Sn-33.0 Zn (mass%) polycrystals.
[1984Mur] evaluated the resistance against degradation due to repeated martensite transformation in Cu-24Zn-6Sn (mass%) alloy through optical reflectivity measurements.

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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
(Cu) < 1084.62	*cF*4 $Fm\bar{3}m$ Cu	a = 361.46	pure Cu [V-C2] dissolves up to 9.1 at.% Sn at 586°C [Mas2, 1994Sau] and up to 38.27 at.% Zn at 454°C [2006Leb]
		a = 370.46	at 9.1 at.% Sn [1994Sau]
		a = 369.612 ± 0.014	at 35.84 at.% Zn [2006Leb]
(βSn) 231.9681 - 13	*tI*4 $I4_1/amd$ βSn	a = 583.18 c = 318.18	pure Sn at 25°C [Mas2, 1994Sau], dissolves 0.6 at.% Sn at 198.5°C [2002Per]
(αSn) < 13	*cF*8 $Fd\bar{3}m$ C(diamond)	a = 648.92	[Mas2, 1994Sau]
(Zn) < 419.58	*hP*2 $P6_3/mmc$ Mg	a = 266.50 c = 494.70	pure Zn at 25°C [Mas2], dissolves 0.0039 at.% Sn at 198.5°C [2002Per]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
β, {($Cu_{17}Sn_3$),(CuZn)}	*cI*2 $Im\bar{3}m$		13.1 to 16.5 at.% Sn [Mas2, 1994Sau]
$Cu_{17}Sn_3$ 798 - 586	W	*a* = 297.81 to 298.71	at 13.4 to 15.7 at.% Sn [1994Sau] 36.1 to 55.8 at.% Zn [2006Leb]
CuZn 903 - 454		*a* = 295.39	at 47.5 at.% Zn [V-C2, 2006Leb]
γ 755 - 520	*cF*16 $Fm\bar{3}m$ BiF_3	*a* = 606.05 to 611.76	15.5 to 27.5 at.% Sn [1994Sau] at 16.6 to 25 at.% Sn [1994Sau]
ζ, $Cu_{10}Sn_3$ 640 - 582	*hP*26 $P6_3$ $Cu_{10}Sn_3$		20.3 to 22.5 at.% Sn [1994Sau], the phase is superstructure based on ζ, AgZn [V-C2, 1994Sau]
		a = 733.0 *c* = 786.4	at 23.1 at.% Sn [1994Sau]
δ, $Cu_{41}Sn_{11}$ 590 - ~350	*cF*416 $F\bar{4}3m$ $Cu_{41}Sn_{11}$	*a* = 1798.0	20 to 21 at.% Sn [1994Sau] at 20.5 at.% Sn [1994Sau]
ε, Cu_3Sn < 676	*oC*80 *Cmcm* Cu_3Sn	*a* = 552.9 *b* = 477.5 *c* = 432.3	24.5 to 25.9 at.% Sn [1994Sau] at 25 at.% Sn [1994Sau]
η, Cu_6Sn_5(h) 415 - 186	*hP*4 $P6_3/mmc$ AsNi	*a* = 419.0 *c* = 508.6	43.5 to 44.5 at.% Sn [1994Sau] at 45.45 at.% Sn [1994Sau]
η', Cu_6Sn_5(r) < 189	*h***		45 at.% Sn superlattice based on AsNi-type structure[1994Sau]
		a = 2087.0 *c* = 2508.1	[1994Sau]
β', CuZn (r) < 468	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 295.9	at 49.5 at.% Zn [2006Leb]
$γ_1$, Cu_5Zn_8 < 835	*cI*52 $I\bar{4}3m$ Cu_5Zn_8	*a* = 886.9	57 to 70 at.% Zn [2006Leb] [2006Leb]
$δ_1$, $CuZn_3$ 665 - 548	*hP*3 $P\bar{6}$ $CuZn_3$	*a* = 427.5 *c* = 259.0	72.45 to 76 at.% Zn [2006Leb] [V-C2, 2006Leb]
$ε_1$, $CuZn_4$ < 574	*hP*2 $P6_3/mmc$ Mg	*a* = 274.18 *c* = 429.39	78 to 88 at.% Zn [2006Leb] [2006Leb]

Table 2: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Cu	Sn	Zn
$L + \beta \rightleftharpoons \gamma_1 + \gamma$	705	U_1	L	~69	~19.6	~11.4
			β	~73	~14.6	~12.4
			γ_1	~72.4	~16.9	~10.7
			γ	~70.2	~16.9	~12.8
$\zeta + \gamma \rightleftharpoons \delta + \varepsilon$	588	U_3	ζ	>77.7	~22.1	<0.2
			γ	~79.0	~19.9	~1.1
			δ	~79.0	~20.4	~0.6
			ε_1	>75.2	~24.7	<0.1
$\beta \rightleftharpoons (Cu) + \gamma + \gamma_1$	571	E_1	β	~75.6	~11.7	~12.7
			(Cu)	~78.2	~3.0	~18.8
			γ	~72.5	~16.0	~11.5
			γ_1	~74.7	~15.3	~10.0
$\gamma + \varepsilon \rightleftharpoons \delta + \gamma_1$	550	U_5	γ	~72.2	~17.1	~10.7
			ε_1	>75.2	~24.7	<0.1
			δ	~75.0	~19.3	~5.7
			γ_1	~72.6	~16.7	~10.7
$\gamma \rightleftharpoons (Cu) + \delta + \gamma_1$	528	E_2	γ	~73.6	~15.3	~11.1
			(Cu)	~78.6	~3.0	~18.4
			δ	~75.0	~19.3	~5.7
			γ_1	~75.3	~15.3	~9.4
$L + \varepsilon \rightleftharpoons \varepsilon_1 + \eta$	358	U_7	L	10.0	85.0	5.0
$L + \eta \rightleftharpoons \varepsilon_1 + (\beta Sn)$	218	U_9	L	~0.3	93.5	~6.2
$L \rightleftharpoons (Zn) + (\beta Sn) + \varepsilon_1$	190	E_4	L	0.3	84.5	15.2

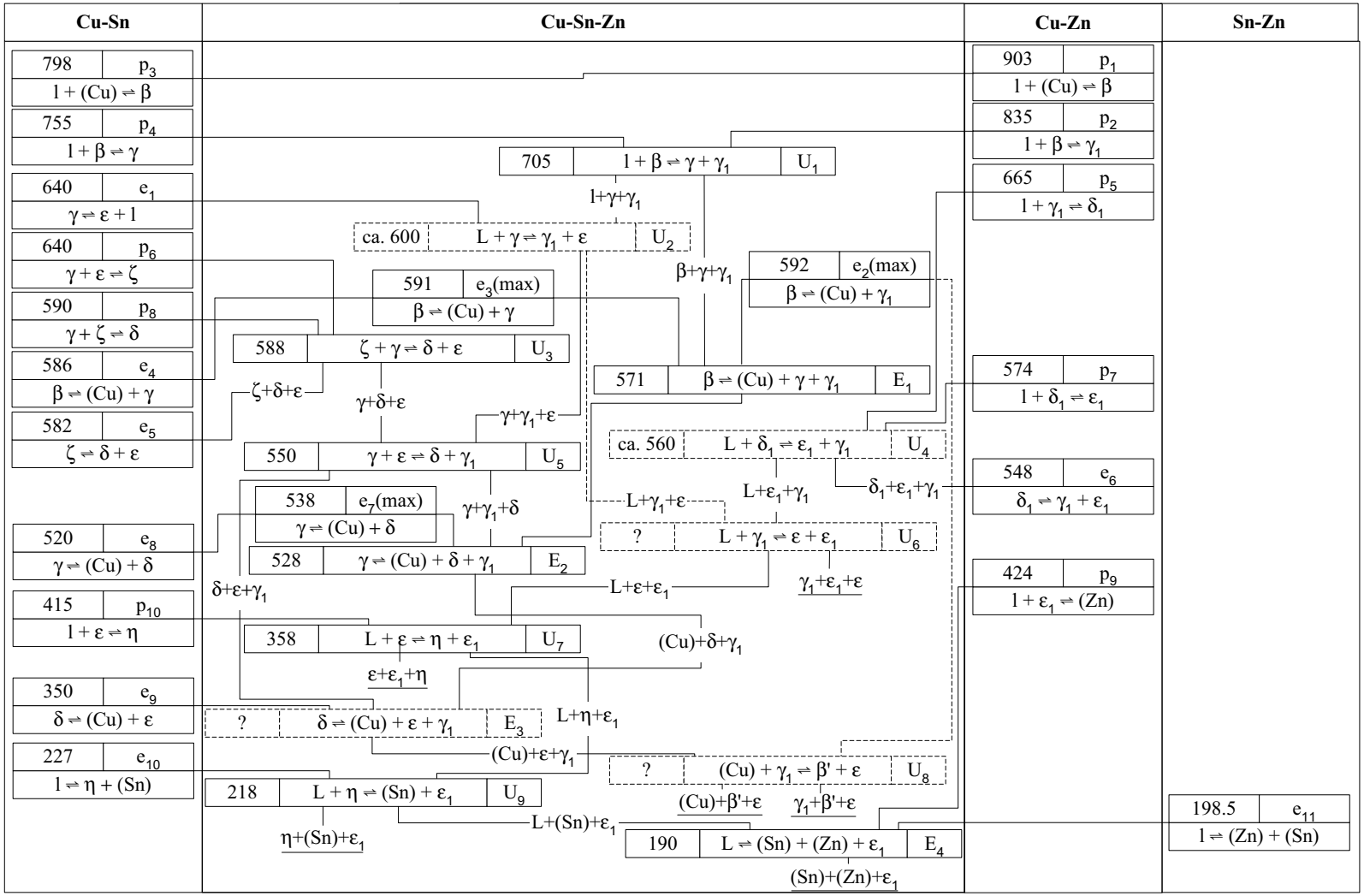

Fig. 1: Cu-Sn-Zn. Reaction scheme

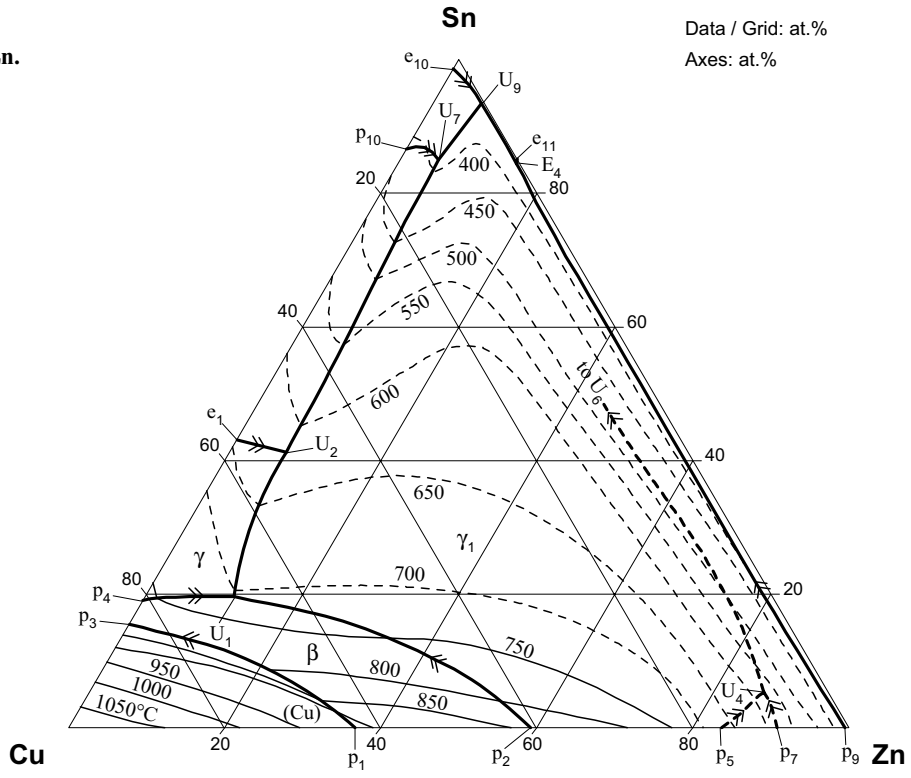

Fig. 2: Cu-Sn-Zn. Liquidus surface projection

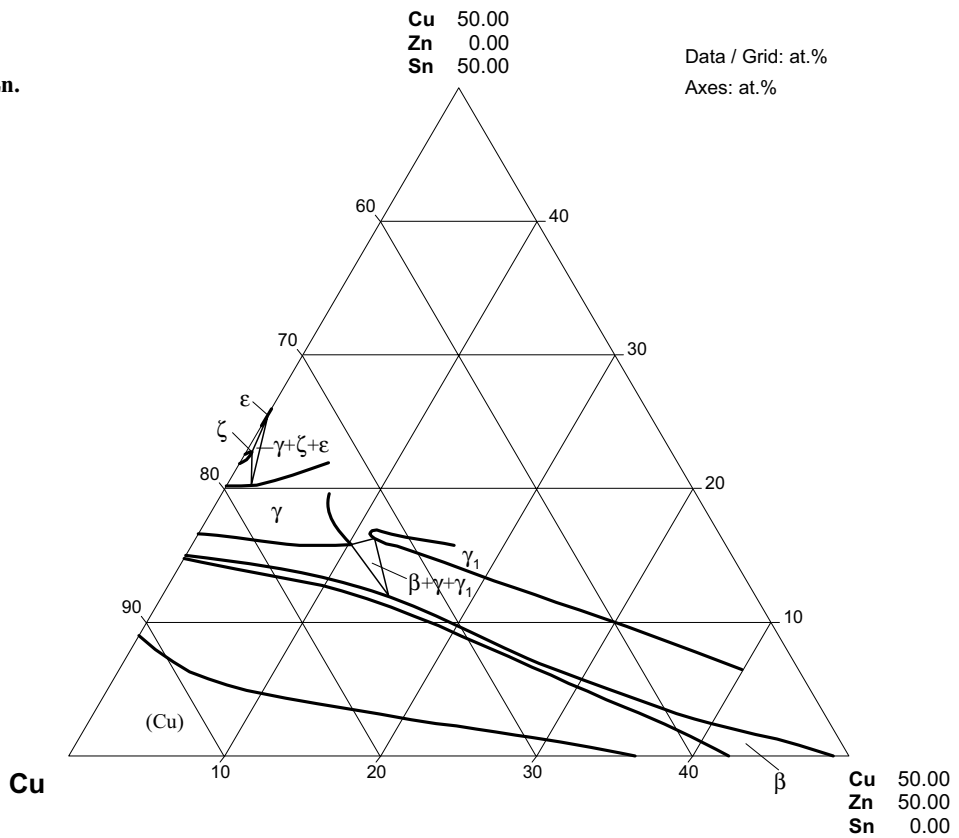

Fig. 3: Cu-Sn-Zn. Cu corner of the isothermal section at 600°C

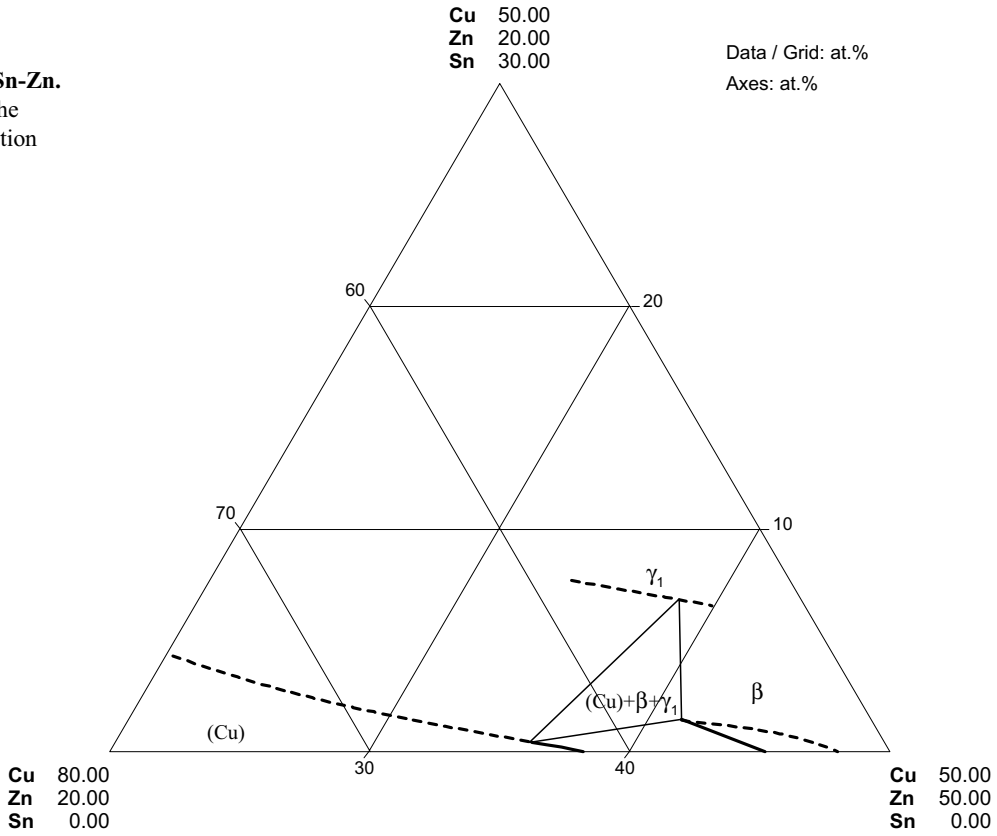

Fig. 4: Cu-Sn-Zn. Cu corner of the isothermal section at 450°C

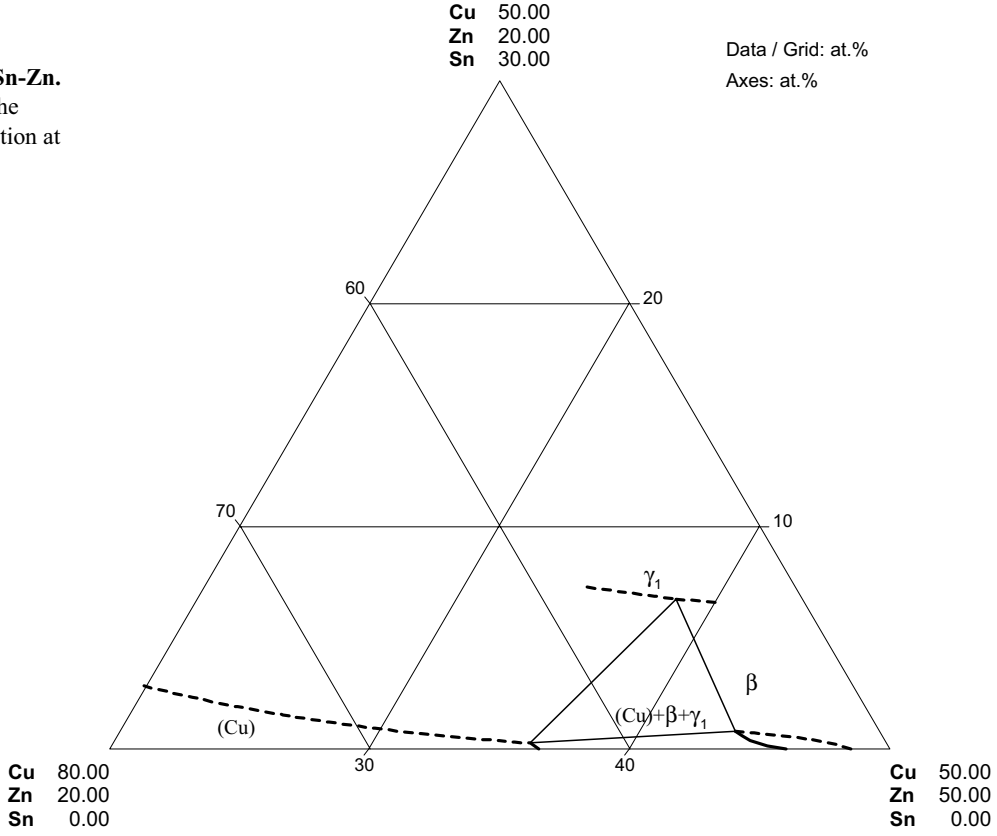

Fig. 5: Cu-Sn-Zn. Cu corner of the isothermal section at 350°C

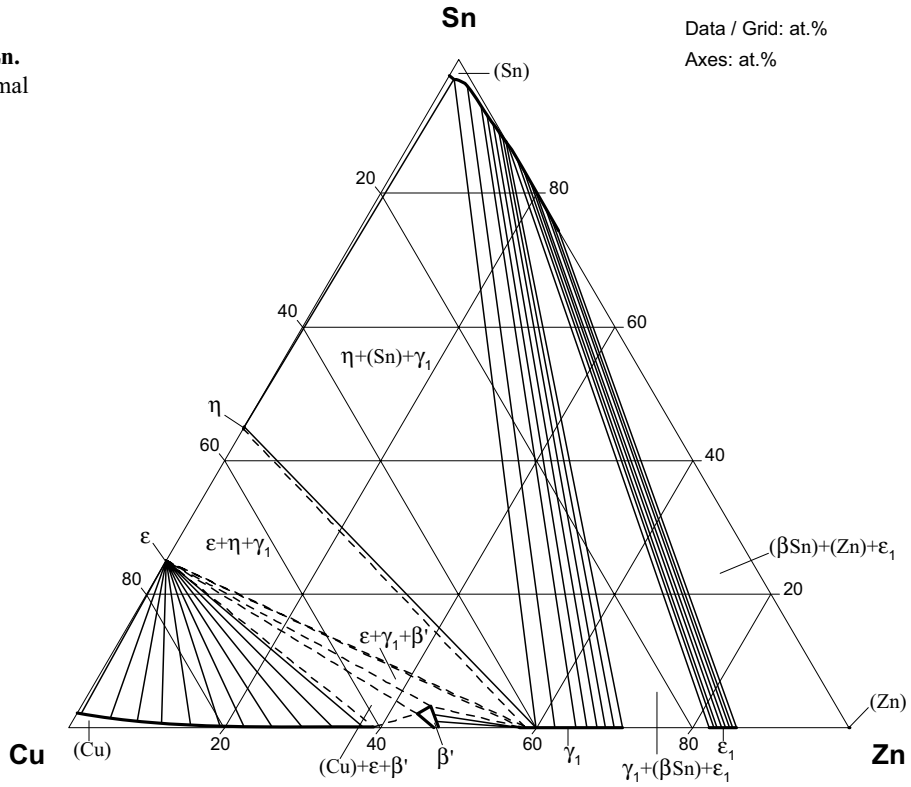

Fig. 6: Cu-Sn-Zn. Calculated isothermal section at 250°C

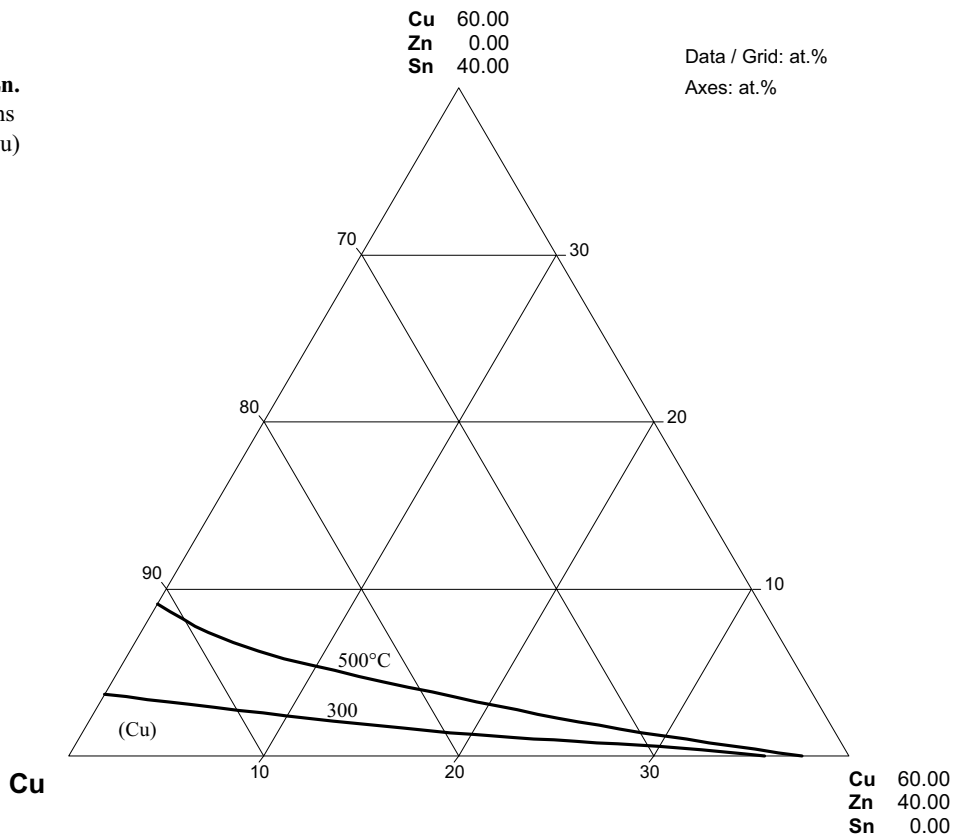

Fig. 7: Cu-Sn-Zn. Solubility isotherms of Sn and Zn in (Cu) at 300 and 500°C

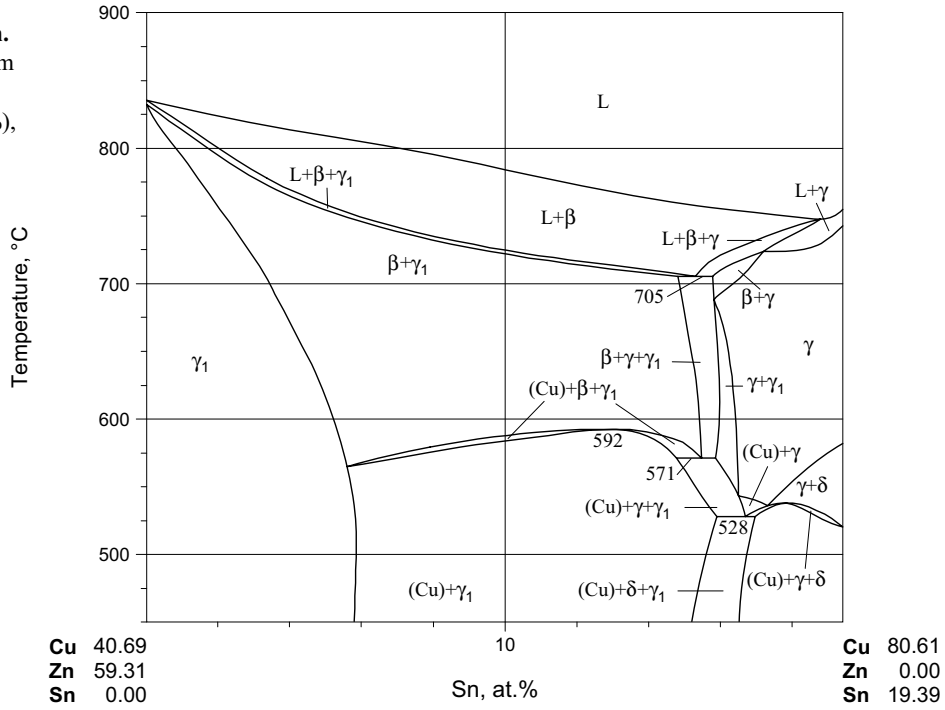

Fig. 8: Cu-Sn-Zn. Vertical section from 69Cu-31Sn to 40Cu-60Zn (mass%), plotted in at.%

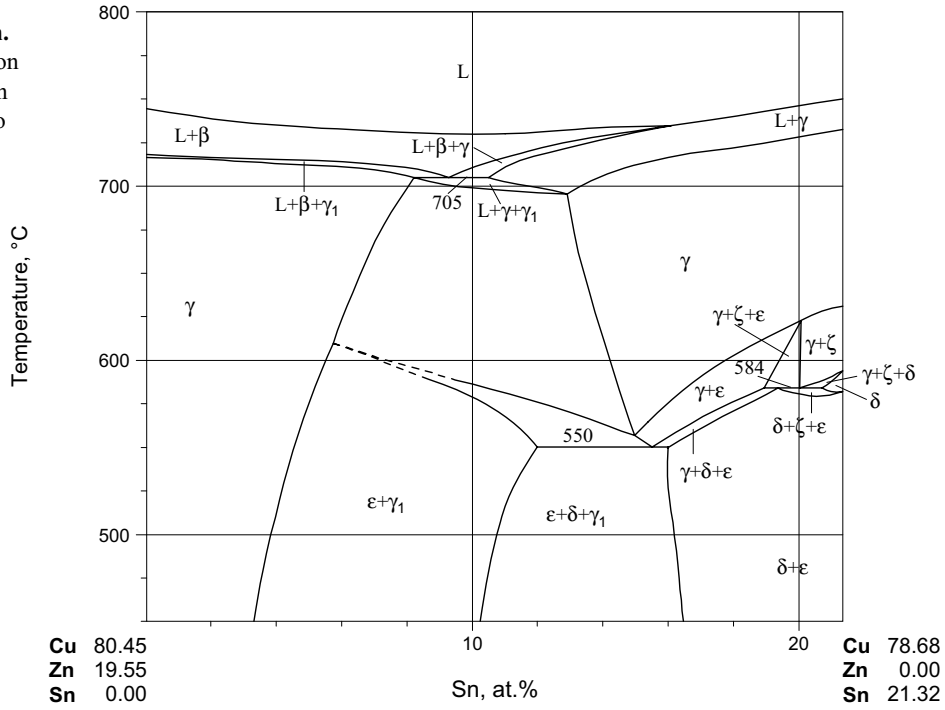

Fig. 9: Cu-Sn-Zn. Partial vertical section from 66.4Cu-33.6Sn to 40Cu-60Zn, up to 20% Zn (mass%), plotted in at.%