

# Copper – Phosphorus – Tin

Peter Rogl

## Introduction

High mechanical strength, wear resistance and sea-water corrosion resistance of Cu–Sn based bronzes have triggered early scientific interest in the constitution of the Cu–P–Sn system. Although the entire diagram still awaits further investigation, several research teams collected experimental phase diagram information on the Cu rich corner of the phase diagram [1910Hud, 1911Lev, 1926Gla1, 1926Gla2, 1933Ver, 1937Ham, 1954Mur, 1987Tak1, 1987Tak2]. Whilst [1933Ver] discussed earlier results of [1910Hud, 1911Lev, 1926Gla1, 1926Gla2], the authors of [1987Tak1, 1987Tak2] seemed to be unaware of previous extensive work in the system. A summary of the constitution of the Cu–P–Sn system was given by [1979Dri], presenting a liquidus projection and partial isothermal sections at 600 and 300°C for the Cu rich region. A thermodynamic assessment for the Cu rich region was recently published [2001Mie].  $\text{Cu}_4\text{SnP}_{10}$  is the only ternary compound hitherto reported for the ternary system [1979Hoe, 1980Hoe], however, phase relations involving the compound are still unknown. The various experimental activities related to the constitution of the ternary Cu–P–Sn system are summarized in Table 1.

## Binary Systems

The binary systems Cu–P and P–Sn are used from the MSIT Binary Evaluation Program [2002Per, 2002Wat]. The Cu–Sn system is adopted from [1994Sau].

## Solid Phases

Crystallographic and melting data pertinent to the Cu–P–Sn system are given in Table 2. Only one ternary compound,  $\text{Cu}_4\text{SnP}_{10}$ , for which a  $\{\text{P}_{10}\}^{6-}$  polyanion of decaphospha-adamantane structure and a  $\{\text{Cu}_3\text{Sn}\}$  four-center 2-electron cluster is remarkable, has so far been reported for the ternary system [1979Hoe, 1980Hoe].

## Invariant Equilibria

Early investigators [1910Hud, 1926Gla1, 1926Gla2, 1937Ham] claimed the existence of a ternary eutectic at  $\text{Cu}80.7\text{Sn}14.8\text{P}4.5$  mass% and 628°C,  $\text{L} \rightleftharpoons (\text{Cu}) + \beta + \text{Cu}_3\text{P}$ . Experiments by [1911Lev, 1933Ver] indicated that the “ternary eutectic” should rather be a transition reaction,  $\text{L} + (\text{Cu}) \rightleftharpoons \beta + \text{Cu}_3\text{P}$ , for which [1933Ver] gave composition and temperature:  $\text{Cu}79.6\text{Sn}16.2\text{P}4.2$  mass% and 637°C. It has to be noted, that the composition of the liquid reported is close to the tie line  $\text{Cu}_3\text{P} - \beta$  but still within the triangle  $(\text{Cu}) + \text{Cu}_3\text{P} + \beta$ , thus rather indicating a ternary eutectic. Metallographic inspection and DTA-data from [1954Mur, 1987Tak1, 1987Tak2] were however, resolved in terms of a transition reaction at 655°C [1954Mur] or at 642°C [1987Tak1, 1987Tak2], respectively:  $\text{L} + (\text{Cu}) \rightleftharpoons \beta + \text{Cu}_3\text{P}$ . The composition of the liquid was reported at significantly lower Cu- and P-contents,  $\text{Cu}77.5\text{Sn}20.7\text{P}1.6$  mass% [1954Mur] on a practically straight line connecting the binary eutectic,  $\text{L} \rightleftharpoons (\text{Cu}) + \text{Cu}_3\text{P}$ , with the binary peritectic point,  $\text{L} + (\text{Cu}) \rightleftharpoons \beta$ . The composition of the ternary liquid L would fall on the line connecting  $\text{Cu}_3\text{P}$  with  $\beta$  ( $\text{Cu}_{17}\text{Sn}_3$ ), assuming a minor change in composition of the  $\beta$  phase ( $\text{Cu}76.2\text{Sn}23.8$  mass%) from only a small phosphorus solubility. Essentially based on DTA and metallographic inspection (no details on X-ray data and EMPA were given), [1954Mur] reported a composition of  $\text{Cu}81.5\text{Sn}17.8\text{P}0.7$  mass% (point B in figure 7 of [1954Mur]) for presumably the vertex of the four-phase reaction plane at the ternary  $\beta$  phase, 655°C. Similarly, the vertex at the (Cu) solid solution was located at a surprisingly low Sn content ( $\text{Cu}97.8\text{Sn}2\text{P}1.2$  mass%) with respect to a maximal Sn solubility in (Cu) at 650°C of 15.6 mass% Sn. A redetermination of the vertices of the isothermal reaction plane will thus be necessary in order to resolve the doubts in the compositions given as well as to resolve the discrepancies between the data of [1910Hud, 1926Gla1, 1926Gla2, 1933Ver, 1937Ham] and the results of [1954Mur, 1987Tak1, 1987Tak2]. Although

somewhat doubtful but as the only experimental information available, the parameters for the ternary reaction taken at 642–655°C after [1954Mur] are listed in Table 3. It should be furthermore noted that the  $\gamma$  phase ( $\text{Cu}_3\text{Sn}$ ) was not observed [1954Mur, 1987Tak1, 1987Tak2] probably due to insufficiently fast quenching rates. This fact devaluates somewhat the vertical sections presented by [1954Mur] (at 1 mass% P, 6 and 10 mass% Sn) as well as those given by [1987Tak1, 1987Tak2] for 3, 5, 7 mass% P and 10, 15 mass% Sn). The  $\gamma$  phase was retained in the experiments by [1933Ver], however, the different position of the ternary reaction isotherm at 637°C makes a comparison difficult.

All experiments agree on a eutectoid ternary decomposition of the  $\beta$  phase (and  $\gamma$  phase?): from vertical sections the authors of [1954Mur, 1987Tak1, 1987Tak2] concluded a eutectoid decomposition of the  $\beta$  phase at 515°C ( $\text{Cu}_{75.5}\text{Sn}_{23.7}\text{P}_{0.8}$  mass%), ( $\beta \rightleftharpoons \text{Cu}_3\text{P} + (\text{Cu}) + \delta$ ), whereas [1933Ver] seemed to indicate the decomposition:  $\beta \rightleftharpoons \text{Cu}_3\text{P} + (\text{Cu}) + \gamma$  at 587°C. The data of [1954Mur, 1987Tak1, 1987Tak2] have to be taken with care as these authors were unable to quench and observe the  $\gamma$  phase ( $\text{BiF}_3$  type). The proper reaction thus will be  $\gamma \rightleftharpoons \text{Cu}_3\text{P} + (\text{Cu}) + \delta$  as indicated by [1933Ver] at about 500°C. No details on the composition of the corresponding phases are available.

A tentative Schultz-Scheil diagram summarizing the invariant reactions in the Cu rich part of the diagram is given in Fig. 1.

### Liquidus, Solidus and Solvus Surfaces

A liquidus projection for the Cu rich region was presented by [1933Ver, 1954Mur, 1987Tak1, 1987Tak2] superseding older data by [1926Gla1, 1926Gla2] on the melting trough running from the binary Cu– $\text{Cu}_3\text{P}$  eutectic to the binary Cu–Sn peritectic  $\text{L} + (\text{Cu}) \rightleftharpoons \beta$  (see also discussion in section Invariant Equilibria). The liquidus projection is shown in Fig. 2 accepting an invariant ternary transition reaction.

### Isothermal Sections

Four isothermal sections at 300, 550, 600 and 660°C were prepared by [1933Ver] for the Cu rich region up to 27 mass% Sn and 9 mass% P. All solid state phase equilibria are characterized by tie lines from  $\text{Cu}_3\text{P}$  to the various binary Cu–Sn phases. For the 300°C section a tie line  $\text{Cu}_3\text{P}$  – “ $\text{Cu}_4\text{Sn}$ ” ( $\delta$  phase,  $\text{Cu}_{41}\text{Sn}_{11}$ ) was indicated [1933Ver], although more recent phase diagrams assume decomposition of  $\text{Cu}_{41}\text{Sn}_{11}$  below about 350°C. The isothermal section for the Cu rich region at 550°C is presented in Fig. 3 showing also the location of the ternary phase  $\tau_1$ ,  $\text{Cu}_4\text{SnP}_{10}$ . The corresponding isothermal section at 600°C reveals similar phase relations, however, all binary tin-phosphides are already liquid (see Fig. 4).

### Temperature – Composition Sections

[1933Ver] derived a set of isopleths with constant contents of 1, 2 and 3 mass% P (from 0 to 25 mass% Sn) as well as with constant content of 5, 10 and 20 mass% Sn (from 0 to 5 mass% P). Independently [1954Mur, 1987Tak1, 1987Tak2] determined isopleths with constant contents of 6, 10, 15 mass% Sn (from 0 to 8 mass% P) as well as with constant content of 1, 3, 5 and 7 mass% P (from 0 to 15 mass% Sn). Comparison of the two sets of data reveals liquidus temperatures of [1933Ver] to be generally lower by about 30°C and shifted to lower P contents of 4.2 mass% P for the monovariant liquid trough. In both data sets we encounter a series of inconsistencies with the solid state equilibria: (i) [1954Mur, 1987Tak1, 1987Tak2] have not observed the  $\gamma$  phase; (ii) their vertical section is inconsistent with the intersections of the  $\text{L} + \text{solid}$  phase lines on the four phase plane; (iii) although the  $\gamma$  phase was included in the sections of [1933Ver] and measurements were carried out on a finer sample grid, there are some misinterpretations of the TA data including several violations of the phase rule; (iv) whilst [1933Ver] shows invariant solid state reactions at 587°C (involving the  $\gamma$  phase) and 500°C (involving the  $\delta$  phase), [1954Mur, 1987Tak1, 1987Tak2] only report an invariant temperature of 500–515°C neglecting the  $\gamma$  phase completely. The isopleth at 6 mass% Sn (up to 5 mass% P) and the isopleth at 10 mass% Sn (up to 5 mass% P) are shown in Fig. 5 and Fig. 6, respectively.

A major point of discrepancy is the location of the four-phase plane near the Cu–Sn boundary for the transition reaction at 642–655°C.

## Thermodynamics

No experimental thermodynamic data are presently available for the ternary system. A thermodynamic CALPHAD type description of the Cu rich part of the system up to to 32 mass% Sn and 14 mass% P is due to [2001Mie]. The calculation includes a thermodynamic modelling of the Cu-P and P-Sn systems up to 30 and 50 at.% P, respectively. For the ternary system [2001Mie] based their calculation exclusively on experimental phase relations as described by [1987Tak1]. Serious discrepancies were encountered between calculated and experimental extents of phase regions.

## Notes on Materials Properties and Applications

Technical use of Cu based friction bearings for automotive industry was summarized by [1992Bog]. A special band-casting technology for various Cu based alloys (including alloying constituents such as Sn, P) was patented by [1993Due]. The technical use of copper alloys in electric and electronic appliances and communication systems have been addressed by [1992Sch, 1990Seg, 1982Sak]. Development and properties of a high-conductivity/high strength cold worked copper alloy containing a submicron dispersion of intermetallic compounds in a Cu-matrix (Mg and P in the ratio of  $\text{Mg}_3\text{P}_2$ ) revealing high resistance to heat softening has been reported and was compared to  $\text{Cu}_{95}\text{Sn}_5\text{P}_{\text{min}0.03}$  mass% and  $\text{Cu}_{92}\text{Sn}_8\text{P}_{\text{min}0.03}$  mass% alloys [1970Fis]. The dispersion pins dislocations and grain boundaries thus retaining high temperature strain-hardening. Effects of phosphorus on the friction and wear characteristics of a  $\text{Cu}_{95}\text{Sn}_5\text{P}_{1-5}$  at.% alloy were studied using a pin-disc apparatus [1979Yag, 1979Tag]. The coefficient of friction and the rate of wear decreased with increasing amount of matrix- $\text{Cu}_3\text{P}$ . The P surface content increases after heating to 300°C (P atoms at 400°C dissolved in  $\alpha$ -ss, whereas after cooling to room temperature the top surface layer was covered by a  $\text{Cu}_3\text{P}$  film). [1956Fre] studied the influence of basic composition, microstructure and impurities on the properties of copper tin bronzes as well as the control of metal and casting quality. Examination of the influence of Sn and P contents as well as the effect of casting on the hot-working capacity (including hot forging, hot extrusion and hot rolling) of phosphorized tin bronzes showed the difficulties in handling these materials [1950Sho].

## Miscellaneous

The ability to form amorphous nanosize products (5-10 nm) was investigated via ballmilling 250 mesh elemental powder blends for the compositional range  $\text{Cu}_{86-x}\text{Sn}_x\text{P}_{14}$  ( $x = 2-15$ ) [1999Zha]. After 28 h of mechanical alloying  $\text{Cu}_{84}\text{Sn}_2\text{P}_{14}$  essentially amorphized with some amount of crystallized phase still present. Increased milling time increased the crystalline phase. The periods of complete amorphization of  $\text{Cu}_{86-x}\text{Sn}_x\text{P}_{14}$  for  $x = 4, 5, 8, 10$  were given as 28, 20, 12 and 32 h, respectively. No amorphous phase forms if the Sn content exceeds 15 mass% Sn. The glass forming range was identified within 4-14 mass% Sn. Explanation for the ability to form amorphous products in Cu-P-Sn alloys was attempted by the authors in the framework of the Zhang-Bangwei theory. The effect of Sn on the microstructure and solidus temperatures of Cu-P bronzes was studied by [1989Kra].

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**Table 1:** Investigation of the Cu-P-Sn Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1910Hud]	presumably melting of $\text{Cu}_4\text{Sn} + \text{Cu}_3\text{P} + \text{Cu}(\text{Sn})$ .	Ternary eutectic claimed at $\text{Cu}_{81}\text{Sn}_{14.2}\text{P}_{4.8}$ mass% 620°C.
[1926Gla1] [1926Gla2]	melting of 50 g alloys from electrolytic Sn, Cu and $\text{Cu}_{74.5}\text{P}_{15.4}$ master alloy in graphite crucibles under reducing CO-containing atmosphere. Thermal analysis, chemical analysis, metallography.	Determination of melting trough from binary Cu-Cu <sub>3</sub> P eutectic to peritectic (Cu)+L $\rightleftharpoons\beta$ ; ternary eutectic point $\text{Cu}_{80.7}\text{Sn}_{14.8}\text{P}_{4.5}$ at 628°C.
[1933Ver]	melting of electrolytic Cu, Sn-ingots and a $\text{Cu}_{89.9}\text{P}_{10.1}$ (mass%) master alloy in ceramic (Schamott=fireclay) crucibles under charcoal. Thermal analyses with calibrated Pt/PtRh thermocouples. Casting of 12mm diameter rods in cold iron crucibles. Chemical analyses. Annealing of alloys packed on charcoal powder in wire-wound furnace. Annealing times: 660°C (24h for <15% Sn, 10 min > 15% Sn); 600°C (24h for <15% Sn, 2 h > 15% Sn); 550°C (60h for <15% Sn, 24 h > 15% Sn); 300°C (120 h for <15% Sn, 12 h > 15% Sn). Metallography.	Determination of isopleths with constant contents of 1, 2 and 3 mass% P and from 0 to 25 mass% Sn. Determination of isopleths with constant content of 5, 10 and 20 mass% Sn from 0 to 5 mass% P. Determination of liquidus and solidus isotherms in the Cu rich region (<25 mass% Sn, <9 mass% P). Determination of partial isothermal sections in the Cu rich region (<25 mass% Sn, <9 mass% P) at 650, 600, 550, 300°C.

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1937Ham]	Alloys were melted from 99.9 min purity elements in graphite crucibles under argon and cast into mild steel molds. Chemical analyses, TA.	Determination of liquidus and solidus isotherms in the Cu rich region (< 35 mass% Sn, < 15 mass% P).
[1950Sho]	no details given on alloy preparation but chemical analyses on 7 standard refined grades of tin are given. Various copper contents < 0.129 mass% Cu. Cast cylinders of bronzes containing 0.1 mass% P, 0.5 mass% P.	Examination of the influence of Sn and P contents as well as the effect of casting on the hot-working capacity (including hot forging, hot extrusion and hot rolling) of phosphorized tin bronzes.
[1956Fre]	Various methods of casting and investigation techniques.	Study of the influence of basic composition, microstructure and impurities on the properties of copper tin bronzes. Control of metal and casting quality.
[1954Mur]	Alloys were melted from 99.9 Sn, electro Cu and Cu <sub>15</sub> P under argon and cast into green sand moulds molds at 1100°C and annealed for 24 h in vacuum. Above 550°C annealed in salt bath and quenched in ice-water. Chemical analyses, DTA, TA, metallography were employed.	Determination of isopleths with constant contents of 6 mass% Sn, 10 mass% Sn and from 0 to 4 mass% P. Determination of isopleths with constant content of 1 mass% P from 0 to 25 mass% Sn. Determination of the liquidus surface in the Cu rich region (<35 mass% Sn, <14 mass% P).
[1979Hoe] [1980Hoe]	Single crystals were obtained from a reaction of Cu, P in Sn-flux. The compound can also be obtained from elements in a sealed quartz tube (1000°C, 24 h). X-ray single crystal data, R=0.047.	Crystal structure of Cu <sub>4</sub> SnP <sub>10</sub> .
[1987Tak1] [1987Tak2]	Alloys were melted from 99.99 min purity elements in graphite crucibles under argon and cast into mild steel molds. Chemical analyses, DTA, EMPA, metallography and X-ray powder diffraction were employed.	Determination of isopleths with constant contents of 10 mass% Sn, 15 mass% Sn and from 0 to 8 mass% P. Determination of isopleths with constant content of 3, 5 and 7 mass% P from 0 to 15 mass% Sn. Determination of the liquidus surface in the Cu rich region (<25 mass% Sn, <10 mass% P). Determination of partial isothermal sections in the Cu rich region (<25 mass% Sn, <9 mass% P) at 650, 600, 550, 300°C.

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1999Zha]	Ball milling of elemental powder blends. Characterization by XPD and TEM.	Investigation of amorphous forming ability and determination of glass forming region in the system.
[2001Mie]	Calphad technique. Experimental data for the ternary refer only to phase relations published by [1987Tak1, 1987Tak2].	Thermodynamic description of the Cu rich corner up to 32 mass% Sn and 14 mass% P. Vertical sections were calculated for constant 10 and 15 mass% Sn (0 to 10 mass% P); and for 5, 7 mass% P (up to 20 mass% Sn). Partial isopleths in the Cu rich corner were calculated for 714, 678, 648, 644, 585, 519°C.

**Table 2:** Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\alpha$ , (Cu) < 1084.62	<i>cF4</i> <i>Fm<math>\bar{3}m</math></i> Cu	$a = 361.46$	0 to 3.5 at.% P [Mas2] 0 to 9.1 at.%Sn [Mas2] melting point [1994Sub]
(P)(I)	<i>cP1</i> <i>Pm<math>\bar{3}m</math></i> Po	$a = 237.7$ $a = 229$	high pressure phase, above ~10 GPa [V-C2]
(P)(II)	<i>hR6</i> <i>R<math>\bar{3}m</math></i> As	$a = 337.7$ $c = 880.6$	high pressure phase, 5 to 11.1 GPa [V-C2]
(P)(red) < 417	$c^*66$	$a = 1131$	Sublimation at 1 bar, triple point at 576°C, >36.3 bar; triple point at 589.6 at 1 atm [Mas2], [V-C2]
(P) (white)	$c^{**}$ ? P(white)	$a = 718$	at 25°C [Mas2]
(P) (black)	<i>oC8</i> <i>Cmca</i> P(black)	$a = 331.36$ $b = 1047.8$ $c = 437.63$	at 25°C [Mas2]
( $\gamma$ Sn)	<i>tI2</i> ? $\gamma$ Sn	$a = 370$ $c = 337$	at 25°C, 9.0 GPa [Mas2]
( $\beta$ Sn) 231.96 - 13	<i>tI4</i> <i>I4<math>_1</math>/amd</i> $\beta$ Sn	$a = 583.18$ $c = 318.18$	[Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
( $\alpha$ Sn) < 13	<i>cF8</i> <i>Fd<math>\bar{3}m</math></i> C(diamond)	$a = 648.92$	[Mas2]
$\beta$ Cu <sub>3</sub> P < 1022	<i>hP8</i> <i>P<math>\bar{3}m1</math></i> Cu <sub>3</sub> P	$a = 409.2$ $c = 718.6$	congruent melting at 1 bar, 25 to 31 at.% P [2002Per], at 560°C [V-C2]
$\alpha$ Cu <sub>3</sub> P	<i>hP24</i> <i>P6<sub>3</sub>cm</i> Cu <sub>3</sub> P	$a = 695.93$ $c = 714.3$	Low temperature phase, [2002Per]
CuP <sub>2</sub> < 891	<i>mP12</i> <i>P2<sub>1</sub>/c</i> CuP <sub>2</sub>	$a = 580.04$ $b = 480.63$ $c = 752.63$ $\beta = 112.70^\circ$	Congruent melting at 15.2 bar [2002Per]
Cu <sub>2</sub> P <sub>7</sub> < 850	<i>mC72</i> <i>C2/m</i> Cu <sub>2</sub> P <sub>7</sub>	$a = 1265.8$ $b = 725.6$ $c = 1463.0$ $\beta = 107.46^\circ$	[2002Per]
Sn <sub>4</sub> P <sub>3</sub> $\lesssim 559$	<i>hR21</i> <i>R<math>\bar{3}m</math></i> Bi <sub>3</sub> Se <sub>4</sub>	$a = 396.3 \pm 0.2$ $c = 3530 \pm 2$	[2002Wat]
Sn <sub>3</sub> P <sub>4</sub> $\sim 560$	<i>hR21</i> <i>R<math>\bar{3}m</math></i>	-	[2002Wat]
SnP <sub>3</sub>	<i>hR24</i> <i>R<math>\bar{3}m</math></i> SnP <sub>3</sub>	$a = 737.85 \pm 0.05$ $c = 1051.25 \pm 0.11$	[2002Wat]
SnP, metastable?	<i>hP12</i> <i>P<math>\bar{3}m1</math></i> CdI <sub>2</sub> -derivative	$a = 439.22 \pm 0.07$ $c = 604.0 \pm 0.3$	[2002Wat]
SnP, metastable?	<i>hP16</i> <i>P<math>\bar{3}m1</math></i> ?	$a = 878.0 \pm 0.1$ $c = 598.0 \pm 0.1$	[2002Wat]
SnP, metastable?	<i>cF8</i> <i>Fm<math>\bar{3}m</math></i> NaCl	$a = 553.59$	High pressure [2002Wat]
SnP, metastable?	<i>tI4</i> <i>I4mm</i> GeAs	$a = 383.1 \pm 0.1$ $c = 596.3 \pm 0.1$	High pressure [2002Wat]
Sn <sub>7</sub> P <sub>10</sub> , metastable	<i>h**</i>	$a = 443.30$ $c = 283.94$	[2002Wat]

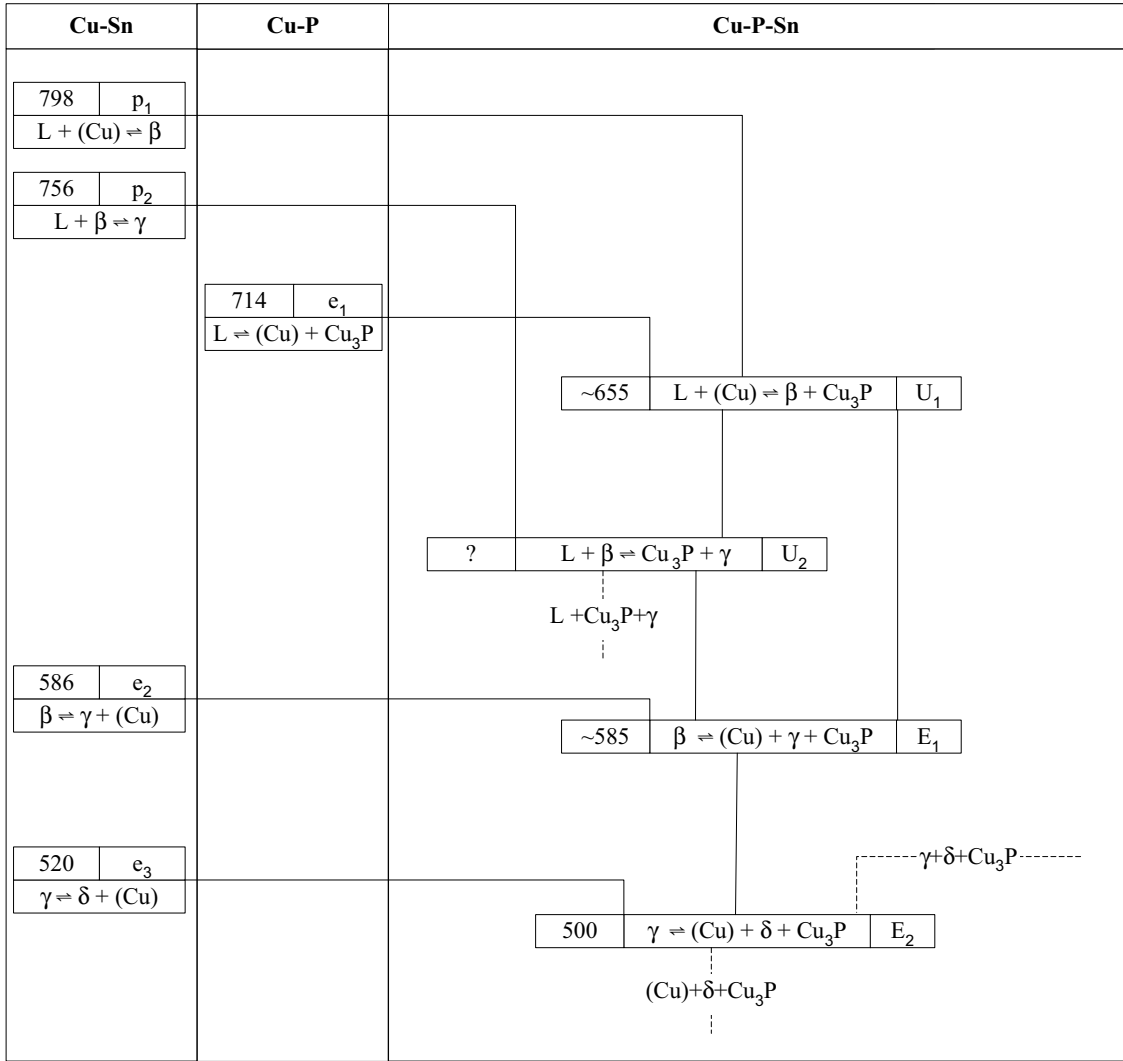


Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\beta$ , Cu <sub>17</sub> Sn <sub>3</sub> 798 - 586	<i>cF2</i> <i>Im<math>\bar{3}m</math></i> W	$a = 302.61$	13.1 to 16.5 at.% Sn [Mas2] at 710°C and 15 at.% Sn [V-C2]
$\gamma$ , Cu <sub>3</sub> Sn 755 - 520	<i>cF16</i> <i>Fm<math>\bar{3}m</math></i> BiF <sub>3</sub>	$a = 611.76$	15.5 to 27.5 at.% Sn [Mas2] at 710°C [V-C2]
$\delta$ , Cu <sub>41</sub> Sn <sub>11</sub> ~585 - 350	<i>cF416</i> <i>F<math>\bar{4}3m</math></i> Cu <sub>41</sub> Sn <sub>11</sub>	$a = 1798.0$	20 to 21 at.% Sn [Mas2, V-C2]
$\zeta$ , Cu <sub>10</sub> Sn <sub>3</sub> ~640 - 582	<i>hP26</i> <i>P6<sub>3</sub></i> Cu <sub>10</sub> Sn <sub>3</sub>	$a = 733.0$ $c = 786.4$	20.3 to 22.5 at.% Sn [Mas2, V-C2]
$\epsilon$ , Cu <sub>3</sub> Sn	<i>oC80</i> <i>Cmcm</i> Cu <sub>3</sub> Sn	$a = 552.9$ $b = 4775$ $c = 432.3$	24.5 to 25.9 at.% Sn [Mas2, V-C2]
$\eta$ , Cu <sub>6</sub> Sn <sub>5</sub> (h) 415 - 186	<i>hP4</i> <i>P6<sub>3</sub>/mmc</i> NiAs	$a = 419.2$ $c = 503.7$	43.5 to 45.5 at.% Sn [Mas2, V-C2]
$\eta'$ , Cu <sub>6</sub> Sn <sub>5</sub> (r) < 189	<i>hP*</i>	-	44.8 to 45.5 at.% Sn, ordered form with superlattice based on $\eta$ [Mas2]
Cu <sub>7</sub> Sn <sub>13</sub>	<i>hP2</i> <i>P<math>\bar{6}m2</math></i> WC	$a = 318.8$ $c = 297.6$	Metastable, rapidly quenched from the liquid phase [V-C2]
$\gamma'$ , ~Cu <sub>7</sub> Sn <sub>2</sub>	<i>hP8</i> Na <sub>3</sub> As	$a = 428.1$ $c = 784.2$	Metastable, martensitic form of quenched $\gamma$ [V-C2]. The $\gamma'$ martensite is found in two composition ranges between 15 and 25 at.% Sn [Mas2]
* $\tau_1$ , Cu <sub>4</sub> SnP <sub>10</sub>	<i>cF60</i> <i>F<math>\bar{4}3m</math></i> Cu <sub>4</sub> SnP <sub>10</sub>	$a = 1028.3$	[1979Hoe]

Two other forms of metastable martensite obtained from quenching the  $\beta$ , Cu<sub>17</sub>Sn<sub>3</sub> phase and a series of metastable phases quenched from the vapor phase are also reported [Mas2].

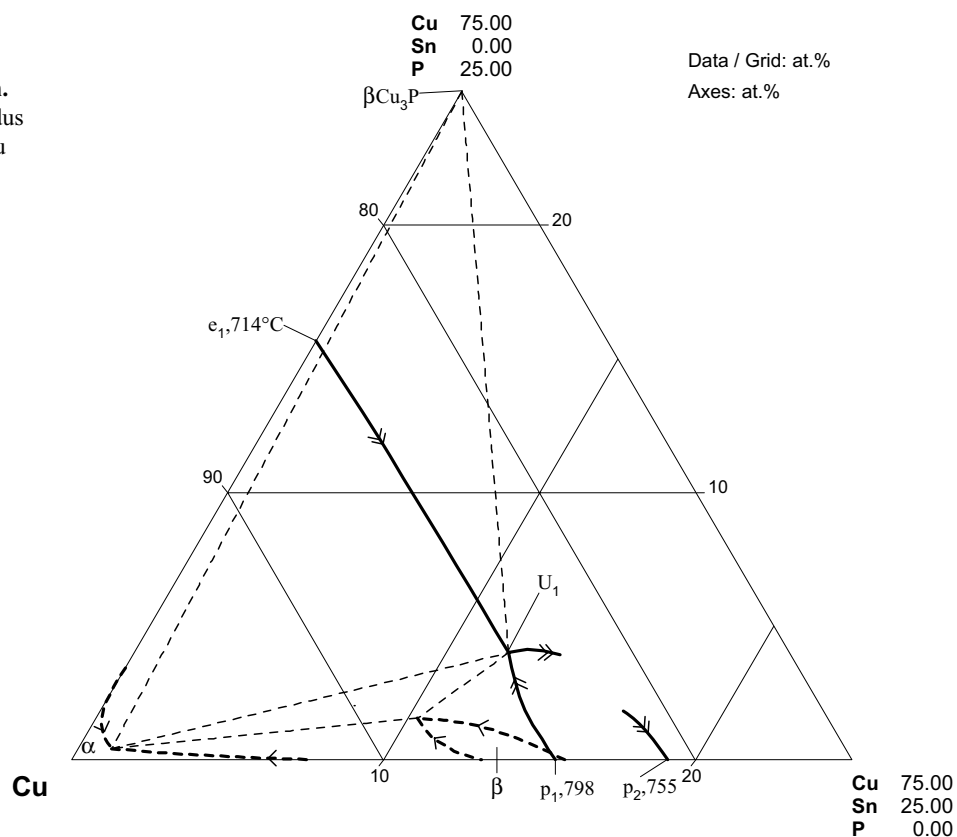
**Table 3:** Invariant Equilibria

Reaction	$T$ [°C]	Type	Phase	Composition (at.%)		
				Cu	Sn	P
$L + \alpha \rightleftharpoons \beta + \text{Cu}_3\text{P}$	642-655	$U_1$	L	84	12	4
			$\alpha$	98.51	1.08	0.41
			$\text{Cu}_3\text{P}$	75	0	25
			$\beta$	88.14	10.31	1.55
$L + \beta \rightleftharpoons \text{Cu}_3\text{P} + \gamma$	?	$U_2$	-	-	-	-
$\beta \rightleftharpoons \alpha + \text{Cu}_3\text{P} + \gamma$	587	$E_1$	$\beta$	84.05	14.12	15.15
$\gamma \rightleftharpoons \alpha + \text{Cu}_3\text{P} + \delta$	~510	$E_2$	-	-	-	-

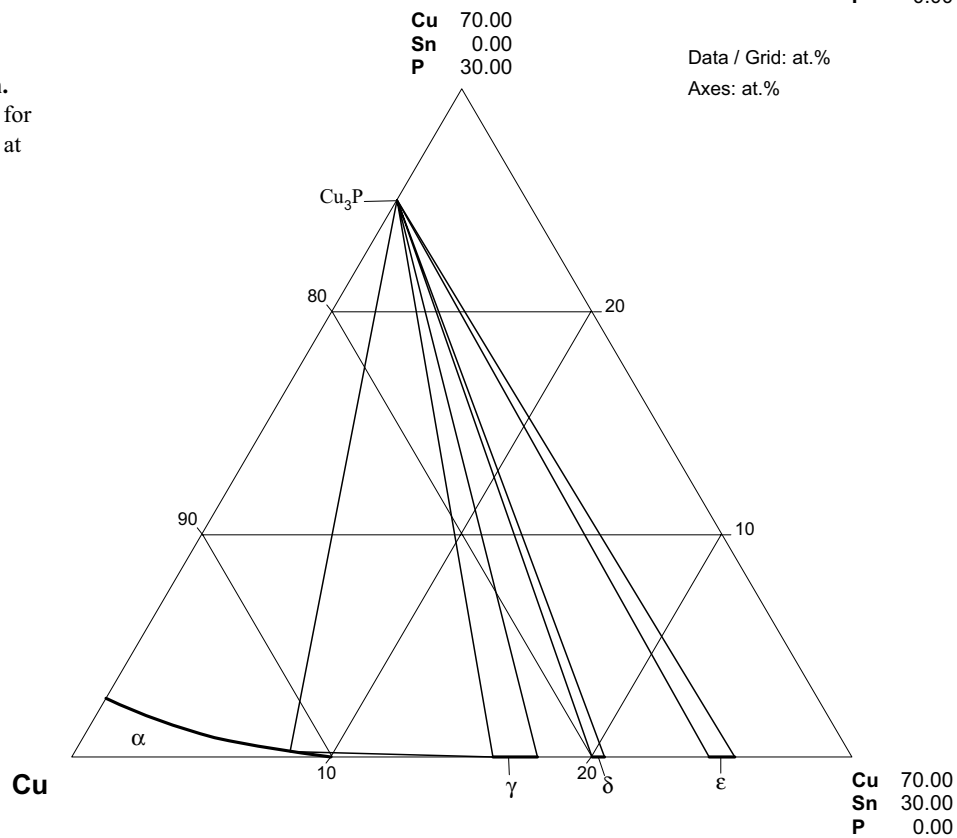


**Fig. 1:** Cu-P-Sn. Tentative reaction scheme for the Cu rich region

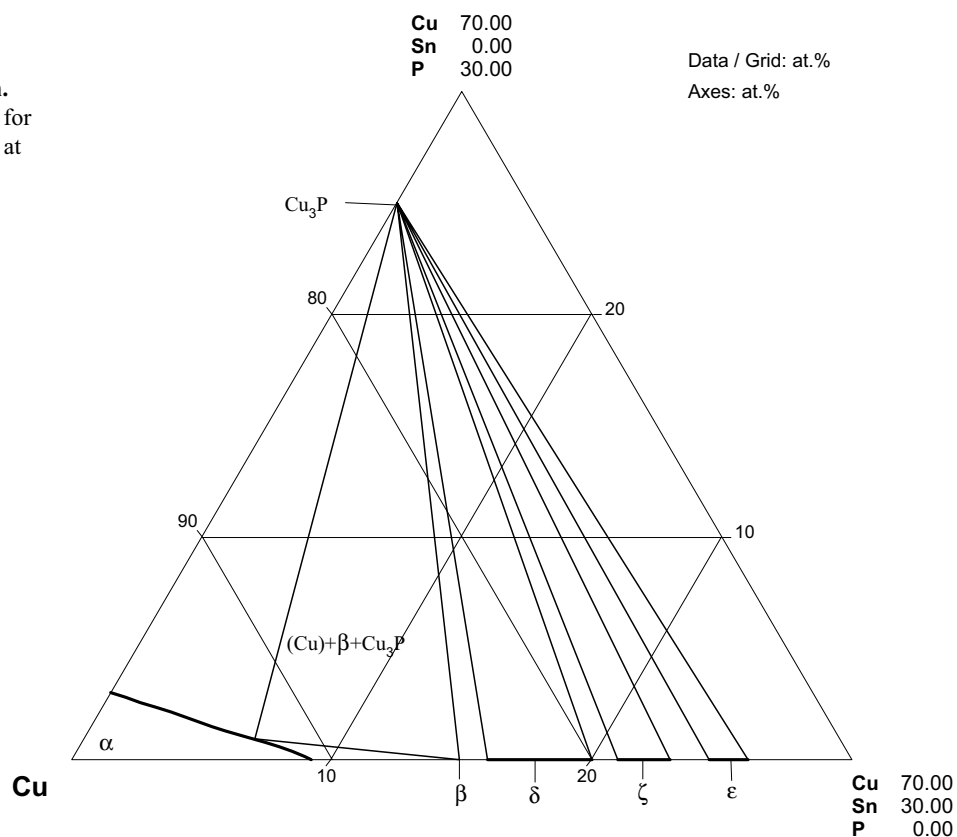
**Fig. 2: Cu-P-Sn.**  
Liquidus and solidus surfaces for the Cu rich region



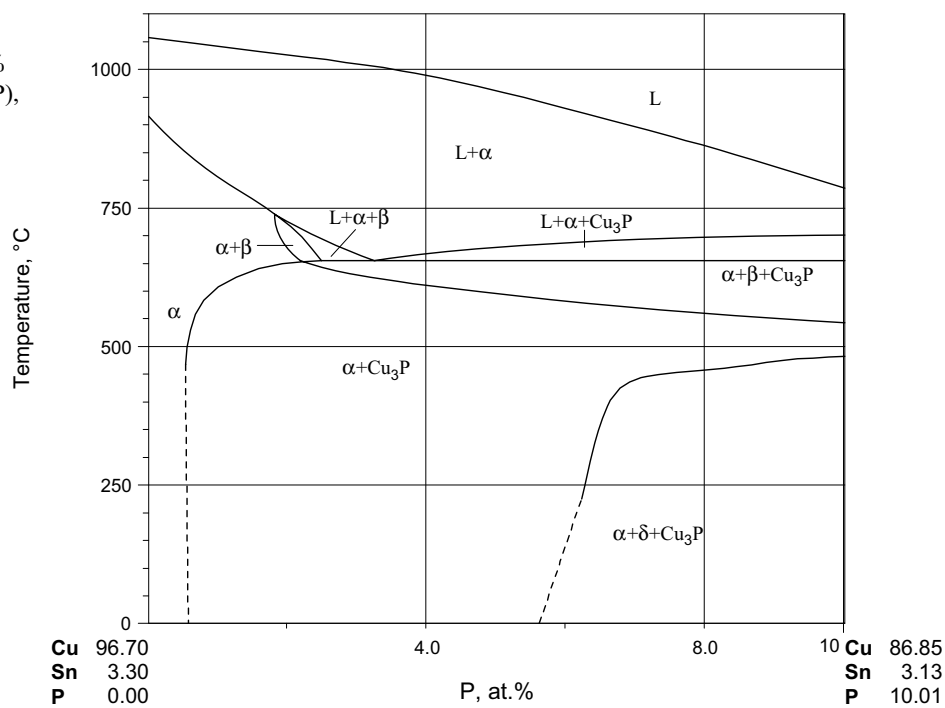
**Fig. 3: Cu-P-Sn.**  
Isothermal section for the Cu rich region at 550°C



**Fig. 4: Cu-P-Sn.**  
Isothermal section for  
the Cu rich region at  
600°C



**Fig. 5: Cu-P-Sn.**  
Isopleth at 6 mass%  
Sn (up to 5 mass% P),  
plotted in at.%



**Fig. 6: Cu-P-Sn.**  
Isopleth at 10 mass%  
Sn (up to 5 mass% P),  
plotted in at.%

