Copper – Nickel – Tin

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Introduction

The phase stability and phase equilibria of the Cu-Ni-Sn system are of significant scientific and technological interests due to following reasons: (i) the occurrence of spinodal decomposition followed by precipitation of ordered phases in Cu rich alloys [1974Sch1, 1974Sch2, 1979Bab, 1980Dit, 1983Mik1, 1984Mik1, 1986Kat, 1987Kra, 1988Sat, 1990Gou, 1994Zha, 1996Oel, 1998Zha1, 1998Zha2], (ii) the occurrence of discontinuous precipitation in Cu- and Ni rich alloys [1982Mik, 1983Mik2, 1984Mik2, 1990Mik, 1991Mik, 1994Mik], (iii) the occurrence of massive and martensitic transformations in γ_1-$(Ni,Cu)_3Sn$ alloys [1981Wat, 1983Mur, 1989Pak, 1990Pak, 1996Oel], (iv) there is a need to design and process Cu rich alloys with high-strength and high-conductivity properties for electrical components and electronic packaging [1982Sak, 1982Ste, 1986Zie], and (v) the usage of lead-free solders [2002Kat, 2002Lin, 2002Zen, 2003Che1] for electronic packaging. As a result, a large number of experimental studies have been carried out to determine the phase equilibria, and the results have been reviewed several times [1936Hum, 1948Ray, 1949Jae, 1969Gue, 1973Lev, 1979Cha, 1979Dri, 1988Gup, 2000Gup].

A summary of experimental studies of phase equilibria is given in Table 1. In earlier investigations [1928Pri, 1932Gui, 1932Ves, 1933Eas], the primarily interest was the solubilities of Ni and Sn in (Cu). A large number of alloys and a variety of experimental techniques, such as hardness [1928Pri, 1932Gui, 1932Ves], metallography [1928Pri, 1932Gui, 1932Ves, 1933Eas], X-ray diffraction (XRD) [1933Eas] and thermal analysis [1932Ves, 1933Eas] were employed to establish the solubility limits in (Cu). [1932Ves] prepared 61 ternary alloys using elements of following purity: 99.93% Cu, Mond's Ni (containing 0.21% Fe, 0.05% Cu, 0.27% C) and 99.96% Sn. They reported six vertical sections and three partial isothermal sections. [1933Eas] prepared 92 ternary alloys using 99.96% Cu, but the purities of Ni and Sn were not mentioned. They [1933Eas] reported five vertical sections and five partial isothermal sections. The results of [1932Ves] and [1933Eas] show a good agreement with each other.

[1940Glu] investigated the interfacial microstructure in diffusion couples made of Cu-Ni alloys and liquid Sn that were reacted at 630°C for up to 8 h. They observed Cu-Sn and Ni-Sn intermetallics in all diffusion couples. Mazzoleni [1953Maz1, 1953Maz2] carried out structural investigation of several ternary alloys, in the composition range of 6 to 38.5 at.% Ni and 36.1 to 58.7 at.% Sn, by XRD. While many of these alloys were found to have NiAs-type structure, presence of a Heusler phase ($NiCu_2Sn$) was also established.

[1971Bas] reinvestigated the phase equilibria of Cu corner, and reported the partitioning ratio of Ni and Sn between (Cu) and liquid, the liquidus and solidus isotherms, six vertical sections and four partial isothermal isothermal sections. They prepared a large number of ternary alloys using 99.994% Cu, 99.95% Ni and 99.99% Sn. The alloys were equilibrated at various temperatures, but in a solid-liquid two-phase field, and quenched in iced water. The partitioning ratio of Ni and Sn, and the tie lines between (Cu) and liquid phases were measured by electron-probe microanalysis (EPMA). [1984Wac] carried out magnetothermal analysis of Cu- and Ni rich alloys, and reported a partial liquidus surface, a partial isothermal section, and the Cu_3Sn-Ni_3Sn isopleth.

The phase equilibria of $Cu_xNi_{75-x}Sn_{25}$ alloys, with $0 \le x \le 30$, have been studied extensively [1981Wat, 1989Pak, 1990Pak, 1996Oel, 1996Rud] using XRD, transmission electron microscopy (TEM), analytical electron microscopy (AEM), and differential thermal analysis (DTA). The vertical section along Ni_2Cu-$(Ni_2Cu)_{1-x}Sn_x$ section was investigated by [1995Bur] to determine the liquidus and solidus using DTA, while the solvus was determined using resistivity and XRD [1996Spr] and magnetometry [1997Spr]. Recently, Chen and co-workers [2002Lin, 2003Wan] have determined the phase equilibria using XRD, DTA and EPMA. They reported the liquidus surface [2002Lin], and isothermal sections at 800 [2003Wan], 240 [2002Lin] and 200°C [2003Che1]. [2002Lin] prepared 28 ternary alloys, containing up to 80 at.% Cu and 75 at.% Ni, by arc melting in an argon atmosphere using 99.98% Cu, 99.98% Ni and 99.95% Sn. After arc melting, the alloys were annealed at 300°C for 336 h and then at 240°C for 1695 h in a vacuum of 8 ·

10^{-3} torr. The isothermal section at 240°C was constructed based on the results of EPMA and XRD. To establish the liquidus surface, heating/cooling experiments were carried out at 5°C·min^{-1}. [2003Wan] prepared 54 ternary alloys by arc melting followed by annealing at 800°C for 30 d. They also prepared three types of diffusion couples, Sn-55 at.% Cu / Ni, Sn-65 at.% Cu / Ni and Sn-75 at.% Cu / Ni, that were reacted at 800°C for up to 20 min. The isothermal section at 800°C was constructed based on the composition analysis of phases by EPMA in bulk samples, and also in diffusion couples. [2003Che1] reported an isothermal section at 200°C based on the observed phases in diffusion couples. [2005Li] determined the phase relations of Sn corner at 240°C, with an emphasis on the phase equilibria involving (Sn), Cu_6Sn_5 and Ni_3Sn_4.
More recently, [2005Li, 2006Li] reinvestigated the phase relations of Sn corner at 240°C, with an emphasis on the phase equilibria involving (Sn), Cu_6Sn_5 and Ni_3Sn_4. They prepared nine alloys, containing 10-25 at.% Cu and 10-30 at.% Ni, by arc melting in an argon atmosphere. Elements of following purity were used: 99.9% Cu, 99.99% Ni, and 99.999% Sn. The alloys were sealed in evacuated quartz tubes and heat treated at 240°C between 1222 to 1700 h. The phases were characterized by XRD and EPMA.
The heat of mixing of liquid alloys was measured by [1979Poo1] and [2004Lue], and the atomic transport kinetics of Ni and Sn in (Cu) was determined by [1972Bas] and [1986Tak]. Thermodynamic modeling of phase equilibria within CALPHAD formalism was reported by [2003Mie].

Binary Systems

The Cu-Ni binary system is accepted from [2002Leb]. The Cu-Sn binary system is accepted from the assessment of [1990Sau] which was later supplemented by thermodynamic modelling [1996Shi, 2000Moo, 2004Liu1] within CALPHAD formalism. In the assessment [1990Sau] and thermodynamic modelling [1996Shi, 2000Moo] of Cu-Sn system, the β_1/γ_1 phase relation is treated as a first-order phase transformation. In contrast, [2004Liu1] reported that a two-stage ordering transition $\beta_1 \rightarrow B2$ (CsCl type) $\rightarrow \gamma_1$ takes place in Cu rich alloys. They used diffusion couples in conjunction with high-temperature electron and X-ray diffraction techniques to study the two-stage ordering transitions. However, in the thermodynamic modelling of Cu-Sn system, [2004Liu1] did not consider the γ_1 phase. Since the two-stage ordering transition is yet to be verified by others, in this assessment the β_1/γ_1 phase relation is treated as a first-order phase transformation. The η phase of Cu-Sn system is believed to be isotypic with $B8_1$-NiAs phase [1990Sau]; however, X-ray and electron diffraction studies have shown that both η and η' phases have monoclinic symmetry [1994Lar, 1995Lar]. The Ni-Sn binary system is accepted from [1985Nas] along with the thermodynamic modeling of [1999Gho, 2004Liu2].

Solid Phases

The addition of Ni at a constant Sn content in Cu rich γ solid solutions decreases lattice parameter while that of Sn at a constant Ni content increases lattice parameter [1995Pal].
The formation of two transient ordered phases, $D0_{22}$ [1977Hel, 1979Bab, 1980Dit, 1983Mik1, 1984Kra, 1984Mik1, 1987Kra, 1994Zha, 1998Zha1, 1998Zha2] and $L1_2$ [1982Ray, 1983Mik1, 1994Zha, 1998Zha1], during aging of supersaturated solid solution is well established. An important fundamental issue that has been debated is whether chemical ordering, leading to $D0_{22}$ and/or $L1_2$ phases, precedes spinodal decomposition. Extensive and systematic transmission electron microscopy study [1998Zha1] showed that spinodal decomposition takes place prior to chemical ordering in a Cu-15Ni-8Sn (mass%) alloy. [1998Zha1] also showed that following spinodal decomposition, $D0_{22}$ ordering takes place prior to $L1_2$ ordering, and both $L1_2$ and $D0_{22}$ may co-exist in a Cu-15Ni-8Sn (mass%) alloy. However, only $L1_2$ phase has also been observed in a Cu-9Ni-6Sn (mass%) alloy aged at 350°C [1982Ray], and in a Cu-20Ni-8Sn (mass%) alloy aged at 400°C [1983Mik1, 1984Mik1] and only $D0_{22}$ phase has been observed after aging at 450°C [1983Mik1, 1984Mik1]. All these results suggest that the formation sequence and co-existence of $L1_2$ and $D0_{22}$ phases depend on both the alloy composition and aging temperature.
γ_1-Cu_3Sn dissolves substantial amount (up to 30 at.% Ni) of Ni [1937Rah, 1984Wac]. Dissolution of Ni in δ-$Cu_{41}Sn_{11}$ phase increases its thermal stability [1953Maz2, 1977Boo] and lattice parameter [1977Boo]. In

both studies, $NiCu_9Sn_3$ alloy was quenched from 800°C yet its structure is found to be the same as δ-$Cu_{41}Sn_{11}$.
Experimental studies show that γ_1-Ni_3Sn ($D0_3$) dissolves at least 25 at.% Cu above 977°C [1932Ves, 1981Wat, 1984Wac, 1989Pak, 1990Pak, 1996Oel]. Dissolution of Cu in γ_1-Ni_3Sn enhances its thermal stability to temperatures well below the binary limit [1981Wat, 1989Pak, 1990Pak, 1996Oel], and also causes a decrease in lattice parameter [1981Wat]. At 600°C, γ_2-Ni_3Sn ($D0_{19}$) dissolves about 5 at.% Cu with an increase of both *a*- and *c*-lattice constants [1981Wat]. Ni_3Sn_2 dissolves about 24 at.% Cu at 240°C [2002Lin] and 30 at.% Cu at 800°C [2003Wan].
In the temperature range of 125 to 240°C, Ni_3Sn_4 dissolves up to 7 at.% Cu [2001Che, 2001Gho, 2002Lin, 2003Che1, 2004Gho], while other studies report slightly higher values of 9 at.% at 240°C [2005Li, 2006Hsi, 2006Li], 9.4 at.% at 245°C [2005Jan], and 10.28 at.% at 265°C [2004Jan, 2005Jan]. In the temperature range of 125 to 240°C, Cu_6Sn_5 dissolves about 24 at.% Ni [2001Gho, 2002Lin, 2003Che1, 2004Gho, 2005Li, 2006Hsi, 2006Li]. At 265°C, Cu_6Sn_5 may dissolve up to 26.2 at.% Ni [2005Jan].
Three ternary phases, τ_1, τ_2 and τ_3, have been reported. The Heusler phase $NiCu_2Sn$ (τ_1) was first reported by [1953Maz2], and subsequently confirmed by [1979Sch, 1984Wac]. However, a detailed study of $NiCu_2Sn$ using DTA, X-ray diffraction and resistivity techniques show that the $L2_1$ structure is stable between 500 and 700°C [1979Sch]. It has been reported that between 245 and 400°C, the Heusler phase (τ_1) decomposes into two hcp structures (hcp1: a = 412 pm, c = 1260 pm; hcp2: a = 414 pm, c = 1240 pm) and an fcc structure (a = 363 pm) [1979Sch]. The Ni_2CuSn alloy was also suspected to be a Heusler phase; however, Mössbauer spectrum (^{119}Sn) shows an unusual splitting that is inconsistent with the cubic symmetry. This splitting is explained on the assumption of disordering in Ni and Sn sublattices, so that it is effectively a $D0_3$ structure [1971Dok]. Furthermore, transmission electron microscopy and X-ray diffraction investigations [1989Pak, 1990Pak] failed to make a distinction between $D0_3$ and $L2_1$ structures in Ni_2CuSn.
The ternary phase τ_2 ($Ni_{5-x}Cu_xSn_2$) with $0.8 \le x \le 1.41$), isotypic with β-Cu_3Ti, was first reported by [1981Wat], and subsequently confirmed by others [1983Mur, 1984Mik1, 1989Pak, 1990Pak, 1996Oel, 1996Rud]. The stability of this phase clearly underscores the influence of Cu, as the binary Ni_3Sn phase with β-Cu_3Ti structure is metastable [1973Pak].
Massive [1981Wat, 1983Mur] and martensitic transformations [1981Wat, 1983Mur, 1989Pak, 1990Pak, 1996Oel] in $Cu_xNi_{75-x}Sn_{25}$ alloys with $0 \le x \le 30$ have been studied by a variety of techniques, such as optical metallography, DTA, XRD and TEM. Slow cooling leads to massive (γ_1 ($D0_3$) → τ_2 (2H)) while fast cooling leads to martensitic (γ_1 ($D0_3$) → τ_2 (2H)) transformation [1983Mur]. Upon furnace cooling of alloys containing 11 to 22 at.% Cu from 1000°C, [1990Pak] reported another martensitic transformation γ_1 ($D0_3$) → τ_3 (triclinic) where the product phase may be considered as a distorted structure of τ_2.
The crystallographic details of all solid phases are listed in Table 2.

Invariant Equilibria

A partial reaction scheme of the system, shown in Fig. 1, is based on the results of [1984Wac] and [2002Lin]. While [1984Wac] reported the liquidus surface of Cu- and Ni rich alloys, [2002Lin] determined the liquidus surface of entire system by means of differential thermal analysis and microstructure characterization of 28 ternary alloys. Five U type transitional invariant reactions have been reported. Among these, U_1 was first proposed by [1971Bas] and subsequently confirmed by [1984Wac] and [2002Lin]. The presence of U_2 was reported by [1984Wac] and subsequently confirmed by [2002Lin]. The invariant reaction U_4 was postulated by [1988Gup], but labelled as U_3. In Fig. 1, the temperature of invariant reactions are only approximate, and they are estimated based on the liquidus data of [2002Lin] and the participating binary invariant reactions. The composition of liquid participating in invariant reactions is listed in Table 3; however, the composition of the solid phases are not known.

Liquidus, Solidus and Solvus Surfaces

Figure 2 shows the liquidus surface of the ternary system adopted from [1984Wac, 2002Lin]. There are eight regions of primary crystallization. The locus of monovariant line e_2-U_1-p_1-p_3 and the superimposed

isotherms are taken from [1984Wac]. [1971Bas] also reported liquidus isotherms, but only for Cu rich alloys containing up to 7 mass% Ni and 14 mass% Sn. [1984Wac] was the first to report the presence of invariant reaction U_2; however, the primary crystallization field of ε-Cu_3Sn in [1984Wac] is much smaller compared to [2002Lin]. The Ni content of liquid phase of the invariant reaction U_2 is about 13.3 at.% [2002Lin] compared to 2.2 at.% reported by [1984Wac]. [2002Lin] observed ε-Cu_3Sn as the primary crystallization product in Cu-10Ni-40Sn (at.%) and Cu-10Ni-45Sn (at.%) alloys.
[1971Bas] reported solidus isotherms, but only for Cu rich alloys containing up to 10 mass% Ni and 3 mass% Sn. [1975Ple] determined the solidus and spinodal temperatures of Cu rich alloys by measuring resistivity, and their data are presented in Table 4. It is not known if the spinodal temperature refers to chemical spinodal or coherent spinodal.

Isothermal Sections

Figures 3, 4 and 5 show isothermal sections of Cu corner at 1090, 1050 and 1025°C, along with the tie lines between γ and liquid phase [1971Bas]. Figure 6 shows the isothermal section at 800°C [2003Wan]. [2003Mie] calculated the isothermal section of Cu corner at 800°C by CALPHAD method by treating γ_1-$(Ni,Cu)_3Sn$ as a solution phase and γ_2-$(Ni,Cu)_3Sn$ as an ordered phase. An important difference between experimental [2003Wan] and calculated [2003Mie] isothermal sections is the presence of phase fields involving β_1 that extends up to the Cu-Sn binary edge. However, in the corresponding accepted binary phase diagram the β_1 phase is stable only below 798°C. In the Cu corner, experimental phase diagram shows the presence of a three-phase field (L+γ+γ_1-$(Ni,Cu)_3Sn$) while the calculated phase diagram shows the presence of two three-phase fields (L+β_1+γ_1-$(Ni,Cu)_3Sn$ and γ+β_1+γ_1-$(Ni,Cu)_3Sn$). Therefore, it is necessary that the three-phase field L+β_1+γ_1-$(Ni,Cu)_3Sn$ originates at a temperature higher than 800°C. However, the reaction scheme, which is drawn on the basis of the liquidus surface (Fig. 2), is inconsistent with this three-phase field. This implies that there must be, yet undetected by thermal analysis, a liquidus maxima/minima and/or an invariant reaction involving β_1 phase occurring at a temperature higher than 800°C. Also, the thermodynamic stability of β_1 and γ_1-$(Ni,Cu)_3Sn$ phases must be enhanced in the presence of Ni.
Figure 7 shows experimentally determined isothermal section of Cu corner at 700°C [1971Bas]. [2003Mie] calculated the partial isothermal section by CALPHAD method and obtained a good agreement with the experimental data. It is to be noted that the reaction scheme in Fig. 1 is consistent with the presence of a γ+β_1+γ_1-$(Ni,Cu)_3Sn$ three-phase field at 700°C.
Figure 8 shows experimentally determined partial isothermal section at 550°C. Miki and co-workers [1983Mik1, 1984Mik1] were the first to report the partial isothermal section, and their results were subsequently verified by [1996Oel]. Extensive transmission and analytical electron microscopy results show that the Cu contents of γ phase in the tie-triangles γ+τ_2+γ_2-Ni_3Sn and γ+τ_2+γ_1-$(Ni,Cu)_3Sn$ are higher than that reported by [1983Mik1, 1984Mik1]. Accordingly, the results of [1996Oel] are accepted here. Also, in constructing Fig. 8 the homogeneity range of τ_2 is taken from [1989Pak]. [2003Mie] calculated the partial isothermal section by CALPHAD method. In addition to the above three-phase fields, the calculated diagram shows the presence of a three-phase field, δ+ε-Cu_3Sn+γ_1-$(Ni,Cu)_3Sn$, which is yet to be experimentally verified.
Figures 9 and 10 show the isothermal sections at 240 [2002Lin, 2005Li] and 200°C [2003Che1], respectively. The only difference in phase fields of these two isothermal sections is that in Sn corner the liquid phase at 240°C is replaced by (βSn) at 200°C. The three-phase fields involving the ternary phase τ_2 have not been determined experimentally, therefore, they are shown as dashed. Also, in these recent studies [2002Lin, 2003Che1, 2005Li] the τ_3 phase has not been identified, even though in earlier studies it was reported to be stable below 460°C [1989Pak, 1990Pak].
[1984Wac] reported a partial isothermal section at 647°C; however, as discussed below, their results are inconsistent with subsequent results. Consequently, the results of [1984Wac] are not accepted here.

Temperature – Composition Sections

Experimental determination of vertical sections is summarized as follows: at 2, 4, 7, 10, 15 and 25 mass% Ni [1932Ves]; at 2, 3, 5, 10 and 20 mass% Ni [1933Eas]; along $Ni_{75}Sn_{25}$-$Cu_{30}Ni_{45}Sn_{25}$ [1981Wat]; along Cu_3Sn-Ni_3Sn [1984Wac]; along $Ni_{75}Sn_{25}$-$Cu_{22}Ni_{53}Sn_{25}$ [1989Pak, 1990Pak]; at 14 at.% Ni [1990Che]; along $Cu_{33.3}Ni_{66.7}$-$Cu_{25}Ni_{50}Sn_{25}$ [1995Bur, 1995Kra]; along $Cu_{40}Ni_{60}$-$Cu_{28}Ni_{42}Sn_{30}$ and $Ni_{75}Sn_{25}$-$Cu_{35}Ni_{40}Sn_{25}$ [1996Oel]. Besides, [2003Mie] calculated several vertical sections by CALPHAD method. Using the results of [1928Pri, 1932Ves, 1933Eas, 1971Bas], the vertical sections at 15 mass% Ni [1998Zha1] and 7.5 mass% Ni [1998Zha2] were reconstructed.

The experimental and calculated vertical section at 2 mass% Ni are compared in Fig. 11 [1932Ves] and Fig. 12 [2003Mie], respectively. Similarly, the experimental and calculated vertical section at 4 mass% Ni are compared in Fig. 13 [1932Ves] and Fig. 14 [2003Mie], respectively. In both cases, the calculated vertical sections show a good agreement with the experimental ones with respect to liquidus, solidus and solvus boundaries. Figures 15 and 16 show the vertical sections at 7 and 10 mass% Ni [1932Ves], respectively. Figure 17 shows the vertical section at 14 at.% Ni [1990Che]. The experimental and calculated vertical section at 15 mass% Ni are compared in Fig. 18 [1932Ves] and 19 [2003Mie], respectively, show only a modest agreement for the solidus and solvus boundaries.

The experimental and calculated vertical section along Cu_3Sn-Ni_3Sn are compared in Fig. 20 [1989Pak, 1990Pak] and Fig. 21 [2003Mie], respectively. Along this section, the phase equilibria of Ni rich alloys containing up to 30 at.% Cu are well documented due to several comprehensive studies [1981Wat, 1989Pak, 1990Pak, 1996Oel]. However, the phase equilibria on Cu rich alloys reported by [1984Wac] remain doubtful and warrant further experimental investigation. Besides the corrections made by [2000Gup], a major discrepancy between the results of [1984Wac] and others is the presence of ζ+η-Cu_6Sn_5, γ+ζ+η-Cu_6Sn_5, γ+η-Cu_6Sn_5, γ+γ_1-$(Ni,Cu)_3Sn$+η-Cu_6Sn_5 phase fields at low temperatures. In the phase equilibria studies using bulk samples and diffusion couples at 240 [2002Lin] and 200°C [2003Che1], these phase fields were not observed. Therefore, the solid-state equilibria below 550°C along Cu_3Sn-Ni_3Sn section reported by [1984Wac] are not accepted here. In the calculated vertical section, Fig. 21, the solubility of Cu in γ_2-Ni_3Sn is not reproduced and the ternary phase τ_2 is treated as line compound. Also, the calculated solubility of Sn in γ (~5 at.%) is much lower than the experimental value of 9 at.% [1996Spr].

The experimental and calculated vertical section at a constant ratio x_{Cu}/x_{Ni} of 1:2 are compared in Fig. 22 [1995Bur, 1996Spr, 1997Spr] and Fig. 23 [2003Mie], respectively. [1995Bur] reported only the liquidus and the solidus boundaries. In subsequent investigations, the solvus boundary was determined using resistivity, magnetometry and XRD [1996Spr, 1997Spr]. At 800 and 660°C, the solvus boundary is located at 9 [1996Spr] and 7 at.% Sn [1997Spr], respectively. The presence of L+γ+γ_1 and L+γ_1 phase fields were not mentioned by [1995Bur], but proposed by [2000Gup] and verified by CALPHAD modelling [2003Mie].

Thermodynamics

The heat of mixing of liquid alloys was measured by SETARAM high-temperature calorimeter at 1307°C [1979Poo1] and 1250°C [2004Lue]. [1979Poo1] measured heat of mixing of 163 compositions, of which 119 lie along eleven sections at a constant ratio of x_{Cu}:x_{Sn} (1:9, 1:2, 3:2, 5:1, 1:5, 2:3, 2:1, 9:1, 1:3, 1:1, 3:1), 33 lie along three sections at a constant ratio of x_{Ni}:x_{Sn} (1:1, 3:1, 1:3), and 11 lie along the section at a constant ratio of x_{Cu}:x_{Ni} (3:1). [2004Lue] carried out 90 measurements along three sections at a constant ratio of x_{Cu}:x_{Ni} (1:3, 1:1, 3:1). Figures 24 and 25 show the isoenthalpy (mixing) contours at 1307°C [1979Poo1] and 1250°C [2004Lue], respectively.

The composition dependence of integral enthalpy of mixing of liquid alloys has been modelled using a variety of analytical functions with [1979Poo2, 1984Hoc1, 1984Hoc2, 1995Tom, 2003Mie, 2004Lue] and without [1987Hoc, 1996Heu] ternary interaction parameter(s). It is found that in order to obtain a satisfactory fit of the experimental data by analytical functions, it is necessary to introduce ternary interaction parameter(s). This is attributed to strong asymmetry of the composition dependence of enthalpy of mixing in Cu-Sn and Ni-Sn systems, and also due to strong ternary interaction between Cu, Ni and Sn atoms in the liquid phase. [1979Poo2] used a modified quasi-chemical model containing one ternary

interaction parameter, [1995Tom] employed "Thermodynamic Adapted Power" (TAP)-series with one ternary interaction parameter, and [2003Mie, 2004Lue] used Redlich-Kister-Muggianu polynomial containing three ternary interaction parameters to fit experimental data of enthalpy of mixing of liquid alloys.

[2003Mie] carried out a thermodynamic assessment of the ternary system by the CALPHAD method, and demonstrated the fidelity of thermodynamic models by calculating phase equilibria up to 70 at.% Ni and 25 at.% Sn which agree very well with the experimental data. [2003Mie] treated $(Ni,Cu)_3Sn(h)$ (γ_1) as a solid solution phase, $(Ni,Cu)_3Sn(r)$ (γ_2) as an ordered intermetallic, and considered ternary interaction parameters in liquid, bcc, fcc and $(Ni,Cu)_3Sn(h)$ phases. The ternary phase τ_2 was represented as $Cu_3Ni_{27}Sn_{10}$ instead of Ni_5CuSn_2. The calculated liquidus and solidus isotherms, partial isothermal sections at 800, 700 and 550°C, and isopleths at 2, 4, 15 mass% Ni, 25 at.% Sn, and at a constant ratio x_{Cu}:x_{Ni} of 1:2 as well as the calculated enthalpies of mixing at 1580 K were presented.

[2005Wan] calculated metastable miscibility gaps in the fcc phase along $Cu_{1-w}Sn_w$-$Ni_{1-w}Sn_w$ sections with Sn contents of 2.3, 4, 6 and 8 mass%.

Notes on Materials Properties and Applications

A summary of experimental investigation of properties is given in Table 5. The mechanical and electrical properties of Cu rich alloys have been studied extensively due to their combined properties of high-strength, high-conductivity and resistance to stress relaxation up to 250°C [1978Ger, 1984Sco, 1991And, 1996Leh, 1997Vir1]. Due to these properties, Cu rich ternary alloys find numerous applications as electrical and electronic interconnection material. There is a large body of mechanical properties data (hardness, Young's modulus, yield stress, ultimate tensile stress, ductility, stress relaxation and fracture behavior) [1928Pri, 1932Gui, 1974Sch1, 1974Sch2, 1975Ple, 1978Ger, 1978Lef, 1984Kra, 1984Sco, 1986Kat, 1986Kha, 1987Kra, 1989Kra, 1990Dey, 1991Abd, 1991And, 1992Bog, 1992Hun, 1994Her, 1994Mik, 1996Leh, 1997Her, 1997Vir1, 1997Vir2, 1999Jun, 1999Mor] and electrical properties [1975Ple, 1984Sco, 1996Leh, 1997Vir2, 1999Jun, 1999Mor]. It has been demonstrated that by controlling thermomechanical processing Cu rich alloys with strength up to 1.4 GPa can be developed. [2004Li] obtained the bulk modulus of Ni_2CuSn by means of an empirical relationship.

[1992Kra] measured the steady state creep rates of Ni_2CuSn in the temperature range of 600 to 900°C. Analysis of their data gives an activation energy of 229.3 $kJ \cdot mol^{-1}$ and a stress exponent of 3.9.

[2003Che2] determined tensile properties of Ni/Sn-0.7 mass% Cu/Ni solder joints after aging at 200°C for up to 240 h. Solid state aging causes growth of Cu_6Sn_5 and Ni_3Sn_4 intermetallics at the solder/substrate interface which degrade the tensile properties of solder joints.

Miscellaneous

The decomposition of Cu rich γ solid solutions, containing up to 15 mass% Ni and 13 mass% Sn and in the temperature range of 150 to 850°C, has been studied extensively. For a given alloy, the mechanism of decomposition is strongly related to the aging temperature, and at least six types of decomposition processes have been identified [1998Zha1]: (i) grain boundary and intergranular precipitation of γ_1 phase, (ii) cellular or discontinuous precipitation of γ_1 phase, (iii) precipitation of metastable $D0_{22}$ ($(Ni_{1-x}Cu_x)_3Sn$) phase, (iv) precipitation of metastable $L1_2$ ($(Ni_{1-x}Cu_x)_3Sn$) phase, (v) spinodal decomposition, and (vi) precipitation of a ternary phase (τ_2). Among these, spinodal decomposition [1974Sch1, 1974Sch2, 1975Ple, 1977Hel, 1978Ger, 1978Hel, 1978Lef, 1979Bab, 1980Dit, 1980Ray, 1982Ray, 1984Kra, 1984Sco, 1985Nar, 1986Kat, 1986Kha, 1987Kra, 1988Col, 1988Sat, 1990Dey, 1990Gou, 1991Abd, 1992Hun, 1993Sat, 1994Her, 1994Zha, 1995Pal, 1999Kim, 1998Zha1, 1998Zha2, 1999Jun, 1999Rhu, 2004Sah], and cellular or discontinuous precipitation [1982Mik, 1983Mik1, 1983Mik2, 1984Mik1, 1984Mik2, 1990Mik, 1991Mik, 1994Mik, 1998Vir, 2004Lou] processes have received most attention. [1998Zha1] provided the time-temperature-transformation (TTT) curves of all decomposition processes in a Cu-15Ni-8Sn (mass%) alloy.

Atomic transport kinetics in γ solid solutions has been studied by [1972Bas] and [1986Tak]. Based on the results of four diffusion couples, [1972Bas] reported that the interdiffusion coefficient, D^{Cu}_{SnNi}, at 790°C are $4.96 \cdot 10^{-14}$ $m^2 \cdot s^{-1}$ at 4.7 mass% Ni and 8 mass% Sn, and $1.23 \cdot 10^{-14}$ $m^2 \cdot s^{-1}$ at 13.7 mass% Ni and 5 mass% Sn. In a subsequent and more comprehensive study, [1986Tak] measured interdiffusion coefficients in (Cu) solid solutions in the temperature range of 750 to 850°C, and confirmed the presence of zero-flux plane. They used twelve ternary diffusion couples containing up to 17.7 at.% Ni and 7.1 at.% Sn which were annealed at 750, 775, 800, 825 and 850°C. Their results show that the interdiffusion coefficients D^{Cu}_{NiNi}, D^{Cu}_{NiSn}, D^{Cu}_{SnNi} and D^{Cu}_{SnSn} are very sensitive to Ni and Sn concentrations. In particular, the interdiffusion coefficients in a Cu-6 at.% Ni-3.7 at.% Sn are expressed as:

$D^{Cu}_{NiNi} = 1.4 \cdot 10^{-5} \exp(-189000/RT)$ in $m^2 \cdot s^{-1}$

$D^{Cu}_{NiSn} = -3.1 \cdot 10^{-9} \exp(-120000/RT)$ in $m^2 \cdot s^{-1}$

$D^{Cu}_{SnNi} = -5.8 \cdot 10^{-7} \exp(-153000/RT)$ in $m^2 \cdot s^{-1}$

$D^{Cu}_{SnSn} = 2.1 \cdot 10^{-5} \exp(-175000/RT)$ in $m^2 \cdot s^{-1}$

where the activation energies are in $J \cdot mol^{-1}$, R is the universal gas constant and T is the temperature in K.
One of the major hurdles of conventional processing of Cu rich alloys on a commercial basis is the severe segregation of Ni and Sn. Rapid solidification of such alloys minimizes chemical heterogeneity leading to uniform microstructure and properties [1988Col, 1992Bog, 1999Mor]. The efficacy of thermodynamic and kinetic approach as a predictive tool for homogenization of highly segregated alloys was demonstrated by [2001Pur] for a commercial alloy of Cu-15Ni-8Sn (mass%).
The cellular or discontinuous reaction, $\gamma \rightarrow \gamma' + \gamma_1\text{-}(Ni,Cu)_3Sn$, in ternary alloys has been studied extensively in the temperature range of 350 to 500°C [1982Mik, 1983Mik1, 1983Mik2, 1984Mik1, 1984Mik2, 1990Mik, 1991Mik, 1994Mik]. The discontinuous reaction may be suppressed by adding B and P which segregate in grain boundaries [1983Mik2, 1984Mik2]. The effect of Al, Cr, Fe, In, Mn, Si and Ti on cellular precipitation kinetics has also been investigated [1994Mik]. Among these, Al, Cr, Si and Ti are most effective in retarding the reaction kinetics. In particular, it has been shown that the precipitation of $Ni_{31}Si_{12}$ [1991Mik] and Ni_3Ti [1994Mik] phase in grain boundaries are responsible for the retardation effect.
In view of lead-free solders in electronic packaging, the growth kinetics of Cu_3Sn and Cu_6Sn_5 intermetallic layers has been studied, in the temperature range of 80 to 170°C, using diffusion couples [2001You, 2004Yoo]. [2001You] prepared solder joints using Cu and Sn-2.7Cu-0.2Ni (mass%) alloy that were aged in the temperature range of 100 to 170°C for up to 360 h, while [2004Yoo] prepared solder joints of Cu and Sn-0.6Cu-0.05Ni (mass%) alloy that were aged in the temperature range of 80 to 150°C for up to 60 d. The activation energies for growth of Cu_3Sn was reported to be 57.06 $kJ \cdot mol^{-1}$ [2001You], while that of Cu_6Sn_5 ranges from 66.35 $kJ \cdot mol^{-1}$ [2004Yoo] to 83.8 $kJ \cdot mol^{-1}$ [2001You].
Besides studies on thermal aging of solder joints, [2001Che] prepared Sn-0.7 mass% Cu/Ni/Sn-0.7 mass% Cu solder joints that were subjected to a current density of 500 $A \cdot cm^{-2}$ in the temperature range of 160 to 200°C. They found that in the absence of electrical current only Ni_3Sn_4 grows at both interfaces, while the passage of electric current causes growth of both Cu_6Sn_5 and Ni_3Sn_4 at the solder/Ni interface and only Ni_3Sn_4 at the Ni/solder interface. They also found that the direction of movement of electrons, Cu and Sn is the same at solder/Cu interface, and the growth rates of intermetallic layers are enhanced. Calculation of apparent effective charge, Z_a^*, shows its decreasing magnitude with increasing temperature implying that the electromigration effect becomes insignificant at higher temperatures.
[1971Bas] measured the partitioning ratio of Ni and Sn between (Cu) and liquid in alloys containing up to 9 mass% Ni and 9 mass% Sn.
The Curie temperature of $\gamma\text{-}(Ni_2Cu)_{1-x}Sn_x$ solid solution decreases linearly with Sn concentration up to 7 at.% [1997Spr], from 32°C at $CuNi_2$ to –52°C at $Cu_{31}Ni_{62}Sn_7$.

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1928Pri]	Optical microscopy, hardness	200 - 800°C; 8.9 - 76.5 mass% Ni and 6.5 - 22 mass% Sn
[1932Gui]	Optical metallography, hardness	150 - 450°C; 50 - 70 mass% Ni and 0.5 - 15 mass% Sn
[1932Ves]	Thermal analysis, optical metallography	< 1050°C; 2-22.5 mass% Ni and 5-40 mass% Sn
[1933Eas]	Thermal analysis, XRD, optical microscopy	< 1140°C; 1-20 mass% Ni and 1-31 mass% Sn
[1937Rah]	XRD	$Cu_{45}Ni_{30}Sn_{25}$ ($D0_3$)
[1940Glu]	Optical metallography, XRD	630°C; (Cu-Ni) alloy/liquid-Sn
[1953Maz1]	XRD	900°C; 26.8 - 34.9 at.% Ni and 54-58.7 at.% Sn
[1953Maz2]	XRD	800 - 900°C; 6-38.5 at.% Ni and 36.1-55.5 at.% Sn
[1971Dok]	Mössbauer spectroscopy	$NiCu_2Sn$ ($L2_1$)
[1974Sch1], [1974Sch2]	TEM and XRD	350°C; 9 mass% Ni and 6 mass% Sn
[1975Ple]	Resistivity	300 - 825°C; 3.5-12 mass% Ni and 2.5-8 mass% Sn
[1977Hel]	XRD	200 - 450°C; 8 mass% Ni and 2-5.46 mass% Sn
[1978Ger]	TEM, XRD and hardness	330 - 780°C; 9 mass% Ni and 1-6 mass% Sn
[1978Hel]	TEM and XRD	8 mass% Ni and 5 mass% Sn
[1978Lef]	TEM and XRD	300 - 550°C; 15 mass% Ni and 8 mass% Sn
[1979Bab]	TEM	400 - 825°C; 9 mass% Ni and 6 mass% Sn
[1979Poo1]	SETARAM high-temperature calorimeter	1307°C; x_{Cu}:x_{Sn}=1/9, 1/5, 1/3, 1/2, 2/3, 1/1, 2/1, 3/2, 3/1, 5/1, 9/1; x_{Ni}:x_{Sn}=1/1, 3/1, 1/3; x_{Cu}:x_{Ni}=3/1
[1979Sch]	DTA, XRD and resistivity	≤ 700°C; $NiCu_2Sn$
[1980Dit]	TEM and XRD	350°C, 10 mass% Ni and 6 mass% Sn
[1980Ray]	TEM and XRD	350 - 600°C; 9 mass% Ni and 6 mass% Sn
[1981Wat]	DTA, optical microscopy and XRD	300 - 850°C; $Cu_xNi_{75-x}Sn_{25}$ with $5 \le x \le 30$
[1982Mik]	Optical microscopy, TEM and XRD	350 - 500°C; 10 mass% Ni and 8 mass% Sn
[1982Ray]	TEM and XRD	350 - 600°C; 9 mass% Ni and 6 mass% Sn

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1983Mik1]	Optical microscopy, TEM and XRD	350-850°C; 10-90 mass% Ni and 8-40 mass% Sn
[1983Mik2]	Optical microscopy and SEM	450-850°C; 10-80 mass% Ni and 8 mass% Sn
[1983Mur]	TEM	< 877°C; $Cu_8Ni_{67}Sn_{25}$
[1984Kra]	TEM	300-400°C; 9 mass% Ni and 2-5 mass% Sn
[1984Mik1]	Optical microscopy, TEM and XRD	
[1984Mik2]	Optical microscopy and SEM	450-850°C; 10-80 mass% Ni and 8 mass% Sn
[1984Sco]	Optical microscopy and TEM	350-400°C; 15 mass% Ni and 8 mass% Sn
[1985Nar]	TEM	350-850°C; 8.9 mass% Ni and 6 mass% Sn
[1986Tak]	SEM	750-850°C; 3.5-17.7 at.% Ni and 2.4-7.1 at.% Sn
[1987Kra]	TEM	300-500°C; 9 mass% Ni and 6 mass% Sn
[1988Col]	Optical microscopy and SEM	300-500°C; 10-15 mass% Ni and 2-8 mass% Sn
[1988Sat]	TEM	350°C; 10 mass% Ni and 6 mass% Sn
[1989Pak]	Optical microscopy, DTA, TEM and XRD	< 1000°C; $Cu_xNi_{75-x}Sn_{25}$ with $10 \le x \le 22$
[1990Che]	Optical microscopy, DTA and XRD	< 1100°C; 14 at.% Ni and 10-22 at.% Sn
[1990Dey]	Optical microscopy, EPMA and XRD	400-825°C; 10-15 mass% Ni and 6-12 mass% Sn
[1990Gou]	XRD	350°C; 15 mass% Ni and 8 mass% Sn
[1990Pak]	DTA, TEM and XRD	$Cu_xNi_{75-x}Sn_{25}$ with $11 \le x \le 22$
[1991Mik]	Optical microscopy	450°C; 10 mass% Ni and 8 mass% Sn
[1992Hun]	Optical microscopy and SEM	350-775°C; 15 mass% Ni and 8 mass% Sn
[1992Kra]	XRD and TEM	≤ 900°C; Ni_2CuSn ($D0_3$)
[1994Her]	Optical microscopy and XRD	400°C; 15 mass% Ni and 8 mass% Sn
[1994Mik]	Optical microscopy, TEM and XRD	450-850°C; 10 mass% Ni and 8 mass% Sn
[1995Bur]	DTA	850-1400°C; $(Ni_2Cu)_{1-x}Sn_x$ with $0.11 \le x \le 0.22$
[1995Kra]	TEM/AEM and XRD	490-800°C; 50.2-65.9 at.% Ni and 3.4-24.8 at.% Sn
[1995Pal]	XRD and SEM	450°C; 5-22 mass% Ni and 2.7-13 mass% Sn
[1996Oel]	AEM/TEM and XRD	≤ 850°C; $(Cu_{0.33}Ni_{0.67})_{1-x}Sn_x$, $(Cu_{0.4}Ni_{0.6})_{1-x}Sn_x$ $0 \le x \le 0.3$
[1996Rud]	Dilatometry and XRD	≤ 850°C; Ni_2CuSn and $(CuNi_2)_{0.775}Sn_{0.225}$

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1996Spr]	Electrical resistivity, XRD	< 900°C; $(Ni_2Cu)_{1-x}Sn_x$ with $0 \le x \le 0.143$
[1997Spr]	Magnetometry	< 700°C; $(Ni_2Cu)_{1-x}Sn_x$ with $0 \le x \le 0.07$
[1997Vir2]	Electrical resistivity, TEM/AEM	310-350°C; 2-8 mass% Ni and 7-9 mass% Sn
[1998Vir]	SEM and TEM	800-900°C; 6-9 mass% Ni and 6-7 mass% Sn
[1998Zha1]	TEM	225-840°C; 15 mass% Ni and 8 mass% Sn
[1998Zha2]	TEM	150-800°C; 7.5 mass% Ni and 5 mass% Sn
[1999Jun]	Resistivity	300-850°C; 9 mass% Ni and 6 mass% Sn
[1999Kim]	TEM	350°C; 9 mass% Ni and 6 mass% Sn
[1999Rhu]	Optical microscopy, SEM and TEM	350-850°C; 9 mass% Ni and 6 mass% Sn
[2001Che]	Diffusion couples	160-200°C
[2001You]	Diffusion couples	100-170°C
[2002Lin]	DTA, EPMA and XRD	240-300°C; 0.5-70.5 at.% Ni and 20.7-99.5 at.% Sn
[2003Che1]	Diffusion couples	200°C
[2003Wan]	Optical metallography and EPMA	800°C; < 80 at.% Cu and < 75 at.% Ni
[2004Lou]	Differential scanning calorimetry	≤ 830°C; 9 mass% Ni and 6 mass% Sn
[2004Lue]	SETARAM high-temperature calorimeter	1250°C; x_{Cu}:x_{Ni}=1/3, 1/1, 3/1
[2004Sah]	XRD	400°C; 15 mass% Ni and 5-13 mass% Sn
[2004Yoo]	Diffusion couples	80-150°C
[2005Li] [2006Li]	XRD, EPMA	240°C; 10-25 at.% Cu, 10-30 at.% Ni, bal. Sn

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ, (Ni,Cu)	*cF*4 $Fm\bar{3}m$		
(Ni) ≤ 1455	Cu	a = 352.32	pure Ni at 25°C [V-C2]
(Cu) ≤ 1084.62		a = 361.46	pure Cu at 25°C [V-C2]
		a = 362.25	as-quenched Cu-5Ni-2.7Sn(mass%), at 25°C [1995Pal]
		a = 360.90	as-quenched Cu-15Ni-2.7Sn(mass%), at 25°C [1995Pal]
		a = 359.87	as-quenched Cu-22Ni-2.7Sn(mass%), at 25°C [1995Pal]
		a = 362.04	as-quenched Cu-15Ni-5Sn(mass%), at 25°C [1995Pal]
		a = 363.56	as-quenched Cu-15Ni-9Sn(mass%), at 25°C [1995Pal]
		a = 365.20	as-quenched Cu-15Ni-13Sn(mass%), at 25°C [1995Pal]
		a = 358.06	as-quenched Cu-65.9Ni-3.4Sn(at.%), at 25°C [1996Spr]
		a = 360.10	as-quenched Cu-62.0Ni-5.5Sn(at.%), at 25°C [1996Spr]
(βSn) 231.5 - 13	*tI*4 $I4_1/amd$ Sn	a = 583.18 c = 318.18	pure Sn at 25°C [V-C2]
(αSn) < 13	*cF*8 $Fd\bar{3}m$ C (diamond)	a = 648.92	pure Sn [V-C2]
β_1, $Cu_{17}Sn_3$ 798 - 586	*cI*2 $Im\bar{3}m$ W	a = 297.81 to 298.71	$0.131 \le x_{Sn} \le 0.158$ [V-C2]
ε, Cu_3Sn(r) < 676	*oC*80 *Cmcm* Cu_3Sn	 a = 552.9 b = 4775.0 c = 432.3	$0.245 \le x_{Sn} \le 0.259$ [V-C2] at 25 at.% Sn [V-C2]
δ, $Cu_{41}Sn_{11}$ 590 - 350	*cF*416 $F\bar{4}3m$ $Cu_{41}Sn_{11}$	 a = 1798 a = 1801	$0.203 \le x_{Sn} \le 0.208$ [V-C2], at 20.5 at.% Sn $NiCu_9Sn_3$, at 25°C [1977Boo]
ζ, $Cu_{10}Sn_3$ 640 - 582	*hP*26 $P6_3$ -	 a = 733.0 a = 784.0	$0.209 \le x_{Sn} \le 0.225$ [V-C2], at 23.1 at.% Sn [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
η, Cu_6Sn_5(h) 415 - 186	*mP*36 $P2_1/c$ Cu_5Sn_4	 *a* = 983.0 *b* = 727.0 *c* = 983.0 β = 62.5°	$0.435 \le x_{Sn} \le 0.445$ [Mas2], superstructure of $B8_1$-NiAs type, at 44.44 at.% Sn [1995Lar]
	*mC*54 *C*2 Cu_5Sn_4	*a* = 1260.0 *b* = 727.0 *c* = 1020.0 β = 90°	superstructure of $B8_1$-NiAs type, at 44.44 at.% Sn [1995Lar]
η', Cu_6Sn_5(r) < 186	*mP*44 *C*2/*c* Cu_6Sn_5	 *a* = 1103.6 *b* = 728.8 *c* = 984.0 β = 98.81°	$0.435 \le x_{Sn} \le 0.445$ [Mas2], superstructure of $B8_1$-NiAs type, at 44.44 at.% Sn [1994Lar]
γ_2, Ni_3Sn(r) < 977	*hP*8 $P6_3/mmc$ $NiSn_3$	 *a* = 530.5 *c* = 425.4	$0.241 \le x_{Sn} \le 0.260$ [Mas2], at 25 at.% Sn [V-C2]
		a = 530.5 *c* = 425.4	$Cu_{1.92}Ni_{73.08}Sn_{25}$ quenched from 600°C, at 25°C [1981Wat]
		a = 530.5 *c* = 425.4	$Cu_{3.99}Ni_{71.01}Sn_{25}$ quenched from 600°C, at 25°C [1981Wat]
		a = 530.5 *c* = 425.4	$Cu_5Ni_{70}Sn_{25}$ quenched from 600°C, at 25°C [1981Wat]
λ_1, Ni_3Sn_2(h) 1264 - 600	*hP*4 $P6_3/mmc$ NiAs	 *a* = 414.6 *c* = 525.3	$0.388 \le x_{Sn} \le 0.425$ [Mas2], at 40 at.% Sn [V-C2]
λ_2, Ni_3Sn_2(r) < 794.5	*oP*20 *Pnma* Ni_3Sn_2	 *a* = 711.2 *b* = 521.1 *c* = 823.2	$0.241 \le x_{Sn} \le 0.260$ [Mas2], at 40 at.% Sn [V-C2]
Ni_3Sn_4 < 794.5	*mC*14 *C*2/*m* Ni_3Sn_4	 *a* = 1221.4 *b* = 406.02 *c* = 521.93 β = 105.01°	$0.555 \le x_{Sn} \le 0.57$ [Mas2], [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ_1, $(Ni,Cu)_3Sn$	*cF*16 $Fm\bar{3}m$		
Cu_3Sn(h) 755 - 520	BiF_3	a = 606.05 to 611.76	$0.165 \le x_{Sn} \le 0.279$ [V-C2]
		a = 594.6	$Cu_{45}Ni_{30}Sn_{25}$, at 25°C [1937Rah]
Ni_3Sn(h) 1174 - 850			$0.2325 \le x_{Sn} \le 0.2725$ [Mas2], at 25 at.% Sn [V-C2]
		a = 598.2	
		a = 592.93	$Cu_{20.95}Ni_{54.05}Sn_{25}$ quenched from 600°C, at 25°C [1981Wat]
		a = 593.04	$Cu_{21.98}Ni_{53.02}Sn_{25}$ quenched from 600°C, at 25°C [1981Wat]
		a = 593.20	$Cu_{22.98}Ni_{52.02}Sn_{25}$ quenched from 600°C, at 25°C [1981Wat]
		a = 593.41	$Cu_{25}Ni_{50}Sn_{25}$ quenched from 600°C, at 25°C [1981Wat]
* τ_1, $NiCu_2Sn$ 700 - 500	*cF*16 $Fm\bar{3}m$	a = 579.7	[1953Maz2]
	$AlCu_2Mn$	a = 596.4	[1979Sch]
		a = 596.0	[1984Wac]
* τ_2, Ni_5CuSn_2 < 740	*oP*8 *Pmmn*		$Cu_xNi_{5-x}Sn_2$, with $0.8 \le x \le 1.41$ [1981Wat]
	βCu_3Ti	a = 449.5 b = 538.0 c = 428.5	at x = 1 [1989Pak]
* τ_3, Ni_2CuSn < 460	*aP*?	a = 453.0 b = 531.0 c = 434.0 α = 85° β = 86° γ = 84°	[1990Pak]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Cu	Ni	Sn
$L + \gamma \rightleftharpoons \beta_1 + \gamma_1$-$(Ni,Cu)_3Sn$	~780	U_1	L	77.8	5.5	16.7
$L + \gamma_1$-$(Ni,Cu)_3Sn \rightleftharpoons \varepsilon$-$Cu_3Sn + Ni_3Sn_2$(h)	~620	U_2	L	44.5	12.7	42.8
$L + \varepsilon$-$Cu_3Sn \rightleftharpoons \eta + Ni_3Sn_2$(r)	~400	U_3	L	12.6	2.6	84.8

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Cu	Ni	Sn
$L + Ni_3Sn_4 \rightleftharpoons (Sn) + Ni_3Sn_2(r)$	~230	U_4	L	1.4	2.7	95.9
$L + Ni_3Sn_2(r) \rightleftharpoons (Sn) + \eta$	~228	U_5	L	2.3	1.1	96.6

Table 4: Solidus and Spinodal Temperatures of Cu Rich Alloys

Alloy Composition (mass%)			Solidus Temperature [°C] (±5)	Spinodal Temperature [°C] (±20)
Cu	Ni	Sn		
93.57	3.41	3.02	617	360
90.41	4.89	4.70	692	410
86.14	5.98	7.88	770	450
85.22	9.03	5.75	740	464
84.93	10.41	4.66	751	450
81.32	11.46	7.22	816	490
79.01	14.04	6.95	780	480

Table 5: Investigations of the Cu-Ni-Sn Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1974Sch1], [1974Sch2]	Tensile test	Tensile properties of spinodal microstructure
[1975Ple]	Tensile test	Tensile properties of spinodal microstructure
[1978Lef]	Tensile test	Tensile properties of spinodal microstructure
[1984Kra]	Tensile test	Yield stress
[1984Sco]	Electrical and mechanical tests	Young's and shear moduli, yield and ultimate tensile stress, electrical conductivity
[1986Kat]	Tensile test	Tensile properties of single crystal at 25°C
[1986Kha]	Tensile test	Tensile properties of single crystal at 25°C
[1989Kra]	Tensile test	Tensile properties
[1991Abd]	Tensile test	Hot deformation behavior between 570 and 850°C
[1991And]	Tensile test	Tensile properties, stress relaxation
[1993Sat]	Tensile test	Tensile properties
[1992Bog]	Electrical, mechanical and thermal tests	Hardness, Young's modulus, thermal conductivity, thermal expansion coefficient
[1992Kra]	Creep tests	Creep between 300 and 900°C
[1994Her]	Tensile test	Hardness and tensile properties

Reference	Method/Experimental Technique	Type of Property
[1996Leh]	Electrical and mechanical tests	Tensile properties and electrical conductivity
[1997Her]	Tensile test	Tensile properties
[1997Vir1]	Tensile test	Stress relaxation
[1997Vir2]	Electrical	Electrical resistivity
[1999Jun]	Electrical and mechanical tests	Tensile properties and electrical conductivity
[1999Kim]	Tensile test	Tensile properties
[1999Mor]	Electrical and mechanical tests	Tensile properties and electrical conductivity
[1999Rhu]	Tensile test	Tensile properties
[2001Che]	Electrical test	Electromigration
[2003Che2]	Tensile test	Tensile properties of solder joints

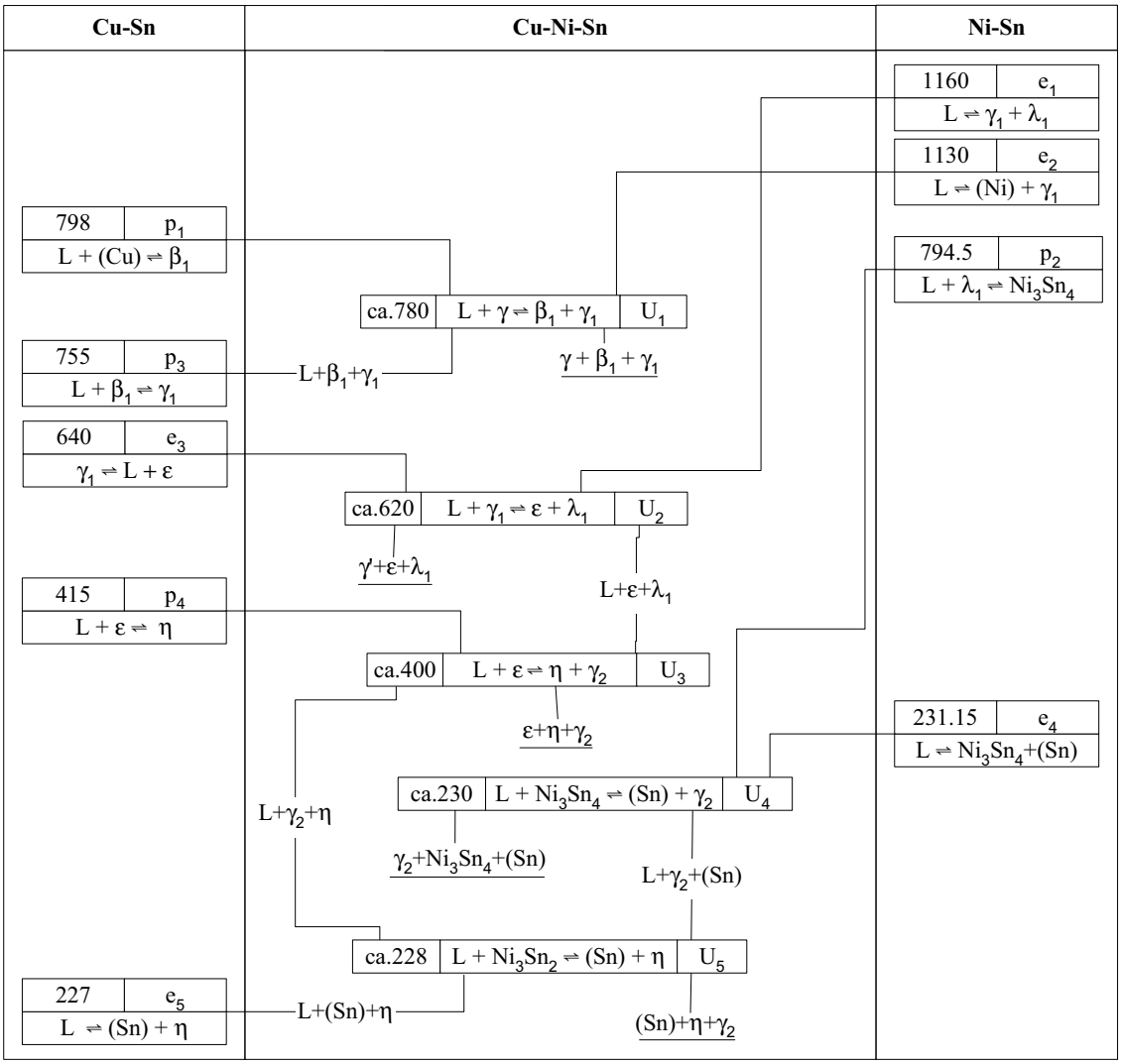


Fig. 1: Cu-Ni-Sn. Reaction scheme for the solidification of Cu-Ni-Sn alloys

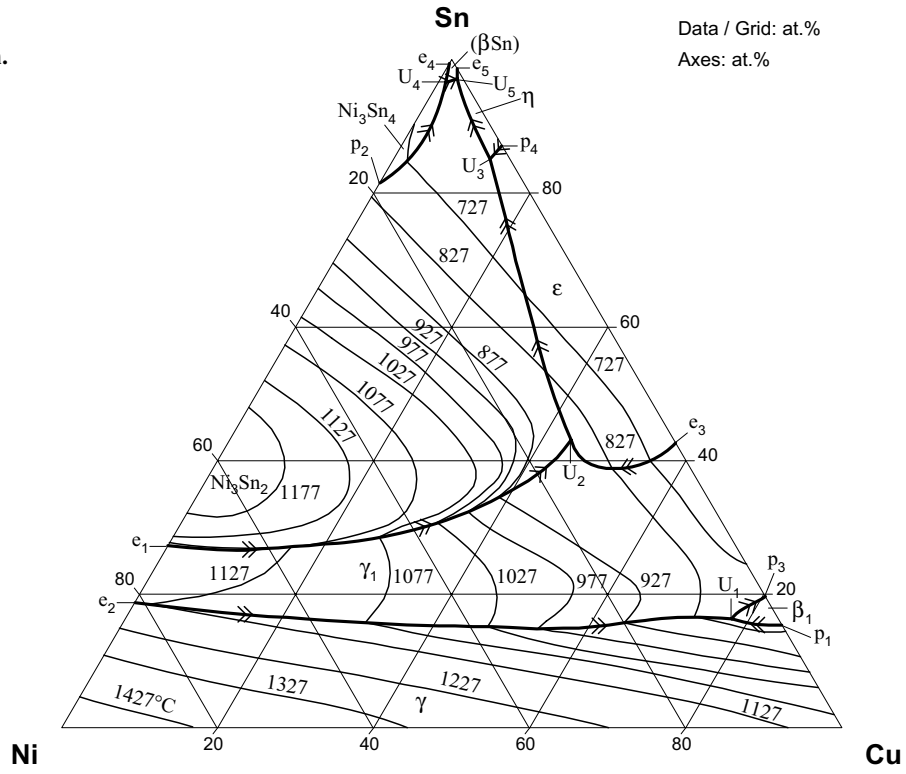


Fig. 2: Cu-Ni-Sn. Liquidus surface projection

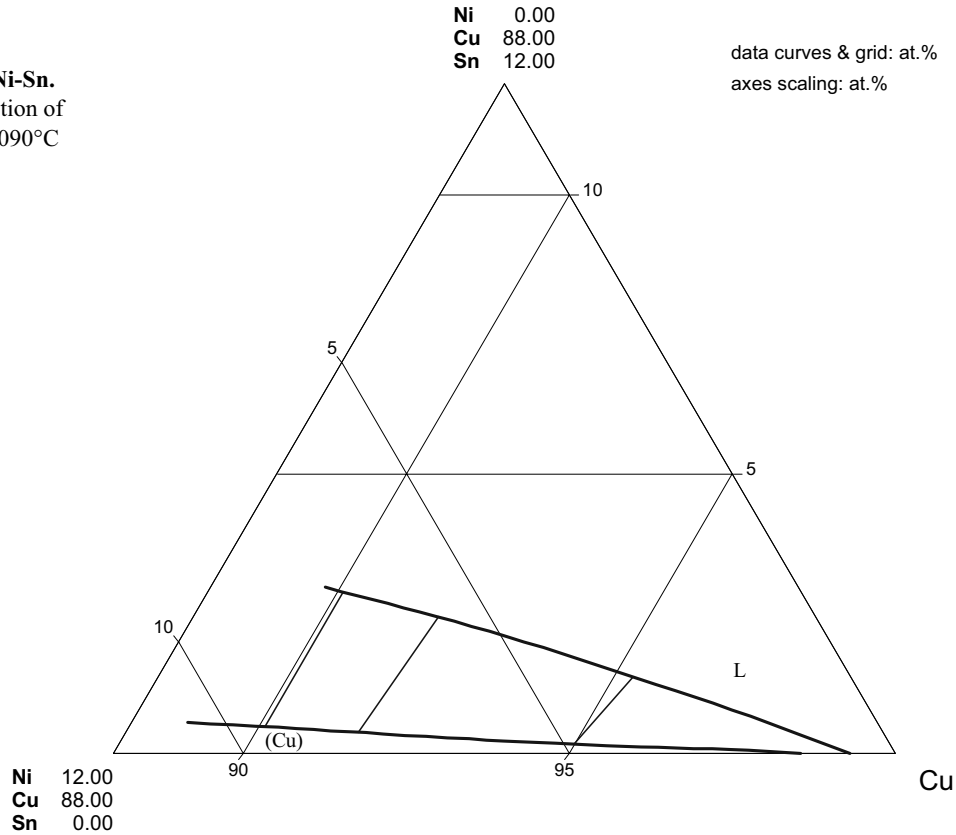


Fig. 3: Cu-Ni-Sn. Isothermal section of Cu corner at 1090°C

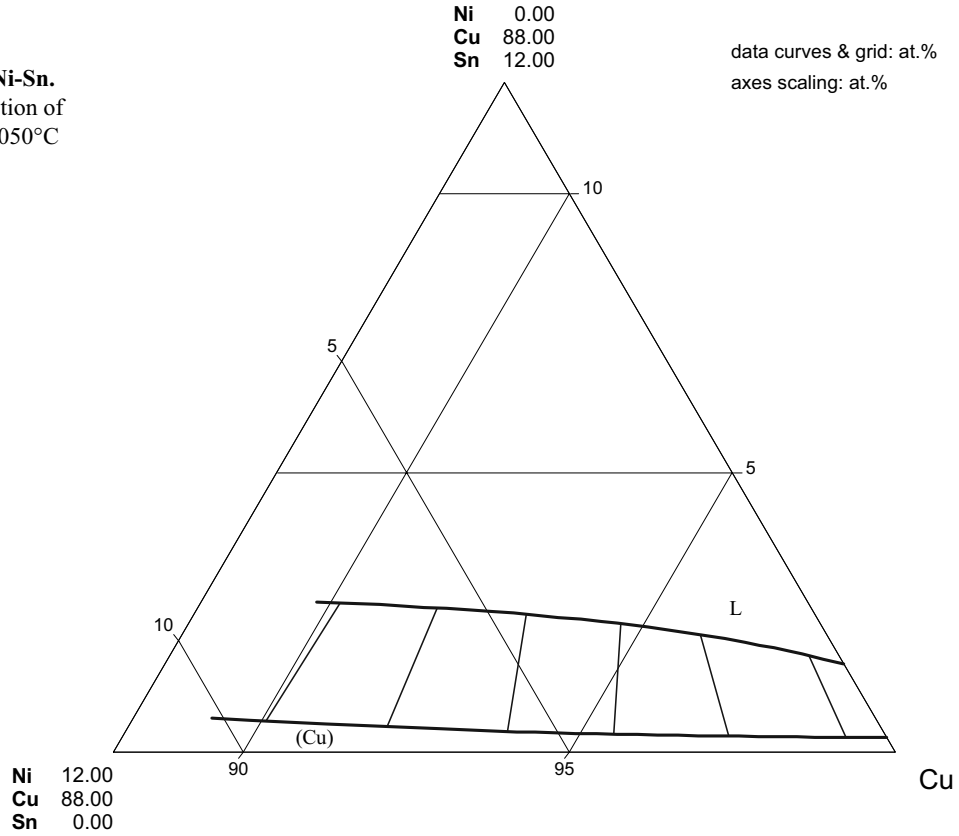


Fig. 4: Cu-Ni-Sn.
Isothermal section of Cu corner at 1050°C

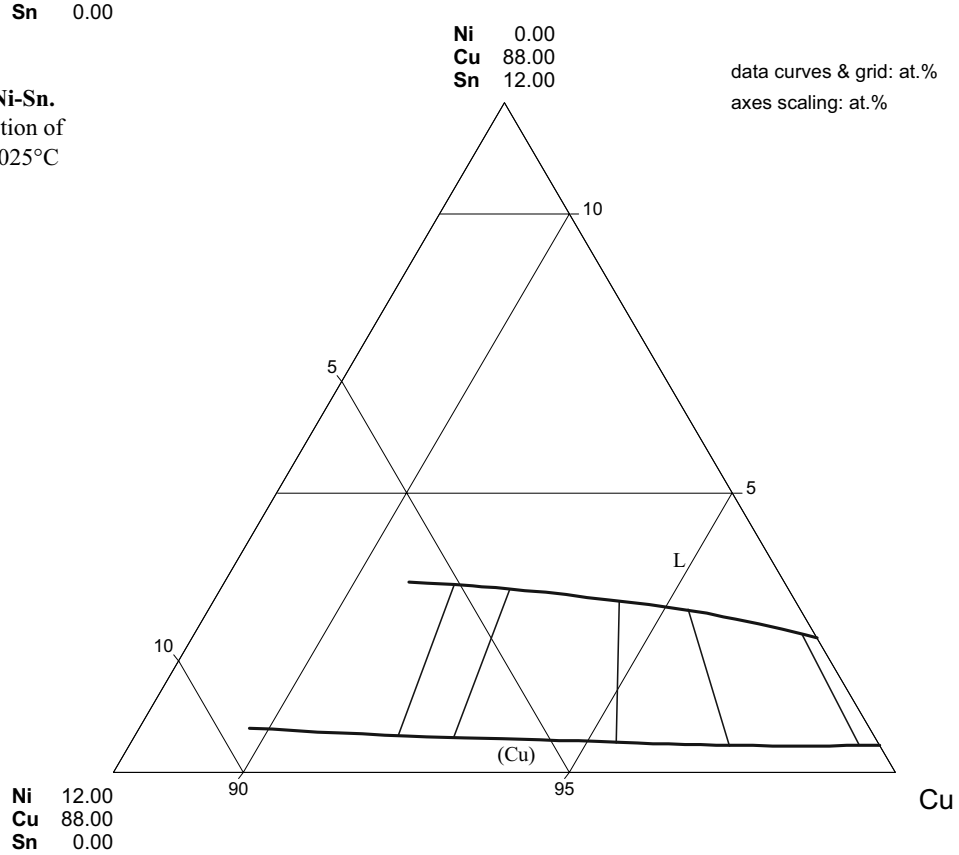


Fig. 5: Cu-Ni-Sn.
Isothermal section of Cu corner at 1025°C

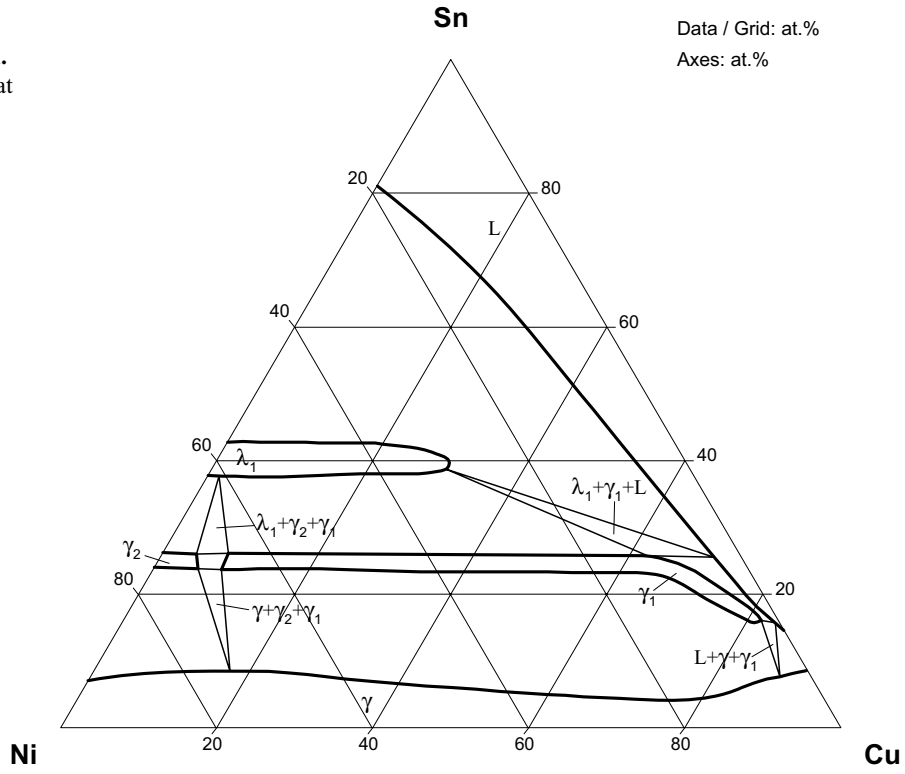


Fig. 6: Cu-Ni-Sn. Isothermal section at 800°C

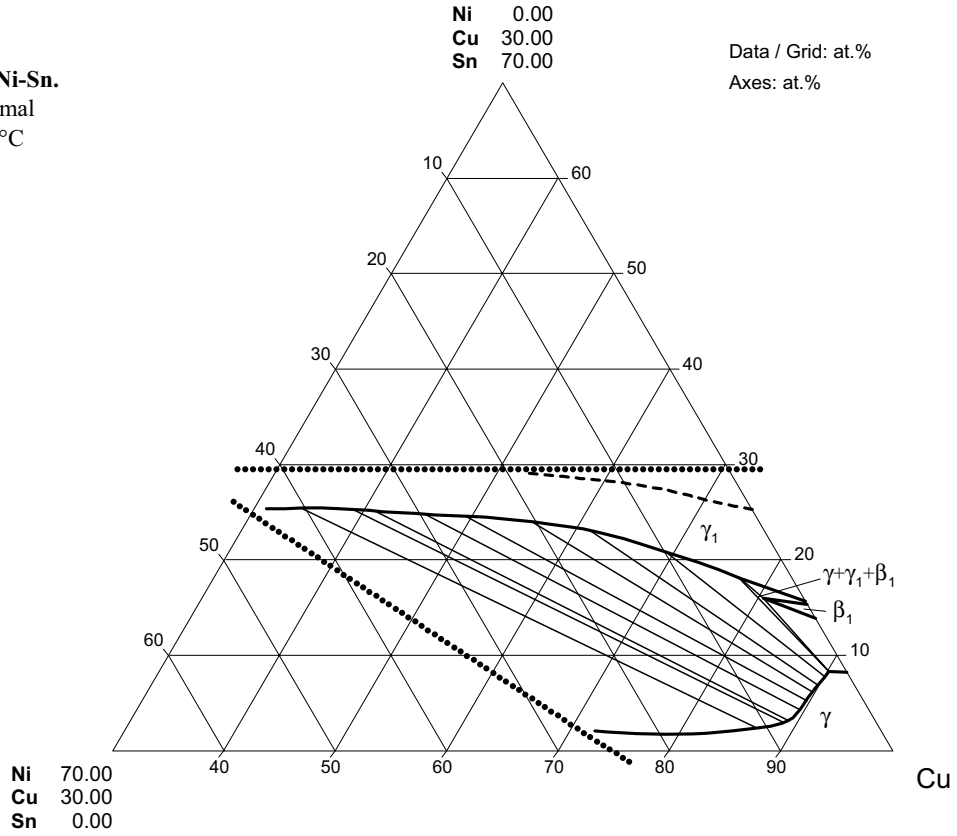


Fig. 7: Cu-Ni-Sn. Partial isothermal section at 700°C

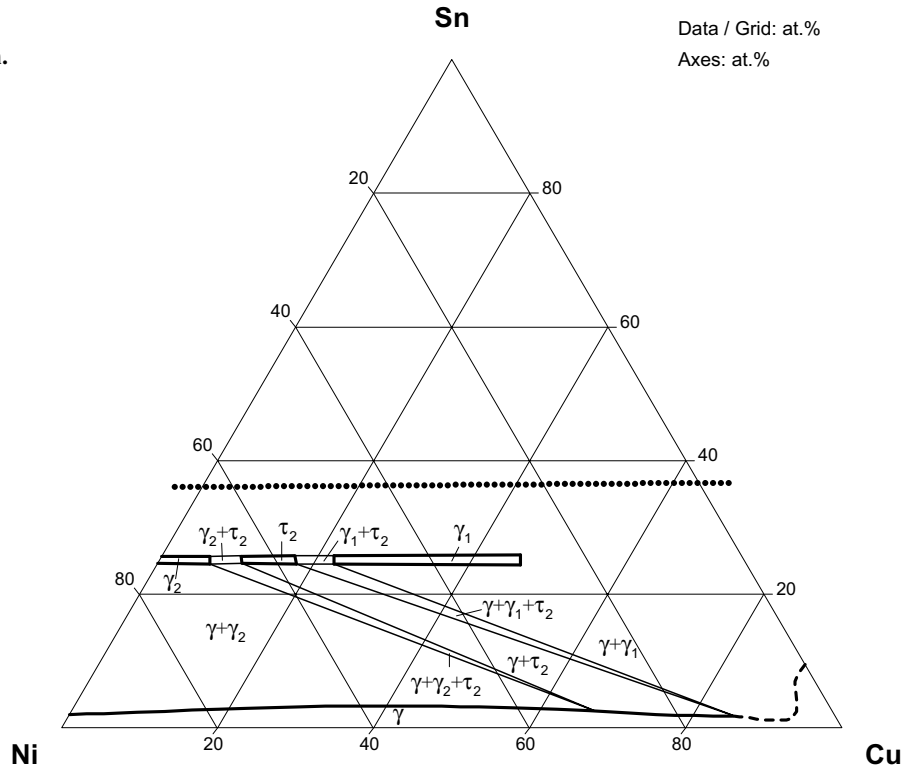


Fig. 8: Cu-Ni-Sn. Partial isothermal section at 550°C

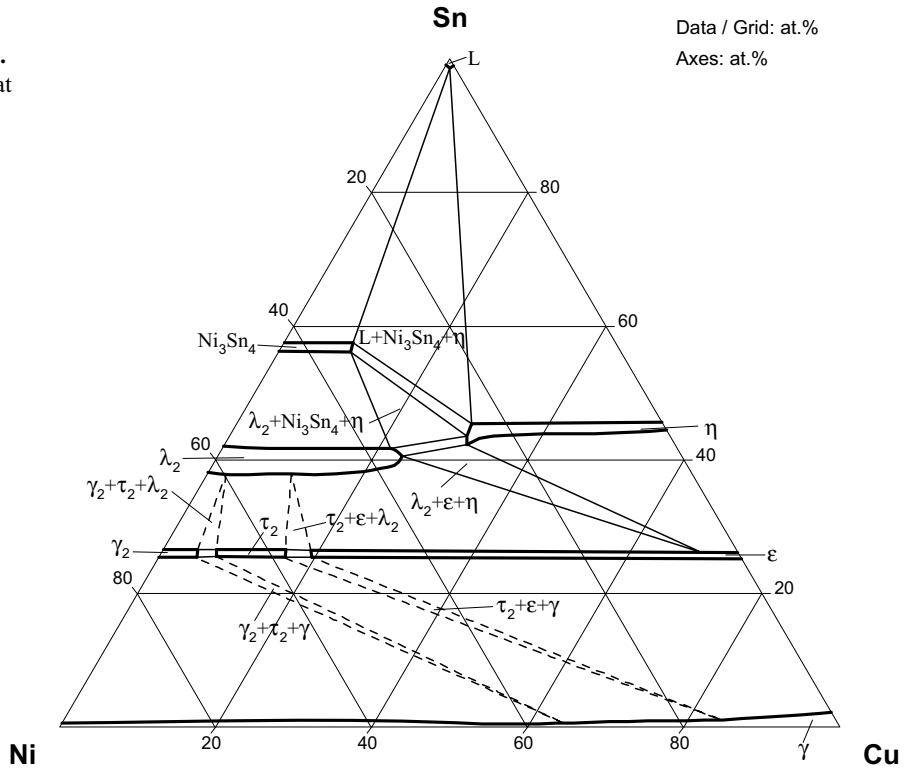


Fig. 9: Cu-Ni-Sn. Isothermal section at 240°C

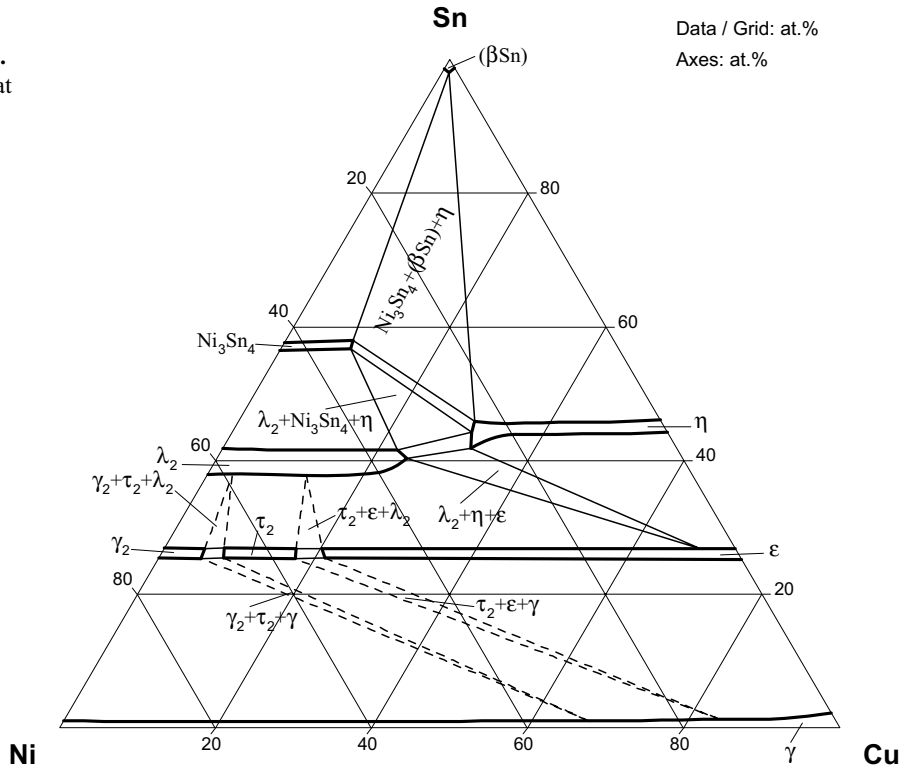


Fig. 10: Cu-Ni-Sn. Isothermal section at 200°C

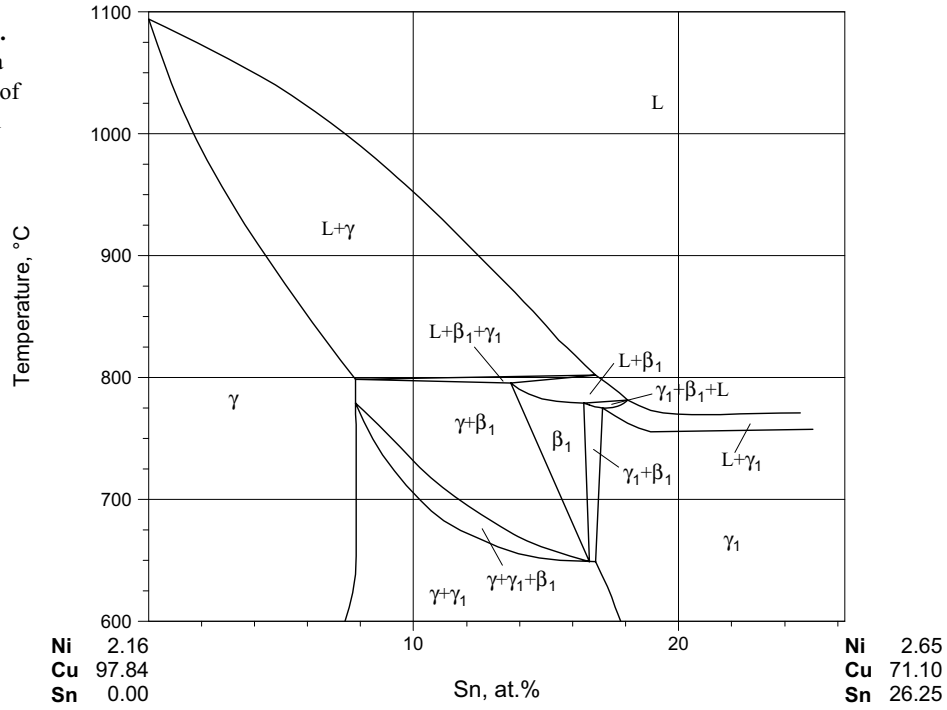


Fig. 11: Cu-Ni-Sn. Vertical section at a constant Ni content of 2 mass%, plotted in at.%

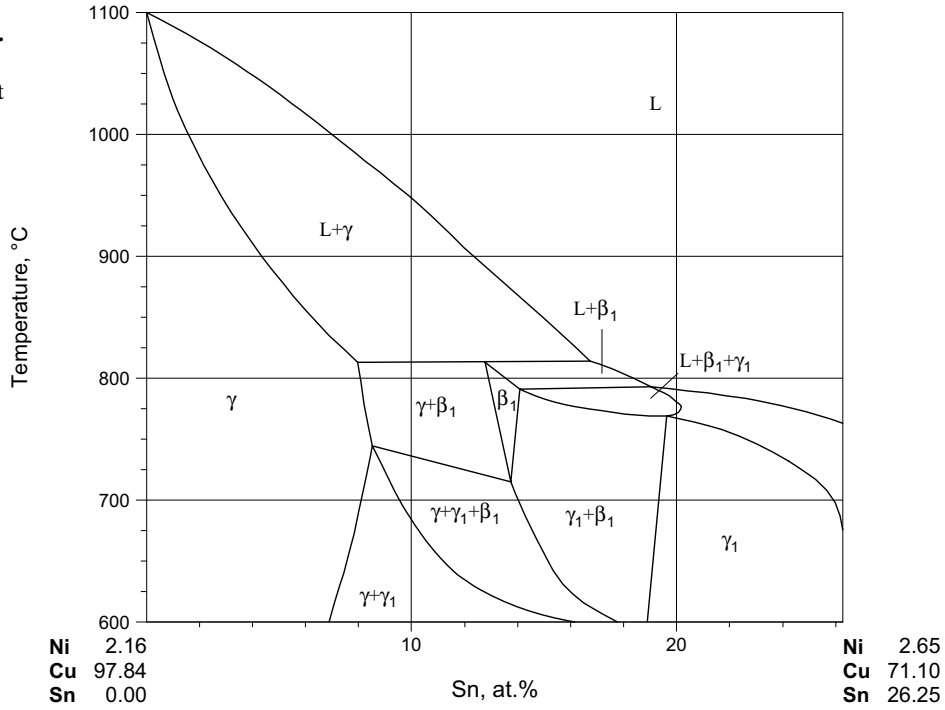


Fig. 12: Cu-Ni-Sn. Calculated vertical section at a constant Ni content of 2 mass%, plotted in at.%

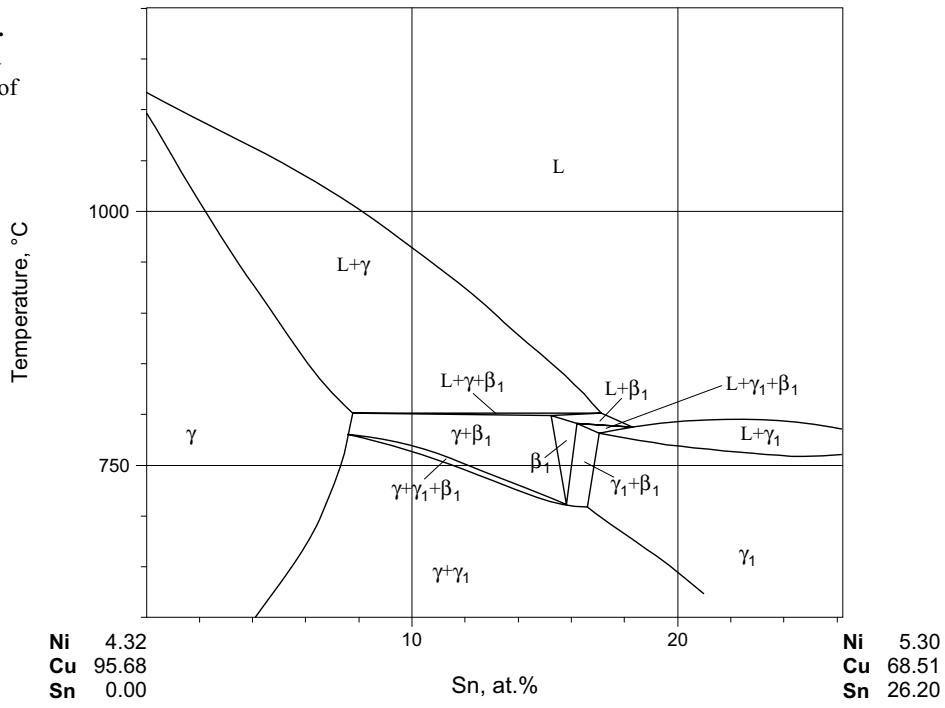


Fig. 13: Cu-Ni-Sn. Vertical section at a constant Ni content of 4 mass%, plotted in at.%

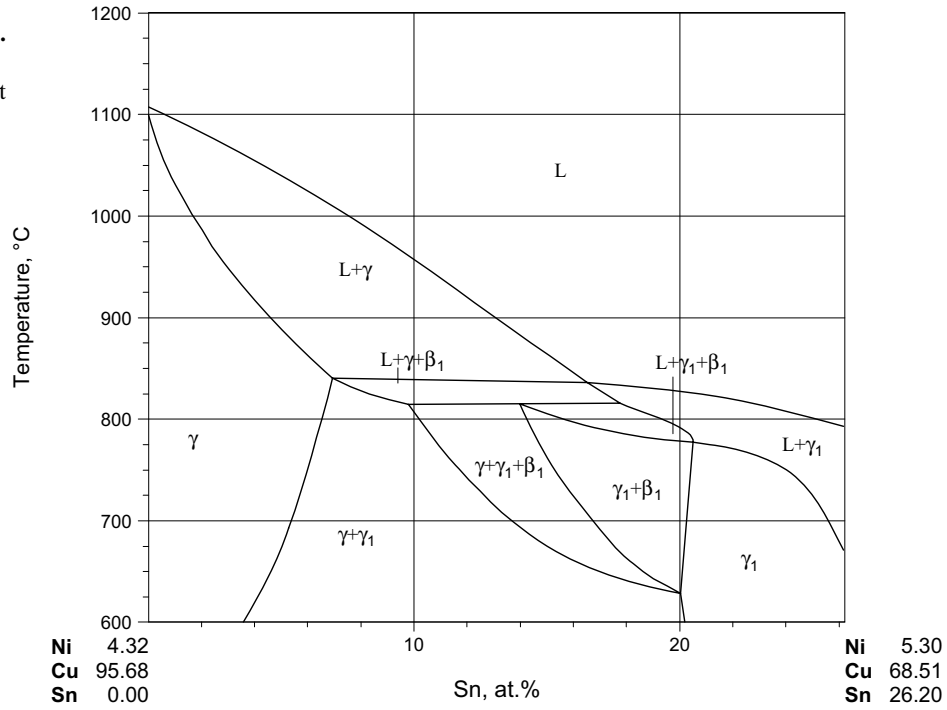


Fig. 14: Cu-Ni-Sn. Calculated vertical section at a constant Ni content of 4 mass%, plotted in at.%

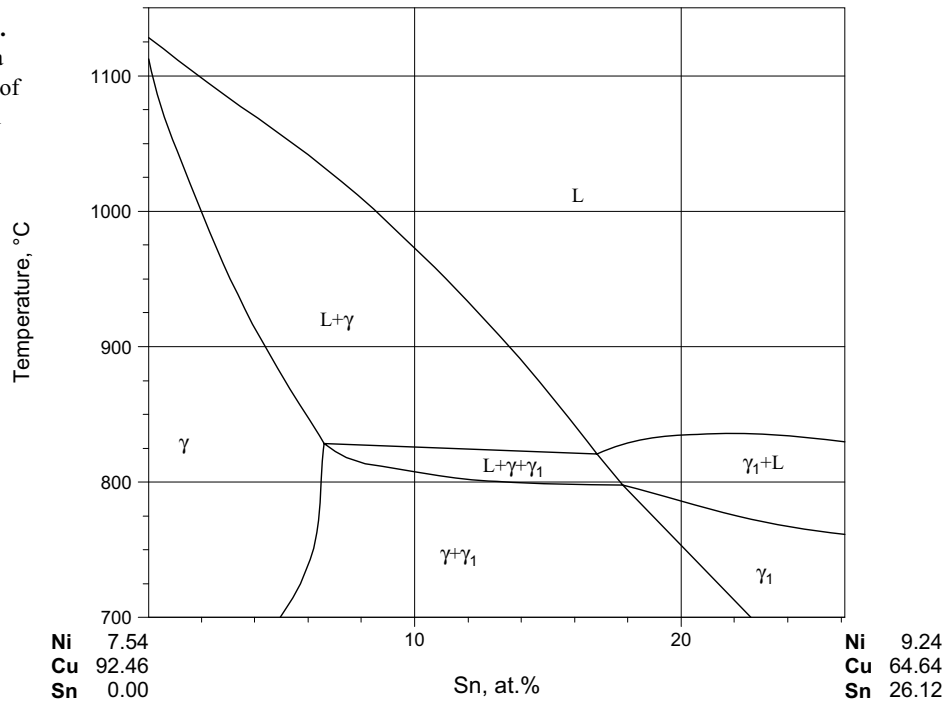


Fig. 15: Cu-Ni-Sn. Vertical section at a constant Ni content of 7 mass%, plotted in at.%

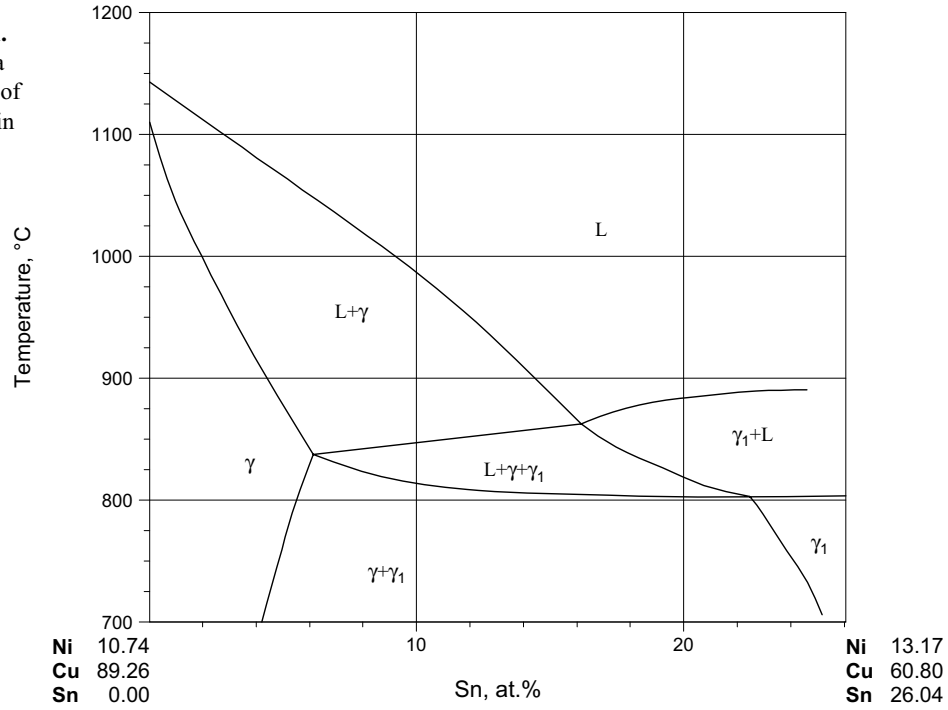


Fig. 16: Cu-Ni-Sn. Vertical section at a constant Ni content of 10 mass%, plotted in at.%

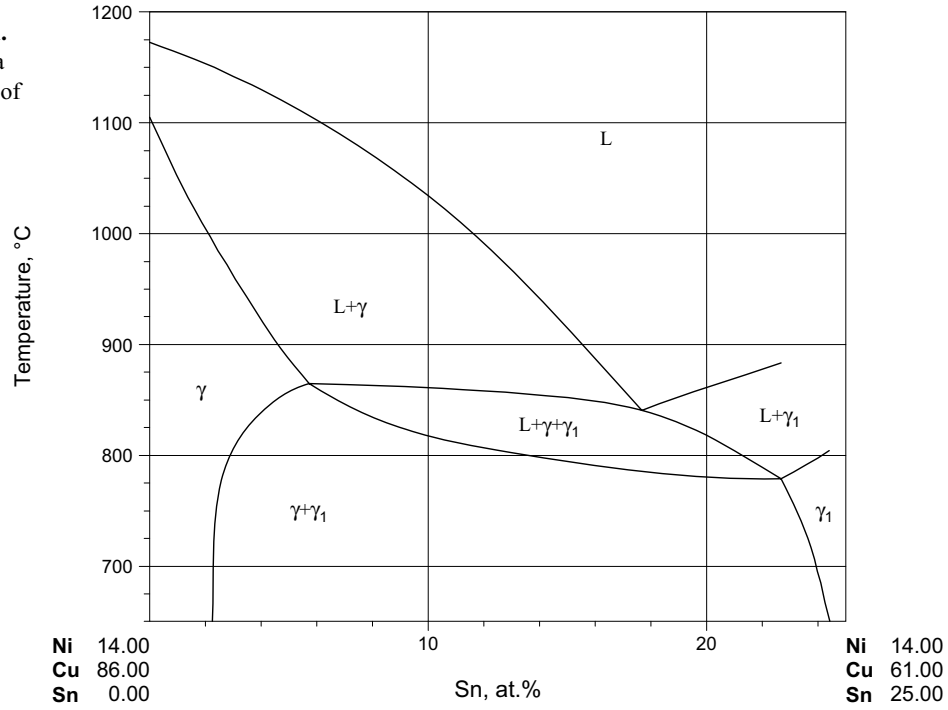


Fig. 17: Cu-Ni-Sn. Vertical section at a constant Ni content of 14 at.%

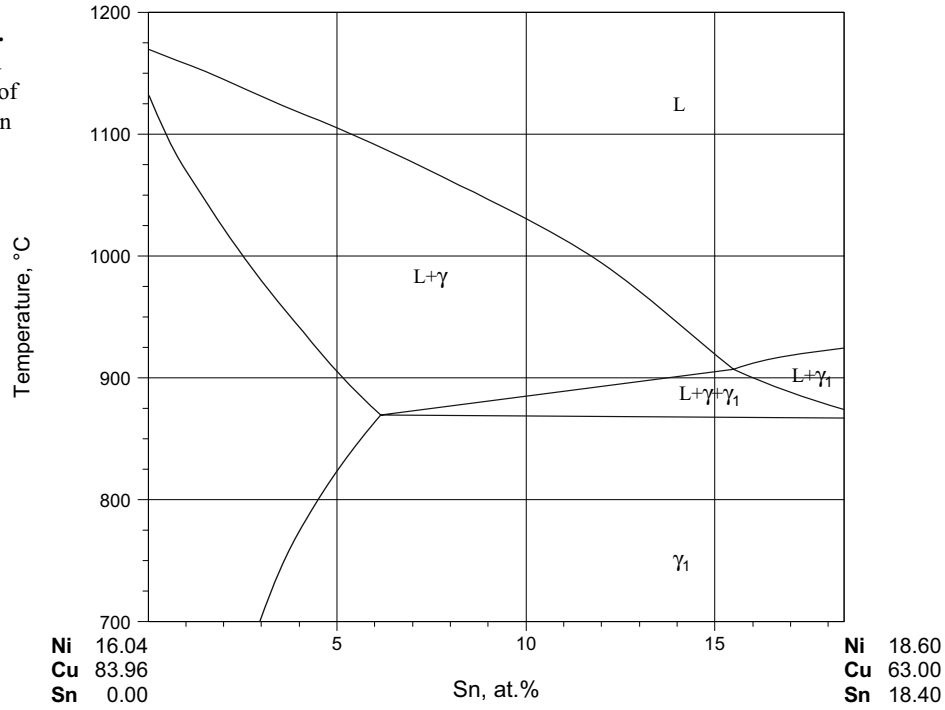
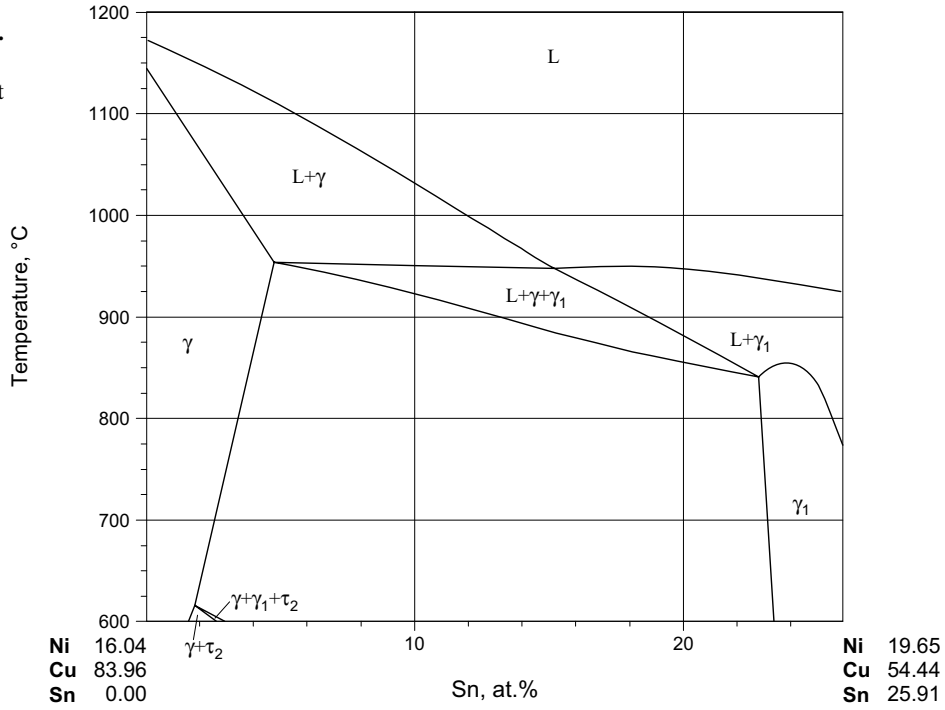


Fig. 19: Cu-Ni-Sn. Calculated vertical section at a constant Ni content of 15 mass%, plotted in at.%



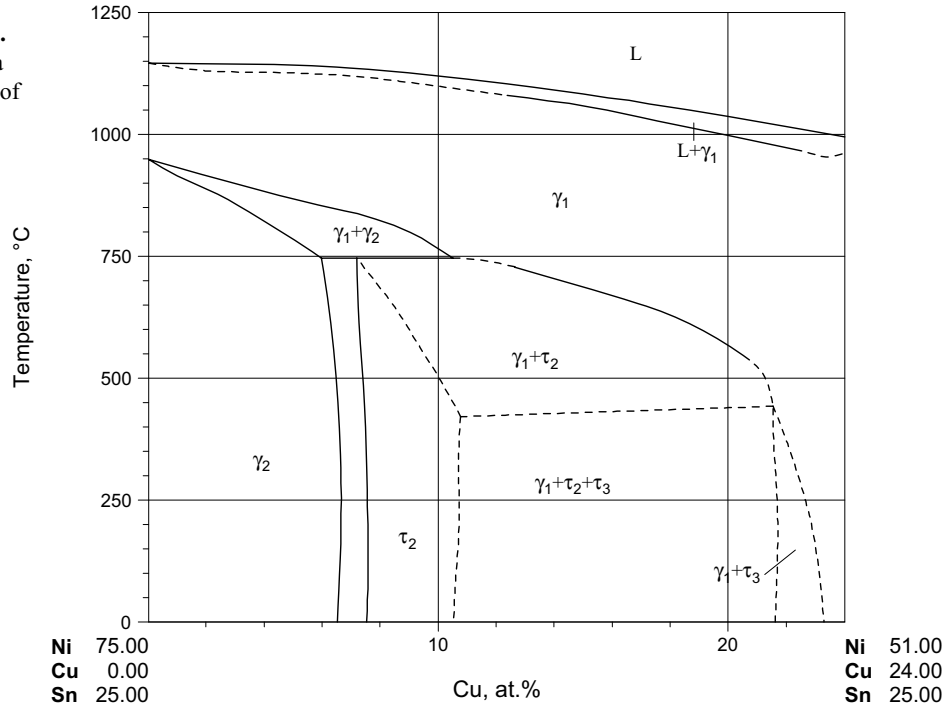


Fig. 20: Cu-Ni-Sn. Vertical section at a constant Sn content of 25 at.%

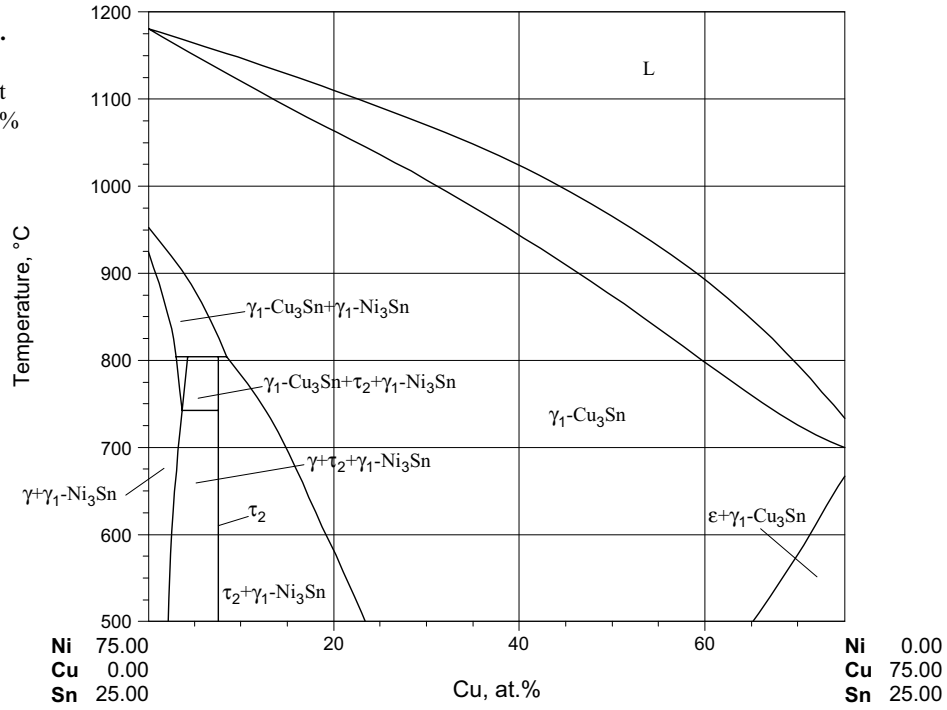


Fig. 21: Cu-Ni-Sn. Calculated vertical section at a constant Sn content of 25 at.%

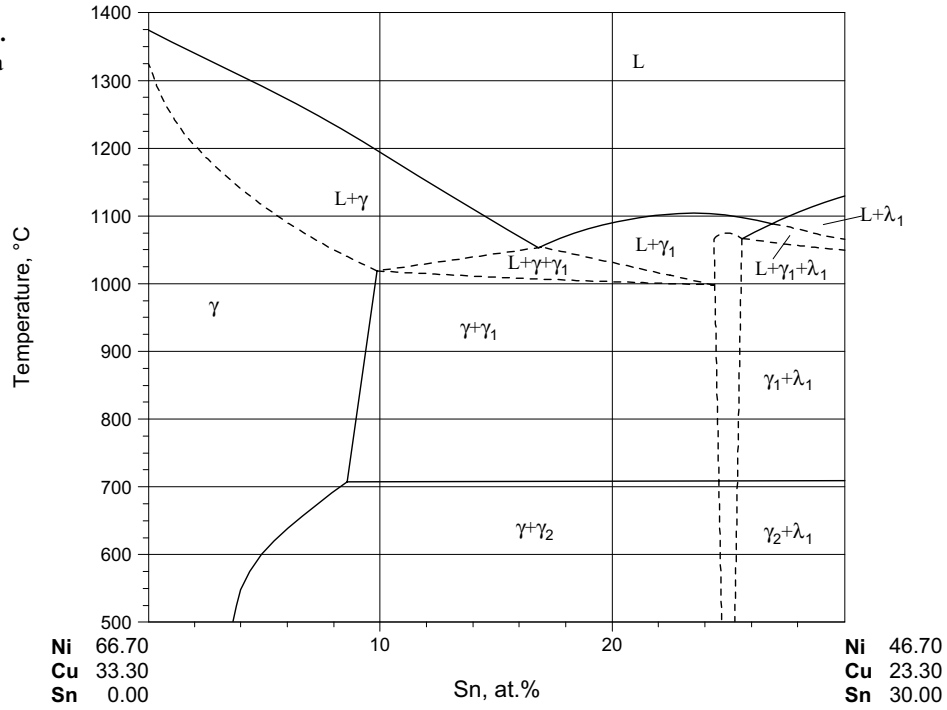


Fig. 22: Cu-Ni-Sn. Vertical section at a constant ratio x(Cu):x(Ni)=1:2

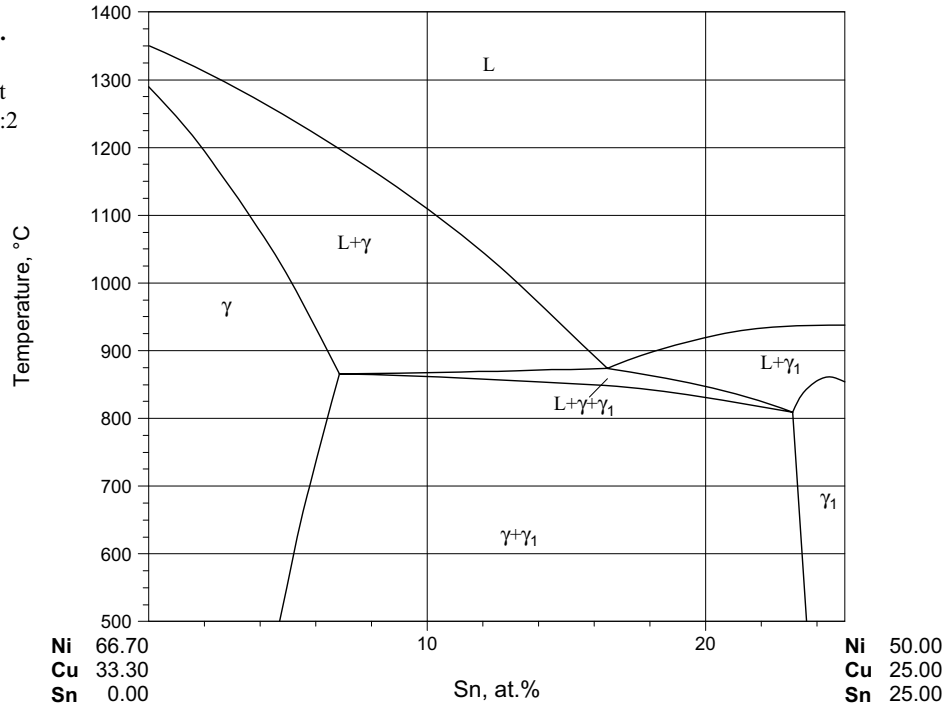


Fig. 23: Cu-Ni-Sn. Calculated vertical section at a constant ratio x(Cu):x(Ni)=1:2

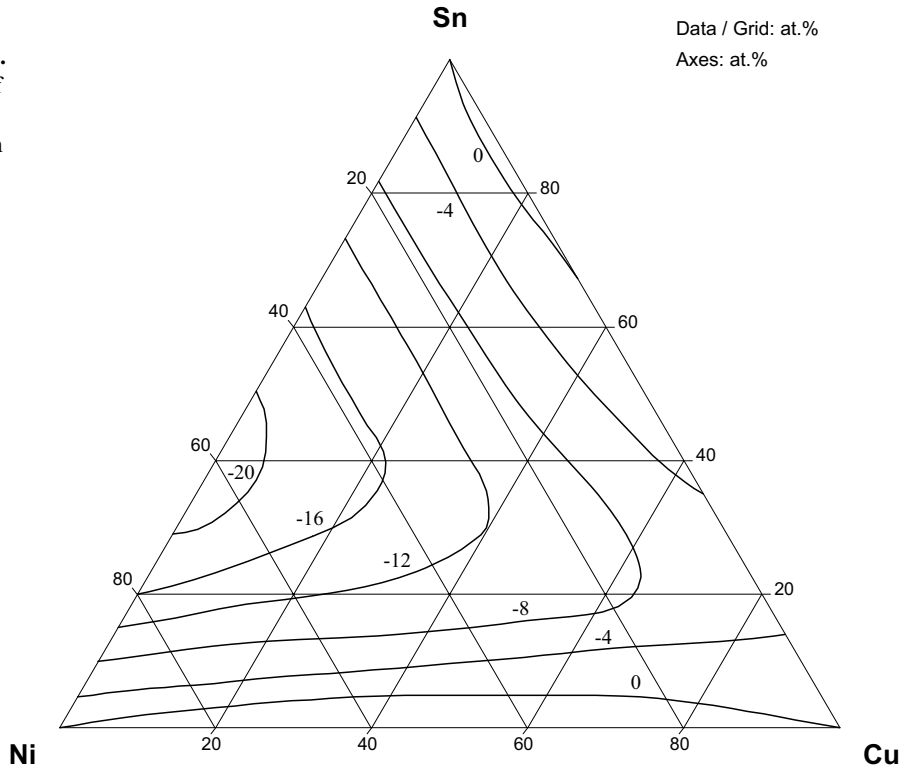


Fig. 24: Cu-Ni-Sn. Integral enthalpy of mixing of liquid alloys at 1307°C, in kJ/mol of atoms

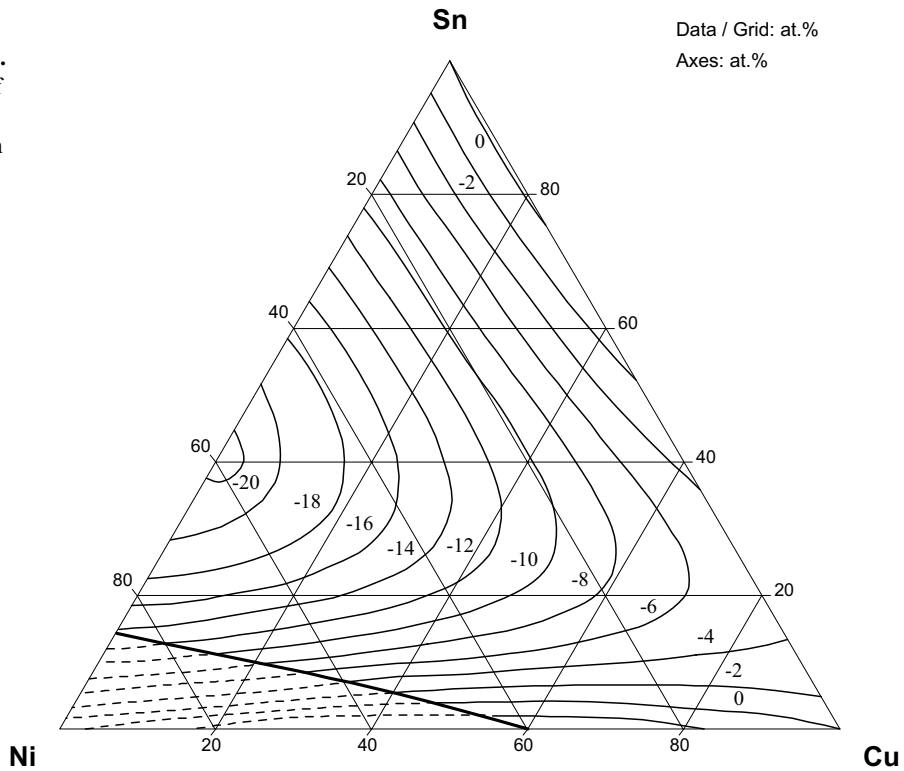


Fig. 25: Cu-Ni-Sn. Integral enthalpy of mixing of liquid alloys at 1250°C, in kJ/mol of atoms