Copper – Nickel – Zinc

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Introduction

In the first telephone exchanges built in 1879, the cables were made of copper and the switches of "nickel silver" (Cu-Ni-Zn alloy) because of its excellent wear and corrosion resistance [1990Seg]. The first liquidus of the Cu-Ni-Zn system was proposed by [1908Taf]. Micrographic observations were reported by [1929Bau2], and isothermal sections at 400, 600 and 800°C were given by [1929Bau1, 1930Bau]. The older information on the metallurgical properties of the alloys was obtained by [1912Car, 1913Gui, 1922Voi, 1924Pri, 1925Gui, 1925Ost, 1926Sma]. The ternary phase diagram has been investigated by [1930Bau, 1934Yam], later reproduced by [1949Jae], then more extensively by [1935Sch]. These diagrams are very similar to those generally accepted and were later confirmed through their intensive use as a basis for diffusion studies at 775°C [1970Tay, 1971Coa, 1977Sis, 1977Wir, 1979Day, 1985Kan]. The most complete work on the phase equilibria in the ternary diagram is that of [1935Sch] whose results were taken into account in the thermodynamic assessment of [2003Mie, 2005Jia]; the isothermal sections at 650°C and 775°C proposed by [1973Lev, 1979Dri] are those of [1935Sch] modified according to the metallographic observations of [1952Haw]. The isothermal section at 775°C was widely confirmed by [1979Day, 1984Kim] which used it to put into evidence the existence of zero flux and flux reversal planes in ternary diffusion experiments, and by [1985Kan] who used it to extend this observation to the quaternary systems. [1936Sch] proposed a low temperature isothermal section accepted by [1956Fre, 1973Lev, 1979Dri]. The equilibria between α and β solid solutions have been investigated by [1930Bau] at 600 and 800°C, [1952Haw] at 672°C and more extensively by [1979May] at 600°C. Investigations related to phase equilibria, structure and thermodynamics are reported in Table 1.

Binary Systems

The binary systems Cu-Zn and Ni-Zn present three isotypical phases α, β and γ in which copper and nickel may replace each other. The β phases present two polymorphic varieties. The label β is used for the *cP*2 structure which corresponds to the high temperature form for β(Ni,Zn) and to the low temperature form for β(Cu,Zn). After [Mas2], the binary phase diagram Cu-Zn has been calculated by [1993Kow] and assessed by [1994Mio, 2001Her, 2003Mie]. [1993Kow] incorporates in its thermodynamic evaluation an explicit description of the ordering in the β phase and a four sublattice model applied to the γ phase. More realistic solid phase boundaries than [1994Mio] have been proposed for the β and γ phases and have been retained in its assessment. The Cu-Zn phase diagram accepted from [2006Leb] is a compilation of [1993Kow, 1994Mio, 2001Her]. The binary phase diagrams Cu-Ni and Ni-Zn were respectively accepted from [2002Leb] and [1991Nas].

Solid Phases

Crystallographic data of solid phases are reported in Table 2. X-ray diffraction measurements of α(Ni,Cu,Zn) alloys show the appearance of superstructure lines with a maximum for the composition $NiCu_2Zn$ indicating a long-range order whose theory has been presented by [1994Fon, 1996Alt]. The long-range order, overwhelming from measurements of physical properties such as electrical resistivity, Hall coefficient [1967Liv], heat capacity, thermal expansion and elastic modulus was also observed by [1965Hir] from neutron diffraction study of a single crystal of $NiCu_2Zn$. The superstructure is $L1_2$ ($AuCu_3$ type), stable between 325 and 501°C, in which Cu and Ni atoms are statistically distributed in the equivalent positions (1/2, 1/2, 0), whereas zinc atoms occupy the equivalent (0,0,0) position [1969Bar, 1981Weg]. Thermal neutron scattering and electron microscopy measurements [1976Vri] show that, below 450°C, ordering of $NiCu_2Zn$ occurs on four interpenetrating simple cubic sublattices: one with Zn, one with Ni and the other two with Cu. [1979Hos] uses the interatomic potentials to predict a value of ordering energy and the critical temperature in the $NiCu_2Zn$ alloy taking into account nearest neighbor interactions. Tetragonal distortion of the lattice upon ordering appears very small. [1960Cha] proposes for the lattice parameter of the α solid solution the following expression

a (pm) = 360.75 + 20.5 x_{Zn} – 11.2 x_{Ni} (x_{Zn} < 0.23, x_{Ni} < 0.33)

Below 325°C, a fully ordered superstructure of the type $L1_0$ is stable around the composition $NiCu_2Zn$ [1981Roo] in which Zn and Ni atoms occupy two different sublattices whereas Cu occupies the remaining two. Long range order parameter of Zn as function of temperature in $NiCu_2Zn$ is determined by neutron diffraction study [1983Weg] and compared with order parameters calculated by Kikuchi's Cluster Variation Method. Using anomalous scattering of synchrotron radiation, [1985Has] pointed out a short range ordering between Ni and Zn atoms and also between Zn and Cu atoms while a correlation of the opposite direction exists between Cu and Ni atoms. These results are consistent with the latter calculations of [1987Has] and with the prediction of ordering energies given by [1980Roo]. Both ordered structures $L1_0$ (AuCu type) and $L1_2$ ($AuCu_3$ type) were shown to have important consequences on the mechanical properties: yield stress, hardening and stacking fault energy of the $NiCu_2Zn$ alloy [1984Hos]. Monte-Carlo simulations based on effective interactions obtained from first principles calculations [1998Sim] reveal the existence of three ordered phases in $NiCu_2Zn$: a modified $L1_0$ (0-600 K), $L1_2$ (600-850 K) and a partially ordered (Cu,Zn)(Ni,Cu)-$L1_0$ (850-1200 K) which contradicts the generally accepted picture which assumes the existence of only two ordered phases.

An increase of resistivity was also measured during slow cooling of the alloy $Cu_3Ni_3Zn_2$, attributed to a long-range order, which was also detected by X-ray methods [1969Sch]. The alloy $Cu_3Ni_3Zn_2$ clearly falls in the α region and a long-range order of the type A_3B is assumed where Cu and Ni atoms are on the A sites and Zn atoms on the B sites. However, no crystallographic evidence is provided.

β-$Ni_xCu_{1-x}Zn$ alloys undergo a martensitic transformation from the CsCl type ordered cubic ($B2$ structure) to the AuCuI type tetragonal ($L1_0$ structure) [1976Shi]. The martensite $L1_0$ phase appears at room temperature when x < 0.325. The $B2$-$L1_0$ transition is also observed on the temperature elastic constants curves in β-$Ni_xCu_{1-x}Zn$.

Liquidus Surface

The liquidus surface shown Fig. 1 is based on the works of [1934Yam, 1935Sch]. It was adjusted to be consistent with the accepted binary systems and the Calphad assessments of [2003Mie] in the domain 0.3 < x_{Zn} < 0.7 and [2005Jia] in the zinc rich corner. No information concerning the monovariant lines in the zinc rich corner is available. The invariant equilibria from [1979Cha] are given in Table 3.

Isothermal Sections

The isothermal section at 850°C given in Fig. 2 is taken from [2003Mie]. The isothermal section at 775°C shown in Fig. 3 is a composite proposed by [1979Cha], based on the 775°C diagram given by [1935Sch] and on the isopleths given by [1934Yam]. The phase equilibria at 775°C are confirmed by the diffusion measurements carried out at this temperature in the single-phase α domain [1979Day] and in the two-phase α + β domain [1970Tay, 1971Coa, 1977Sis, 1977Wir]. The isoactivity lines in the α domain are from [1977Sis].

The isothermal section at 650°C presented in Fig. 4 is from [1973Lev] and takes into account the Calphad assessment of [2003Mie] carried out for x_{Zn} < 0.6. At low temperatures, α alloys undergo an ordering towards the composition $NiCu_2Zn$. The (α + $L1_2$) two-phase field calculated at 427°C is shown in Fig. 5. Below 335°C for the composition $Ni_{26}Cu_{47}Zn_{27}$ (325°C for the stoichiometric composition $NiCu_2Zn$) appears the $L1_0$ ordered phase as shown in Fig. 6. Figure 6 represents the α-$L1_2$-$L1_0$ equilibria at 327°C from [1982Roo], but data above 30 at.% Zn are not shown here, as they are not consistent with the accepted binary diagrams. Also it should be mentioned that the location of the $L1_0$ phase field in Fig. 6 covers the stoichiometric composition $NiCu_2Zn$, but according to the resistivity measuments reported in the same work [1982Roo] at this temperature the $L1_0$ phase field should be rather around the composition $Ni_{26}Cu_{47}Zn_{27}$. The isothermal sections calculated by [1982Roo] at 227and 127°C show the miscibility gap observed in the α solid solution at low temperatures. However these sections are not reproduced in the present evaluation, because they are in disagreement with the accepted binary diagrams Cu-Zn and Ni-Zn.

Temperature – Composition Sections

The cross section $Cu_{0.5}Ni_{0.5-x}Zn_x$ ($0.15 < x < 0.35$) showing α-$L1_2$-$L1_0$ equilibria and given in Fig. 7 was obtained through electrical resistivity measurements [1981Roo] and calculated with the tetrahedron approximation of the Kikuchi's cluster variation method [1980Roo]. The calculated equilibria where ordering occurs are in reasonable agreement with electrical resistivity measurements. Maximum critical temperature for the $L1_2$-α (A_3B-*fcc*) transition is 784 K (511°C) at an overall composition of $Cu_{47}Ni_{26}Zn_{27}$. The critical point for the $L1_0$-$L1_2$ (A_2BC-A_3B) transition has the same composition and occurs at 608 K (335°C). These critical temperatures are 10 K higher than the critical temperatures of the stoichiometric composition [1981Weg, 1982Roo].

Thermodynamics

The activity coefficient of zinc in α solid solution ($x_{Ni} < 0.4$, $x_{Zn} < 0.35$) was determined by vapor pressure measurements [1961Cha] and the partial molar quantities calculated at 727°C. The results confirm the existence of a short-range order in copper-zinc alloys and suggest that a long-range order exists in the Cu-Ni-Zn alloys associated with the composition $NiCu_2Zn$. Based on these measurements and available thermodynamic data for the three binary systems, [1977Sis] calculated the activities of Cu, Zn and Ni and the integral Gibbs energy of mixture at 775°C in the α and β domains. However, they used for their calculation the 775°C isotherm given by [1935Sch] which does not show the order-disorder transformation in the β region. Therefore, the activities in the β region are doubtful.
The activity of Zn in liquid Cu-Ni-Zn alloys have been measured at 1100 and 1200°C by an isopiestic method in the composition range $x_{Zn} < 0.09$ and $x_{Ni} < 0.08$ [1986Sug]. The first and second interaction parameters of Zn in liquid copper were determined as follows:

$$\varepsilon_{Zn}^{Ni} = \lim_{x_{Zn},\, x_{Ni} \to 0} \left(\frac{\partial \ln \gamma_{Zn}}{\partial x_{Ni}} \right) = -3.75 \text{ at } 1150°C \text{ and } -3.76 \text{ at } 1200°C$$

$$\rho_{Zn}^{Ni} = \frac{1}{2} \lim_{x_{Zn},\, x_{Ni} \to 0} \left(\frac{\partial^2 \ln \gamma_{Zn}}{\partial x_{Ni}^2} \right) = 4.68 \text{ at } 1150°C \text{ and } 4.47 \text{ at } 1200°C$$

$$\rho_{Zn}^{Ni,\,Zn} = \lim_{x_{Zn},\, x_{Ni} \to 0} \left(\frac{\partial^2 \ln \gamma_{Zn}}{\partial x_{Ni} \partial x_{Zn}} \right) = 15.1 \text{ at } 1150°C \text{ and } 1200°C$$

By equilibrating Cu-Zn solutions at 1200°C with Cu-Ni-Zn alloys, [1987Ryc1, 1987Ryc2] proposes:

$$\varepsilon_{Zn}^{Ni} = \lim_{x_{Zn},\, x_{Ni} \to 0} \left(\frac{\partial \ln \gamma_{Zn}}{\partial x_{Ni}} \right) = 2.4 \pm 2.8 \text{ at } 1200°C$$

However, the assumption of equilibrium between solid and liquid phases is questionable.

Notes on Materials Properties and Applications

Cu-Zn alloys are the base of materials offering exceptional combination of strength, formability, conductivity and resistance to softening and relaxation, and may be used for high current carrying connectors in the automotive industry [1987Puc]. Nickel acts as a copper replacement element in β brass [1912Car, 1926Sma] and is well known to enhance mechanical properties of Cu-Zn alloys such as yield strength [1968Bar], cold working [1912Gui, 1913Gui, 1991Mar] and resilience [1920Gui2] as well as surface properties [1980Ble]. Analogies have been observed between the mechanical behavior of austenitic steel and Cu-Ni-Zn alloys [1914Tho]: decrease of the grain size by increasing the nickel content [1924Pri, 1926Sma], recrystallization after cold working. Annealing improves mechanical properties of Nickel brasses ($Cu_{50}Zn_{45}Ni_5$) [1920Gui1, 1925Gui]; however, a loss of ductility is observed by overheating [1914Tho]. Tensile tests, compression tests, hardness, electrical resistance, cooling curves of as cast and annealed samples have been carried out by [1916Tho]. Structural hardening is always observed after annealing and quenching followed or not by a tempering [1925Gui, 1925Ost]. Alloys close to the composition $NiCu_2Zn$ were found to show an anomalous hardening effect [1966Phi] on quenching from 600°C and aging at 400°C. This effect is attributed to the lattice strains caused by clustering rather than to a long-range order hardening which is known to occur by annealing between 300 and 350°C [1980Ito, 1988Ito]. Ni reduces also the quantity of β constituent without affecting the hot-working properties of ordinary α-β brasses [1926Sma]. [1935Kih] investigated tensile properties like fluidity, shrinkage, pressure tightness and established correlations between composition, oxidation resistance, hardness and liquidus temperatures for alloys containing up to 30% Ni and 50% Zn.

[1974Mar] pointed out a nonuniformity of the anodic etching of polycrystalline bars of nickel β brasses. The rate of the anodic process on the (001) face is 5 times greater than on the (111) face and 3 times greater than on the (101) face. α/β duplex alloys present a superplastic behavior during tensile straining [1978Liv], whence nucleation and growth of cavities at the α/β boundaries leading to brittle superplastic fracture.

New technologies depend on a large extent on the electrical properties of copper and its alloys with Ni and Zn which play an important role in all communication systems [1990Seg]. These properties have been extensively investigated since [1922Voi, 1957Koe, 1961Phi, 1963Koe] who measured resistivity, Hall effect, thermoelectric effect and electrochemical properties. The combination of high electrical and thermal conductivity, corrosion resistance makes Cu-Ni-Zn alloys useful in various fields such as electronic, electrotechnic and computer industry [1988Pry].

The ordered phase is characterized by higher values of the electrical resistance and the temperature coefficient than disordered state. In both heating and cooling from an initial disordered state, the ordering process is accompanied by an increase of the electrical resistance, known as the K effect [1963Koe]. The electrical resistivity of Cu-Ni-Zn alloys increases during a low temperature anneal, phenomenon also attributed at the appearance of a “K state” that is a special short range ordering [1972Tho, 1973Hor, 1981Ara]. The electrical resistance may change in different way, depending on the conditions of heat treatment and the result may be interpreted by the superposition of two reversible kinetic processes: ordering-disordering and the deposition of a second phase. A maximum of order is observed for the composition $Cu_5Ni_4Zn_{3.5}$ [1988Gur]. Electrical conductivity, heat conductivity, heat capacity measurement have been used on $Cu_{65}Ni_{12}Zn_{23}$ alloys [1973Hor] to explore the influence of the short range ordering on the Debye temperature.

Various observations have been reported in α solid solutions. Stacking faults induced by cold working were investigated by [1977Hal, 1991Mar] from the detailed analysis of X-ray peak shift, peak asymmetry and peak broadening. *In situ* analysis of α(Ni,Cu,Zn) alloys [1977Sch] allow to identify precipitated particles with a cuboidal shape in a semi-coherent relationship with the matrix. These particles, whose lattice parameter is a = 847 pm are identified with an oxide of spinel structure. Disordered α specimens are more sensible to fire cracking than ordered ones [1978Sch]. However, the chemical composition of the alloy and the presence of impurities such as lead are more important than ordering phenomena.

Miscellaneous

Owing the large extent of the α, β and γ solid solutions, the ternary Cu-Ni-Zn system was extensively used for diffusion studies in ternary systems, first by [1940Glu] who investigated the Zn diffusion in Cu-Ni alloys at 630°C, then by [1977Sis, 1979Day, 1984Kim] who used the experimental observations of the diffusion paths in the Cu-Ni-Zn system to propose a general theory of the diffusion in ternary solid solutions.
The Zener relaxation in solid solutions provides a powerful tool to study atomic mobility at low temperatures. The Zener relaxation time τ_r is controlled by the rate of atomic movement and the temperature following: $\tau_r = \tau_o \exp(-Q_r/RT)$. For α alloys of nominal composition $Cu_{70}Ni_{10}Zn_{20}$, $Cu_{60}Ni_{10}Zn_{30}$, $Cu_{60}Ni_{20}Zn_{20}$, the preexponential factor is $\tau_o \approx 10^{-15.5\pm0.5}$ s and the activation energy $Q_r \approx 190 \pm 10$ kJ·mol^{-1} which is also the experimentally measured activation energies for the diffusion of Cu, Ni or Zn into the alloy [1976Ban]. Long range order near the $NiCu_2Zn$ composition have been described by two processes [1979Van]: a fast one involving the redistribution of the most mobile constituent, which is the usual Zener effect and a slow one involving a redistribution in the ordered phase. Using first principles together with the density functional theory of atomic short-range order, [1996Alt] calculates, for $NiCu_2Zn$, two ordered states at low temperatures in good agreement with experimental measurements. However, for Ni_2CuZn [1997Alt], the quality of the fit is much poorer.
Some results regarding solderability, surface roughness, brightness and bendability of tin coated copper alloys strips are reported by [1988Puc]. [1982Ste, 1986Zei] compare hardness of a classical $Cu_{62}Ni_{18}Zn_{20}$ alloy with the best copper alloys. [1974Sht] investigates partial relaxation process in ternary monophased Cu-Ni-Zn alloys by measuring internal friction and elastic deformation coefficients. The bulk modulus B of the $Cu_{25+x}Ni_{25-x}Zn_{50}$ may be evaluated by an empirical formula $B = \eta^2 V$ [2004Li] with an error of ± 16 %, where η is the electron density of the lattice and V is the volume of the lattice in m^3·mol^{-1}. A corrective parameter taking into account the enthalpy of formation may be introduced, which allows the evaluation of B with an error of ± 8%. The experimental values are B = 107.8 GPa, 103.1 GPa and 99.3 GPa for x = respectively 0, 10 and 20.
[1977Sis] investigated diffusion paths in the α and β monophased domains at 775°C. Intrinsic diffusion and interdiffusion coefficients were calculated from tracer diffusion coefficients and thermodynamic data. By using diffusion couples in the monophased α domain, [1979Day] identified zero flux planes, that are planes in which the interdiffusion flux of a component goes to zero. The composition of zero flux planes correspond to composition points of intersection of diffusion paths and isoactivity lines drawn to the terminal alloys of the couple. [1985Kan] by measuring diffusion profiles, calculation of interdiffusion fluxes, identified zero flux planes for individual components in the α domain of the quaternary Cu-Ni-Zn-Mn system. Diffusion in the α + β region at 775°C was investigated by [1970Tay] who described the morphology of the layers, and measured the diffusion paths by microprobe analysis. Morphological stability of the α/β interface at 775°C and diffusion coefficients in the composition range of interest (35 to 50 Zn and 0 to 10% Ni) were provided by [1971Coa]. Diffusion paths between a common γ cubic terminal alloy and a set of α alloys were also measured by [1977Wir]. All sets developed a β (*bcc*) phase with two interface: a planar β/γ interface and an α/β interface showing transitions from planar to non planar. The composition of either side of planar interface were consistent with those based on equilibrium tie lines.

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

Reference	Experimental Technique	Temperature/ Composition/ Phase Range Studied
[1908Taf]	Thermal analysis	The whole diagram, 0-1200°C
[1934Yam]	Thermal analysis	The whole diagram, 400-1300°C
[1935Sch]	Thermal analysis	The whole diagram, 0-1450°C
[1936Sch]	X-Ray investigation	The whole diagram, 298 K
[1952Haw]	α-β equilibrium, annealing and microscopic examination	4-12 at.% Ni, 36-48 at.% Zn, 672°C
[1960Cha]	Lattice parameters measurements	α solid solution (< 24 at.% Zn, < 25 at.% Ni), 298 K
[1960Koe]	Ordering determination by electrical resistance, Hall constant and X-Ray	Ni/Zn = 1, 35-70 at.% Cu, 400-700°C
[1961Cha]	Zinc activities determined from zinc vapor pressure measurements	α solid solutions (< 24 at.% Zn, < 25 at.% Ni), 1000 K
[1965Hir]	Long range order by neutron diffraction	$NiCu_2Zn$ annealed at 300°C
[1966Phi]	Long range order by neutron diffraction	$NiCu_2Zn$ quenched from 600°C and annealed at 400°C
[1969Bar]	Long range order by neutron diffraction	Ni/Zn = 1, 40-60 at.% Cu, 200-600°C
[1969Sch]	Long range order by electrical and X-Ray measurements	$Ni_3Cu_3Zn_2$ annealed at 600°C
[1979May]	Tie-lines determination by X-Ray measurements	(α+β) region: 30-50 at.% Zn, < 35 at.% Ni, 600°C
[1981Roo]	Order-disorder transition by electrical resistance measurements	50 at.% Cu, 15-35 at.% Zn, 250-500°C
[1981Veg]	X-Ray, parameter measurements, order-disorder transition	$NiCu_2Zn$, 200-800°C
[1981Weg]	Order-disorder transition by electron microscopy observations	50 at.% Cu, 20-30 at.% Zn, 350-500°C
[1982Roo]	Order-disorder transition by electrical resistance measurements	α domain, > 30 at.% Cu, 10-40 at.% Zn, 125-500°C

Reference	Experimental Technique	Temperature/ Composition/ Phase Range Studied
[1983May]	Tie-lines determination by X-Ray measurements	(α + β_1) region: 25-50 mass% Zn, < 55 mass% Cu, 600°C
[1983Weg]	Long range order by single crystal neutron diffraction	$NiCu_2Zn$ annealed between 300 and 500°C
[1985Has]	Atomic order by anomalous scattering of synchrotron radiation	$Cu_{0.47}Ni_{0.29}Zn_{0.24}$ annealed at 600°C
[1986Sug]	Zinc activity measurement in liquid alloy by an isopiestic method	Liquid Cu (< 9 at.% Zn, < 8 at.% Ni) 1100-1150°C
[1987Ryc1, 1987Ryc2]	Zinc activity measurement in liquid alloy by an isopiestic method	Liquid Cu (< 12 at.% Zn, < 10 at.% Ni), 1200°C
[2003Mie]	Calphad assessment	< 70 mass% Zn, 600-1400°C
[2005Jia]	Calphad assessment	The whole diagram, 600-1400°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α, (Ni,Cu,Zn)	*cF*4 $Fm\bar{3}m$		
$Cu_{0.5}Ni_{0.25}Zn_{0.25}$ 1100 - 501	Cu	a = 363.9	[1981Veg]
(Cu) < 1084.62		a = 361.46 a = 369.61	pure Cu at 25°C [1994Cha] 38.27 at.% Zn in solid (Cu) at 454°C [1997Von] 35.84 at.% Zn in solid (Cu) at 300°C
$Cu_{0.5}Ni_{0.5}$		a = 356.6	[1994Cha]
(Ni) < 1455		a = 352.410	pure Ni at 25°C [Mas2] 48.3 at.% Zn in solid Ni at 1040°C [Mas2]
η, (Zn) < 419.58	*hP*2 $P6_3/mmc$ Mg	a = 266.50 c = 494.70	pure Zn at 25°C Dissolves 2.83 at.% Cu at 425°C [Mas2] Dissolves 0.2 at.% Ni at 418.5°C [Mas2]
β, (Ni,Cu)Zn	*cP*2 $Pm\bar{3}m$		
NiZn 1040 - 675	CsCl	a = 290.83	High temperature phase of β Ni-Zn Lattice parameter from [V-C2] at 890°C
CuZn < 468		a = 295.9	Low temperature phase of β Cu-Zn Lattice parameter at 49.5 at.% Zn [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
β_1, NiZn < 810	*tP*2 *P*4/*mmm* AuCu	*a* = 274.1	45% Zn [1983May] Ordered form of β Ni-Zn ($L1_0$ superstructure)
β', CuZn 902 - 454	*cI*2 $Im\bar{3}m$ W	 *a* = 295.39	High temperature form of β-CuZn (labelled β in binary diagrams) Lattice parameter at 47.5 at.% Zn [V-C2]
γ	*cI*52 $I\bar{4}3m$		
Cu_5Zn_8 < 835	Cu_5Zn_8	*a* = 893.57	57.7 to 70.6 at.% Zn in the Cu-Zn binary Lattice parameter from [V-C2]
Ni_4Zn_{22} < 881		*a* = 893.57	70 to 85 at.% Zn in the Ni-Zn binary Lattice parameter for Ni_4Zn_{22} [1993Ham] at 500°C
δ, $CuZn_3$ 700 - 560	*hP*3 $P\bar{6}$ $CuZn_3$	 *a* = 427.5 *c* = 259.0	High temperature phase Lattice parameters from [V-C2] at 500°C
ε, $CuZn_4$ < 598	*hP*2 $P6_3/mmc$ Mg	 *a* = 274.18 *c* = 429.39	78 to 88 at.% Zn [Mas2] Lattice parameters from [V-C2]
ζ, (Ni-Zn) < 490	*mC*6 *C*2/*m* $CoZn_{13}$	 *a* = 1337.6 *b* = 751.1 *c* = 762.7 β = 113.256	~89 at.% Zn (labelled δ in the Ni-Zn binary) Lattice parameters for Ni_3Zn_{22} [1993Ham] at 500°C
* $NiCu_2Zn$(h) 501 - 325	*cP*4 $Pm\bar{3}m$ $AuCu_3$	*a* = 363.7	at 400°C [1981Veg] Ordered form ($L1_2$ superstructure) of the α phase [1979Hos, 1981Weg]
* $NiCu_2Zn$(r) < 325	*tP*2 *P*4/*mmm* AuCu	*a* = 363.5 *c* ≈ 363.5	at 300°C [1981Veg] Ordered form ($L1_0$ superstructure) of the α phase [1979Hos, 1981Roo]

Table 3: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Ni	Cu	Zn
L + α + β ⇌ β'	935	P	L	22.67	26.93	50.4
L + β ⇌ β' + γ	860	U	L	24.88	11.99	63.13

Fig. 1: Cu-Ni-Zn.
Liquidus surface projection

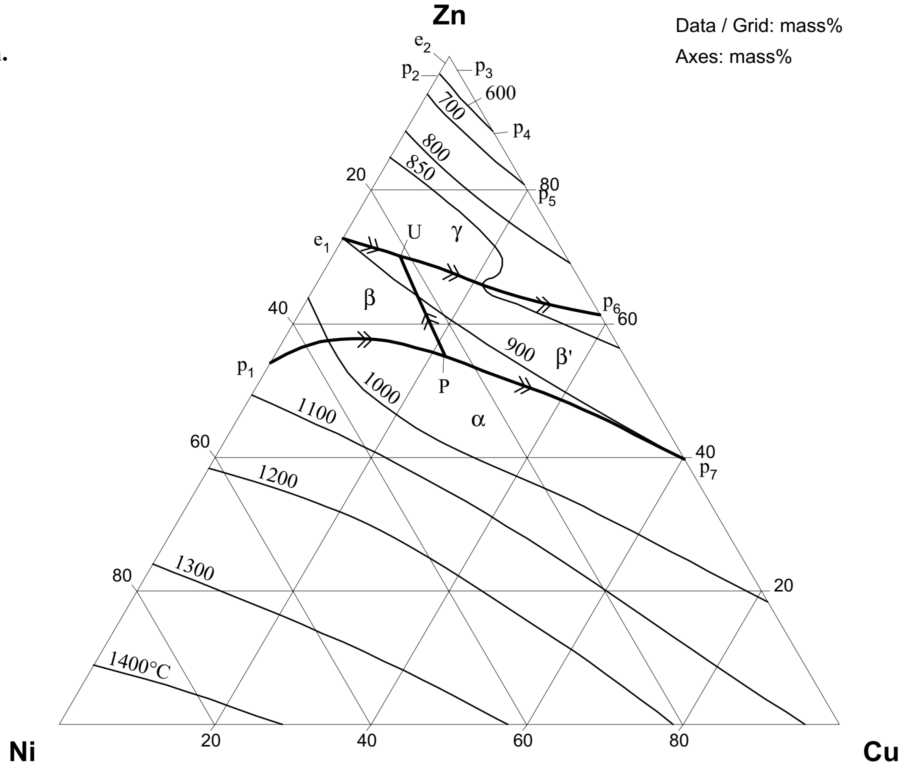


Fig. 2: Cu-Ni-Zn.
Isothermal section at 850°C

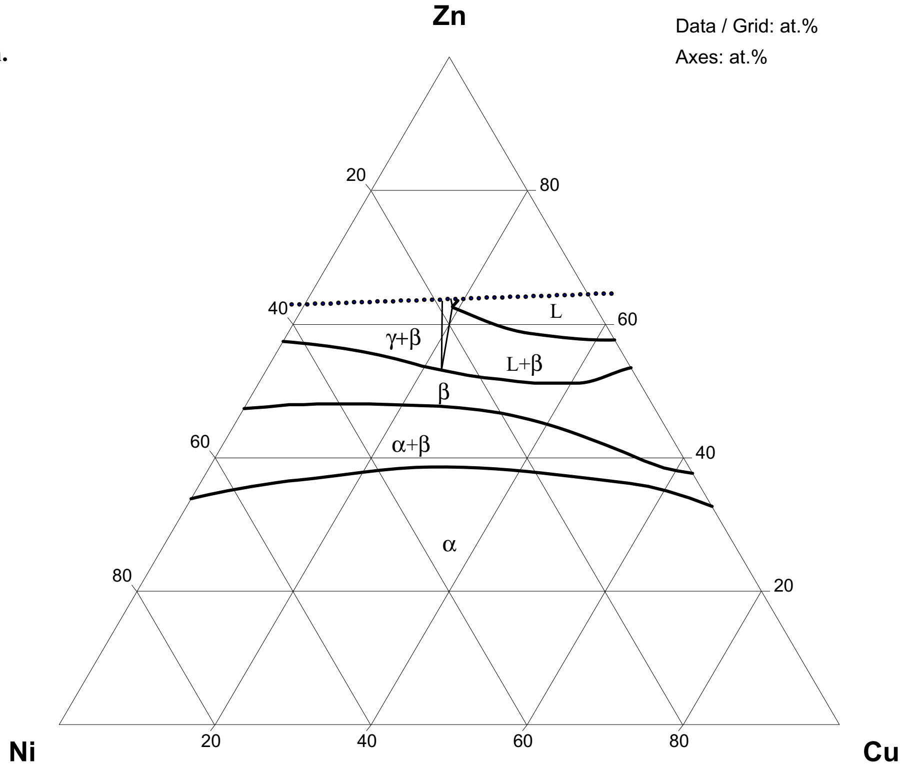


Fig. 3: Cu-Ni-Zn.
Isothermal section at 775°C showing isoactivity lines in α solid solution from [1977Sis]

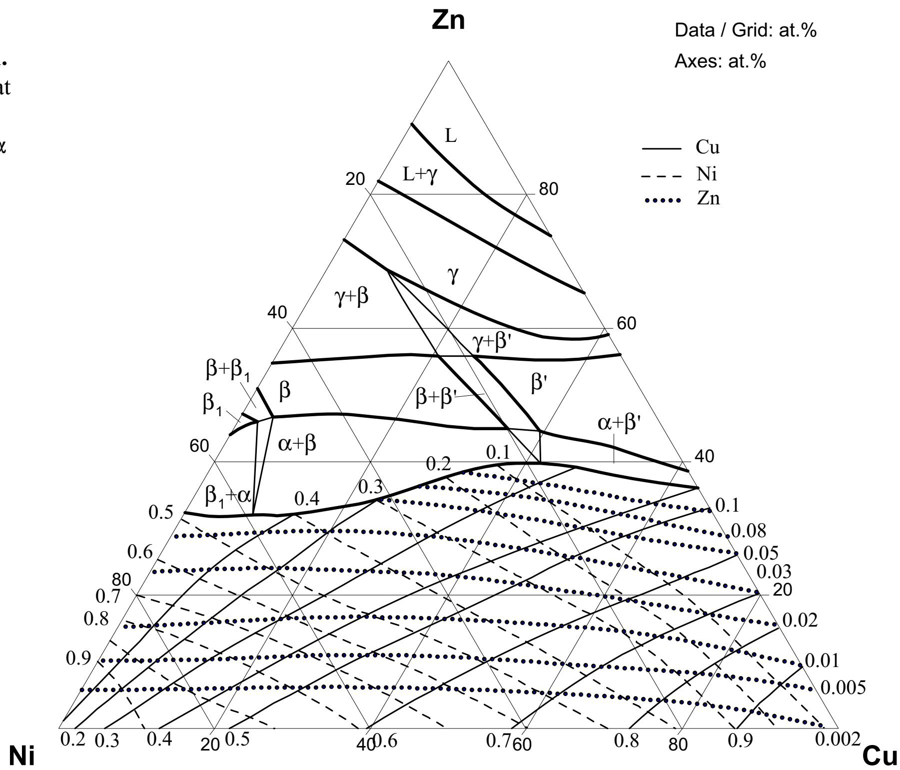
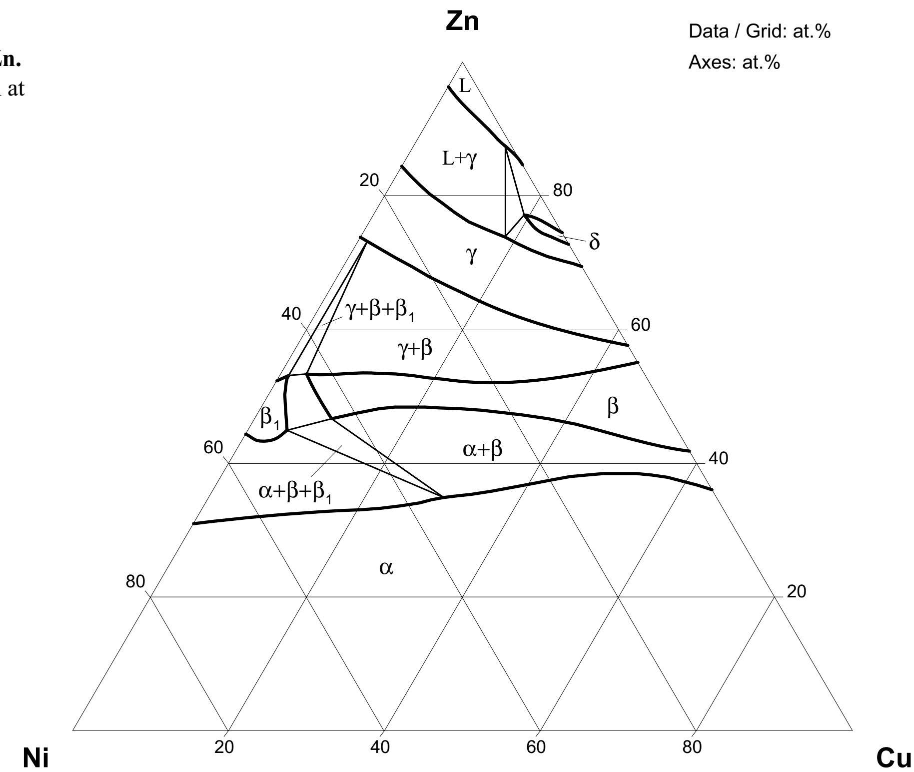


Fig. 4: Cu-Ni-Zn.
Isothermal section at 650°C



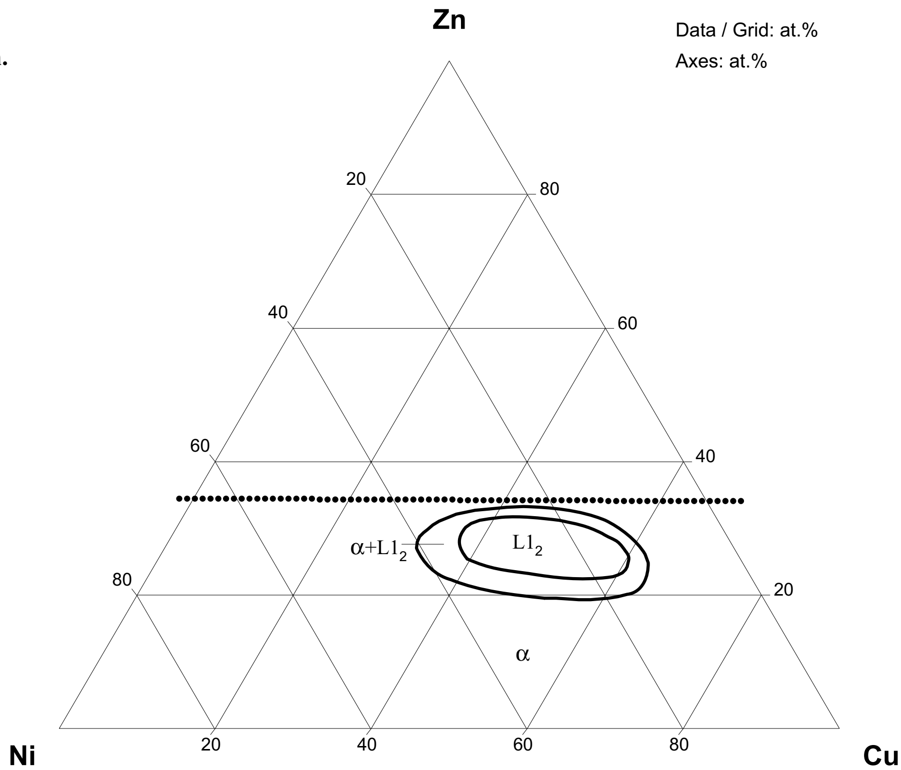


Fig. 5: Cu-Ni-Zn. Calculated partial isothermal section at 427°C

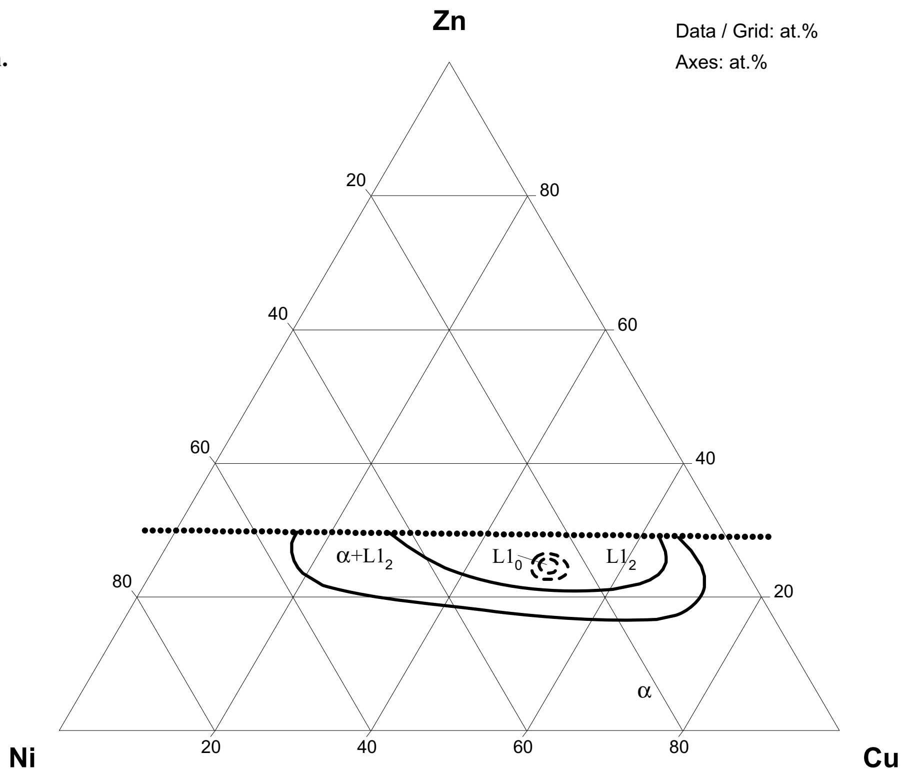


Fig. 6: Cu-Ni-Zn. Calculated partial isothermal section at 327°C

Fig. 7: Cu-Ni-Zn.
Vertical section
$Cu_{0.5}Ni_{0.5-x}Zn_x$
$(0.15 < x < 0.35)$