

## Aluminium – Copper – Zinc

*Gautam Ghosh and Jan van Humbeeck, updated by Pierre Perrot*

### Literature Data

This ternary system contains many technologically important alloys, present and future applications. Accordingly, the phase equilibria of the system have been reviewed [1934Fus, 1943Mon, 1952Han, 1961Phi, 1969Gue, 1973Wil, 1976Mon, 1979Cha] from time to time. Köster [1941Koe3] was the first to report the entire liquidus surface and it was subsequently modified by [1960Arn2]. Isothermal sections in the temperature range of 200 to 700°C have been determined by several researchers [1932Bau1, 1932Bau2, 1932Bau3, 1940Geb, 1941Geb1, 1941Koe1, 1941Koe2, 1941Koe3, 1942Geb, 1942Koe, 1960Arn1, 1960Arn2]. After a gap of four decades, [1980Mur] reinvestigated the solid state equilibria, using 31 ternary alloys containing about 40.8 mass% Cu, in the temperature range of 250 to 350°C by means of metallography, X-ray diffraction and electron probe microanalysis. Thermodynamic descriptions of the system were mainly carried out by [1998Lia, 2002Mie]. Except for the sequence of solid state phase transformations, the basic features of the phase equilibria in all of the above investigations are consistent with each other. The present evaluation continues the detailed critical review made by [1992Gho], which took into account the data published until the year 1988.

Al–Cu–Zn alloys exhibit high damping capacity, shape memory effects and super elasticity which allows a wide variety of possible use. The physical properties are associated with the reversible thermo-elastic martensitic transformation [1987Lon, 1987Sca, 1988Mun, 1988Yev, 1990Gui, 1992Gui, 1993Lex, 1994Bou, 1995Pri1, 1995Pri2, 1997Zha, 1998Buj, 1999Ago1, 1999Lon, 2000Pel, 2000Zel]. So, interest in these materials is grown and a large amount of literature is devoted to their physical properties.

The enthalpy of formation of the ternary phase  $\tau'$  has been measured by dissolution calorimetry [2000Leg]. Calphad assessment has been carried out by [1998Lia, 2002Che, 2002Mie]. [2000Kra] calculated solidification maps below the solidus at different cooling rates.

### Binary Systems

The edge binary systems were recently critically evaluated, Al–Cu by [2003Gro], Al–Zn by [2003Per] and Cu–Zn by [2003Leb] in the MSIT Binary Evaluation Program. These works are accepted here.

### Solid Phases

The maximum solid solubility of Cu in ( $\alpha$ Al) is up to 5.5 mass% in absence of Zn, and that of Zn is up to 83.1 mass% in absence of Cu. In equilibrium with  $\theta$  the Cu solubility in (Al) increases with addition of Zn, whereas in the ( $\alpha$ Al)+ $\tau$  two phase field it decreases with increasing Zn content. The solid solubility limits of Cu and Zn in (Al) are shown in Fig. 1 [1961Phi]. Within the composition range covered in Fig. 1, the locus of the apex of the ( $\alpha$ Al)+ $\theta$ + $\tau$  three-phase field is also shown. The apex of the ( $\alpha$ Al)+ $\tau$ +( $\eta$ Zn) three-phase field was not given by [1961Phi]; it is estimated in Fig. 1 and given by a dashed line. The solid solubilities of Cu in (Al), given by [1942Geb] at 350, 300 and 240°C agree reasonably well with those of [1961Phi]. However, the solid solubility of Zn in (Al) given by [1942Geb] are systematically higher than those of [1961Phi]. [1941Koe1] reported that (Al) contains 1.5 mass% Cu and 33.5 mass% Zn when it is in equilibrium with  $\theta$  and  $\tau$  phases at 350°C (annealed for 336 h), whereas [1942Geb] reported the composition of (Al) to be about 1.5 mass% Cu and 43.0 mass% Zn after annealing at the same temperature for 1680 h. Hume-Rothery [1948Hum] discussed the solid solubility limits of Al and Zn in (Cu) in terms of the electron concentration factor. He noticed that, when Al is added to Cu–Zn alloys, the solubility range of the (Cu) phase against  $\beta$  remains at a constant electron concentration over a wide range of composition, whereas when Zn is added to Al–Cu alloys there is an immediate departure from the simple electron concentration rule. The solid solubility of Al and Cu in (Zn) were reported by [1936Bur, 1940Geb, 1940Loe, 1941Geb1, 1942Geb, 1949Geb] and [1980Mur]. The maximum solubility are about 1.3 mass%

Al and 2.8 mass% Cu at 375°C and 0.8 mass% Al and 1.7 mass% Cu at 275°C. The saturation concentrations of Al and Cu in (Zn) [1940Loe], as a function of temperature, are listed in Table 3. It should be noted that the solubility found by [1940Geb, 1940Loe, 1941Geb1] and [1942Geb] agree well. Those of [1980Mur] indicate a higher Cu solubility. The  $\beta$  phase shows a continuous series of solid solutions from  $\text{Cu}_3\text{Al}$  to  $\text{CuZn}$ ; it has a disordered  $cI2$ , W type structure at high temperatures. The stability of the  $\beta$  phase alloys decreases with decreasing temperature, and centers around an electron concentration of 1.48 for both the binary and ternary alloys. [1948Ray] predicted the lower temperature limit of the stability of the ternary  $\beta$  phase in terms of an effective size factor. At lower temperatures, the  $\beta$  phase undergoes ordering to a CsCl or  $\text{Fe}_3\text{Si}$  type superlattice depending on the alloy composition. Comprehensive reviews of the stability of the  $\beta$  phase and the effect of ordering on the subsequent martensitic transformation can be found elsewhere [1977Rap, 1978Sin, 1980Ahl, 1986Ahl1, 1986Ahl2, 1995Ahl]. Also the  $\gamma$ -brass phases form a continuous series of solid solutions at high temperatures [1941Koe3] which shows a miscibility gap below about 400°C. The behavior of the binary and ternary  $\gamma$  phases has been investigated by a number of experimental techniques, such as resistivity and thermo-emf [1972Kan1, 1973Ash], X-ray diffraction [1972Kan2, 1974Ash, 1988Kis], and thermo-graphymetry and dilatometry [1974Umu]. The solid solubilities of Al in  $\text{Cu}_5\text{Zn}_8$  at 20 and 350°C are about 3.5 and 7.0 mass% Al, respectively [1973Ash]. At the same temperatures, the  $\gamma_1$  phases of the Al–Cu binary system dissolve about 30 mass% Zn [1973Ash]. With the addition of Al in  $\text{Cu}_5\text{Zn}_8$ , the lattice parameter is reported to decrease continuously [1928Bra]. [1941Koe2] and [1941Koe3] assumed  $\eta$ ,  $\tau$  and  $\tau'$  to have one common field of homogeneity at higher temperatures. The same was assumed for the  $\epsilon_2$  and  $\delta$  phases. The phases  $\eta$  and  $\tau$  were shown to be different phases at any temperature by [1960Arn2]. The phases  $\epsilon_2$  and  $\delta$  have such different unit cells that it is very improbable to have one continuous series of solid solutions between them. The  $\epsilon_2$  phase of the Al–Cu binary system was assumed to be completely soluble with the  $\delta$  phase of the Cu–Zn binary system above about 680°C [1941Koe3] and [1960Arn2]. Below this temperature, separation occurs through the intrusion of equilibrium between the  $\gamma$  and  $\tau$  phases. The  $\theta$  phase of the Al–Cu binary system can dissolve up to 2 to 3 mass% Zn with little change in lattice parameter and properties [1941Koe3]. The  $\epsilon$  phase of the Cu–Zn binary system can dissolve up to about 12 mass% Al [1941Koe3] at about 600°C, and this solid solubility decreases with decreasing temperature. The ternary  $\tau$  phase, below 250°C has two separate ranges of homogeneity  $\tau$  and  $\tau'$  [1960Arn1] due to the maximum of the three-phase field  $\tau+\epsilon+\eta_1$  [1941Koe1] and [1941Koe2]. The different structures do not exclude a single range of homogeneity at higher temperatures since the  $hR9$  structure of  $\tau'$  is a superstructure of the CsCl type with ordered vacancies. It may be formed from a CsCl structure with random distribution of vacancies by a second order transformation. The possible formulas of  $\tau$  and  $\tau'$  phases can be represented as  $\text{Cu}_5\text{Zn}_2\text{Al}_3$  and  $\text{Cu}_3\text{ZnAl}_4$ , respectively. The  $\tau$  phase is formed by a univariant peritectic reaction between  $\epsilon_2$  and liquid at about 740°C. The ternary  $\tau'$  phase appears between 600 and 550°C near the Al-rich end of the homogeneity range of the  $\tau$  phase. At 550°C, the  $\tau$  phase has a wide range of homogeneity (Fig. 7). At 200°C, the  $\tau$  phase has a relatively narrow range of homogeneity surrounding 13 mass% Al, 56 mass% Cu and 31 mass% Zn and the  $\tau'$  phase also has a narrow homogeneity range surrounding 32 mass% Al, 56 mass% Cu and 12 mass% Zn (Fig. 13). A metastable X phase has been reported [1988DeG] in both Al–Cu and ternary  $\beta$  phase alloys which were quenched from 900 to 950°C to room temperature or in ice water, and subsequently annealed at 300 to 348°C. This X phase has a long period superlattice structure and can be described in terms of 18R or monoclinic unit cell. The details of the crystal structures and the lattice parameters of all stable solid phases are listed in Table 1.

### Invariant Equilibria

Figures 2a and 2b show the reaction scheme based on the investigations of [1940Geb, 1941Geb1, 1941Geb2, 1941Koe3, 1942Geb, 1949Geb, 1960Arn1, 1960Arn2] and [1980Mur]. The univariant reaction,  $p_8$ , occurs at about 740°C and feeds both the invariant reactions  $U_4$  and  $U_6$ . Some of the four-phase equilibria involving the compositions of the phases are listed in Table 2 after [1940Geb, 1941Geb1, 1941Geb2, 1941Koe3, 1942Geb, 1942Wei, 1949Geb, 1960Arn1, 1960Arn2, 1967Coo] and [1980Mur]. For most of the invariant reactions, both the temperatures and the compositions of the invariant points as

reported by [1925Han] and [1927Nis] differ substantially from the above authors. The sequence of the solid state reactions in the temperature range of 275 to 350°C is adopted from [1980Mur]. The solid state reactions in the temperature range of 268 to 288°C proposed by [1941Geb1] and [1941Geb2] have been experimentally verified by [1980Mur]. This involves three U type reactions instead of one U type and one E type reaction proposed by [1960Arn2]. To comply with the accepted Al–Zn binary phase diagram, the temperature of the four-phase reaction  $U_{12}$  is taken as 278°C instead of 276°C as proposed by [1980Mur]. In contrast to the results of [1941Koe3] and [1980Mur], [1969Cia] reported that the four-phase reaction  $U_{14}$ ,  $(Al)+\epsilon\rightleftharpoons\tau'+(Zn)$ , can take place at as low as 50°C. In the original papers the reaction scheme was simplified, as the phases  $\gamma_0$  and  $\gamma_1$ ,  $\epsilon_1$ ,  $\epsilon_2$  and  $\delta$ ,  $\eta_1$  and  $\eta_2$ ,  $\zeta_1$  and  $\zeta_2$  were not distinguished and the invariant equilibria evolving from solid state three-phase reactions containing  $\alpha_2$  and  $\delta$  phases of the Al–Cu system were neglected. In Figs. 2a and 2b the phases  $\gamma_0$  and  $\gamma_1$ ,  $\epsilon_1$ ,  $\epsilon_2$  and  $\delta$  are tentatively distinguished. It must be emphasized that the reaction scheme in Figs. 2a and 2b is still incomplete as the participation of some binary solid state invariant reactions has not been considered;  $\eta_1$  and  $\eta_2$  as well as  $\zeta_1$  and  $\zeta_2$ , are not distinguished and are called  $\eta_1$  and  $\zeta_1$ , respectively. Nevertheless, the assessed reaction scheme is consistent with the experimental phase diagrams.

### Liquidus Surface

Figure 3 shows the liquidus surface after [1941Koe2] and [1960Arn2] and the monovariant curves separating different areas of primary crystallization. The valley projection not yet determined are given tentatively by dashed lines. [1911Lev] and [1912Lev] reported the primary crystallization temperature of a number of ternary alloys, but their results differ significantly from [1941Koe2] and [1960Arn2]. The partial liquidus surface determined by the earlier workers [1912Car, 1919Jar, 1920Ros, 1921Hau, 1925Han, 1927Nis] agree only qualitatively with the results of [1941Koe2] and [1960Arn2]. Even though [1926Nis] and [1927Nis] performed a thorough investigation of the Al–Cu–Zn phase equilibria, some of their results concerning the liquidus surface could not be reproduced later by [1928Ham]. The liquidus surface of the Zn-corner reported by [1957Wat] does not agree with those of [1941Koe1] and [1960Arn2]. Approximate isotherms at 50 K intervals are also shown in Fig. 3. The Cu-rich part of the system was optimized by [2002Mie]. The calculated liquidus surface ( $x_{Zn} < 0.5$ ,  $x_{Al} < 0.35$ ) agrees well with the experimental one represented in Fig. 1.

### Isothermal Sections

The isothermal sections at 700°C [1941Koe2, 1960Arn2], 650°C [1960Arn2], 600°C [1941Koe2, 1960Arn2], 550°C [1941Koe2, 1960Arn2], 500°C [1941Koe2], 400°C [1941Koe2], 350°C [1941Koe1, 1941Koe2, 1942Geb, 1960Arn1], 300°C [1942Geb], 240°C [1942Geb] and 200°C [1942Koe, 1960Arn1] are shown in Figs. 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13, respectively. The Cu-rich regions are particularly derived from [1932Bau1, 1932Bau2, 1932Bau3, 1970Fle] and the Al- and Zn-rich regions are derived from [1940Geb, 1941Geb1, 1942Geb, 1949Geb] and [1980Mur]. The partial isotherms at the Zn-corner reported by [1920Ros] and [1921Hau] in the temperature range of 200 to 400°C and those for other alloys by [1925Han] at 370 and 385°C agree only qualitatively with the results of the above authors. The isothermal section at 700°C (Fig. 4) shows the continuous solid solutions  $\beta$  (between  $\beta$  of Al–Cu binary system and  $\beta$  of Cu–Zn binary system) and  $\gamma$  (between  $\gamma$  of Al–Cu binary system and  $\gamma$  of Cu–Zn binary system). In Fig. 4, the phases  $\epsilon_2$  and  $\delta$  are tentatively distinguished by dashed lines. Figure 7 shows the isothermal section at 550°C. Here, the ternary phase  $\tau'$  appears in the Al-rich region of the  $\tau$  phase field. Even though two different superstructures, for  $\tau$  and  $\tau'$  phases, have been reported, no two-phase field has been detected [1941Koe1, 1941Koe2]. The isothermal sections shown above are also consistent with the results of  $\beta$  phase decomposition studies by several authors [1934Ful, 1970Fle, 1984Man, 1986Myk, 1986Yan]. Below 350°C, the Cu-rich portion of the isothermal sections are still in doubt. In the isothermal sections, minor adjustments have been made to comply with the accepted binary phase diagrams. The liquidus isotherms in Figs. 4, 5, 6, 7, 8 and 9 are adjusted to those given in Fig. 3. (Al)' and (Al)'' correspond to the de-mixing of ( $\alpha$ Al) below 352°C.

## Temperature – Composition Sections

A large number of temperature-concentration diagrams, cutting vertically through the ternary phase diagram are reported as isopleths or polythermal sections, e.g. by [1919Jar], and by [1919Sch] at constant Cu contents of 2, 4, 6, 8 and 10 mass% Cu. [1921Hau] determined the isopleths at 1, 2, 3, 4, 5, 7, and 9 mass% Cu and also at 2, 4, 6, 8, 10, 12 and 15 mass% Al. [1925Han] determined the isopleths at 5, 10, 15, 20 and 25 mass% Cu. [1926Nis] reported the polythermal sections at 1, 2, 3, 5, 7.5 and 10 mass% Cu. [1949Geb] reported three isopleths at 1, 2 and 3 mass% Cu. [1960Arn2] determined two isopleths at 10 and 20 at.% Zn. [1957Wat] determined three polythermal sections at 2.5, 5.0 and 10.0 mass% Cu. The earlier results [1919Jar, 1919Sch, 1921Hau, 1925Han, 1926Nis] agree only qualitatively with each other. In general, there is substantial disagreement between the earlier results [1919Jar, 1919Sch, 1921Hau, 1925Han, 1926Nis] and later investigations by [1949Geb, 1957Wat] and [1960Arn2] which are considered to be accurate and reliable. However all data have been considered in the course of this critical evaluation.

## Thermodynamics

Heat capacities of the  $\beta_1$  and  $\beta'_1$  phases has been measured on the Cu-13.9Zn-17.3Al (at.%) [1988Tsu]. [1993Ahl] evaluates the phase stabilities of martensitic and equilibrium phases and discusses the contribution which controls the Gibbs energy of the different phases. The first expressions of the chemical potentials changes were proposed by [1988Kuz] for the transition  $\alpha \rightleftharpoons$  liquid and by [1994Hsu] for the martensitic transformations of the  $\beta$  phase. The thermodynamic properties of the ternary alloys containing 25 to 62 at.% Al have been determined in [1994Van] by emf measurements between 420 and 920°C by an aluminum concentration cell. [1998Lia] presents a thermodynamic description of the Al-Cu-Zn system with an emphasis on the Al-Zn binary. The descriptions of the binary systems accepted by [1998Lia] are those of [1993Che] for Al-Zn and [1993Kow] for Cu-Zn. The liquid, fcc-(Cu), fcc-(Al), cph-(Zn),  $\beta$  and  $\gamma$  disordered solutions are modeled by a disordered solution with the introduction of a ternary interaction parameter. The two binary  $\gamma$  phases:  $\gamma\text{Al}_4\text{Cu}_9$  and  $\gamma\text{Cu}_5\text{Zn}_8$ , isomorphous and forming a continuous solid solution are of a rather complex structure.  $\gamma\text{Cu}_5\text{Zn}_8$  has a superlattice in which one unit cell corresponds to 27 unit cells of the W type;  $\gamma\text{Al}_4\text{Cu}_9$  is an ordered variant of that structure in which every Zn position of  $\text{Cu}_5\text{Zn}_8$  splits into two positions, one occupied by Al, the other by Cu. Models with 4 to 6 sublattices have been proposed for the solid solution [2000Ans, 2000Sat]. The model used by [1998Lia] is a simple Redlich-Kister description with hypothetical lattice stabilities used for the  $\gamma$  phases and does not take into account the ordering; it describes reasonably well the solubility range. The  $\gamma_0$  phase was modeled as  $\text{Cu}_8(\text{Cu,Zn,Al})_1(\text{Zn,Al})_4$  and the ternary  $\tau$   $\text{Cu}_5\text{Zn}_2\text{Al}_3$  as  $(\text{Al,Cu})_1\text{Cu}_4\text{ZnAl}_4$  that is as formed by two hypothetical stoichiometric compounds  $\text{Cu}_4\text{ZnAl}_5$  and  $\text{Cu}_5\text{ZnAl}_4$ . Using the Pandat software, [2001Che, 2002Che] propose an isothermal section of the diagram at 277°C (550 K) showing a miscibility gap in the fcc-(Cu) solid solution which does not appear in the experimental diagrams drawn between 200 and 300°C (Figs. 11, 12 and 13).

## Notes on Materials Properties and Applications

Al-Cu-Zn based alloys are important materials with shape-memory effect, more economic than Ni-Ti alloys [1997Zha]. In addition to the martensitic transformation ensuring shape-memory effect [1995Gue, 1999Lov], these alloys are characterized by ordering occurring in the  $\beta$  phase after annealing at 450°C and below. Before turning into martensite, the parent phase  $\beta$  (austenite) undergoes an ordering reaction which transforms the unit cell  $\beta$  (A2) into ordered  $\beta_1$  ( $\text{L2}_1$ ) or  $\beta_2\text{CsCl}$ . During the direct martensitic transformation, the above parent phases change respectively into  $\beta'_1$  (monoclinic) and  $\beta'_2$  (orthorhombic) martensites [1995Cha, 1998Buj]. Between 300 and 600°C, the  $\beta$  phase can decompose by the following reaction:  $\beta \rightleftharpoons (\alpha\text{Cu}) + \gamma\text{Cu}_5\text{Zn}_8$  [2000Zel]. The heat exchange associated with the martensitic transformation has been recorded for three alloy compositions, Cu-24.8Zn-9.2Al at.% [1995Cha], Cu-16.49Zn-15.75Al at.% (alloy R) [2000Pel] and Cu-8.83Zn-22.09Al at.% (alloy H) [2000Pel]. On cooling, the martensitic transformation starts at  $M_S$  and is completed at  $M_F$ ; on heating, the reverse transformation (austenitization),

starts at  $A_S$  and terminates at  $A_F$ . The temperature intervals ( $M_S - M_F$ ) and ( $A_F - A_S$ ) for the phase transformations depend on the martensitic structure, but not on the grain size. A similar dependence applies for the width of the hysteresis ( $A_F - M_S$ ).

The martensitic transformations has been investigated by various methods, recording the nuclear magnetic resonance [1991Dim], measuring the associated caloric effects [1988Mun, 1995Cha, 1998Wei, 2000Pel] and observing the response of the material's structure in X-ray diffraction and electron microscopy [1989Tol, 1998Buj, 2000Dor, 2000Zel]. One of the resulting conclusions is that the relative stabilities of different martensitic phases are related to the lattice distortion [1992Ahl, 1992Pel, 1992Sau, 1995Sau, 1995Ahl].

Other important features such as the influence of quenching and aging on the transformation temperatures were investigated by [1988Ara, 1989Cha, 1994Wu, 1998Man]. [1990Gui] and [1996Gar] studied the influence of compositional changes on the transformation temperatures. Effects on the transformations attributed to the stress-state of the material were studied by [1992Ame, 1995Isa, 1998Gal]. The work of [2001Bek] investigates the influence of pressure, up to 1.5 GPa.

The Gibbs energy of the martensitic transformation of both thermal and mechanical origin has been evaluated by [1988Ort, 1991Gui1, 1991Gui2]. [1999Ago2] developed a thermo-mechanical model allowing the simulation of the shape-memory effect on Cu-14.1Zn-17.0Al (at.%). Point defects in  $\beta$ Cu-Zn-Al single crystals alloys have been investigated by means of positron lifetime spectroscopy [1997Som, 1999Rom]. The formation and growth of  $\alpha_1$  plates from a  $\beta'$  matrix by a bainitic transformation has been studied by [1992Tak, 1994Men]. The shape memory effect has also been observed in alloys with dual phase  $\alpha - \beta'$  structure, obtained by quenching from the equilibrium  $\alpha - \beta$  [1999Lon]. Martensites in shape-memory alloys often exhibit unusual pseudo-elasticity referred to as the rubber-like behavior which has been investigated by [1987Sak, 1995Pri1, 1995Pri2, 1995Tsu, 2000Yaw] and thermodynamic models [1993Lex, 1994Bou] as well as thermo-mechanical models [1999Ago2] has been proposed.

Small Cu-additions to as-cast Al-Zn alloys close to the eutectoid composition show a relatively low ductility but also instabilities [1992Cia], which can be reduced by relatively simple heat treatments [1992Bob].

### Miscellaneous

[1986Sug] reported the chemical activity of Zn in liquid Al-Cu-Zn alloys at 1150 and 1100°C in the composition range  $x_{Zn} < 0.09$  and  $x_{Al} \leq 0.08$ . [1964Day] determined the solid/liquid distribution coefficients by centrifugal method in Al-rich and Zn-rich alloys. The partition coefficients are reported to be consistent with the phase diagram features.

As early as in the beginning 20<sup>th</sup> century [1905Gui] and [1906Gui] performed systematic studies of replacing Zn by Al, Fe, Mg, Mn, P, Pb, Sb, Si and Sn in a number of Cu-Zn brasses. They determined the volume fraction of the  $\beta$  and  $\gamma$  phases in Cu-Zn alloys and their mechanical properties with the addition of these alloying elements. Comparable systematic studies were made by [1925Sma] replacing Zn by Al, Fe, Ni and Sn in Cu-Zn brasses. Similar alloy development studies, regarding the effect of Si and Sb on the microstructure of Al-Cu-Zn bronzes, were also performed by [1930Sev]. All these laborious alloy development studies were performed by carefully examining the microstructure and determining the mechanical properties.

[2001Liu] investigated the influence of zinc and other elements on the  $\alpha$  (fcc),  $\beta$  (bcc) and  $\alpha$ (Cu)  $\gamma$ Cu<sub>9</sub>Al<sub>4</sub> equilibrium in the Al-Cu system and develop a quantitative method to determine the effect of the alloying elements on the two-phase microstructure. [2001Zhu1] analyses by electron back-scatter diffraction the microstructure of an alloy Zn85-Cu11-Al4 (mass%) in which both hexagonal phases ( $\eta$ Zn) and  $\epsilon$  are present. The microstructure evolution in Zn76-Al22-Cu2 and Zn86-Al11-Cu3 (mass%) alloys during ageing between 100 and 200°C were followed respectively by [2000Dor] and [2001Zhu2]. The evidence of a spinodal decomposition of the ( $\eta$ Zn) phase and the occurrence of a four phase reaction  $\alpha + \epsilon \rightleftharpoons \tau + \eta$  is shown. Prolonged ageing causes the disordered  $\tau$  phase to transform into an ordered  $\tau'$ , which confirms previous observations made by [1999Zhu]. The measured composition of the  $\tau'$  phase 57.7Al-34.9Cu-7.4Zn (at.%) agrees with the composition given by [1975Mur] and is incorporated in the Figs. 7 to 13.

Mechanical alloying of Al-Cu-Zn alloys [1998Lop] allows to form metastable phases such as ternary compounds, supersaturated solutions and also amorphous alloys; this opens another large spectrum of possible applications for this ternary system.

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**Table 1:** Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
( $\alpha$ Al) $\leq 660.452$	$cF4$ $Fm\bar{3}m$ Cu	$a = 404.96$	pure Al at 25°C, [Mas2] dissolves up to 2.48 at.% Cu at 548.2°C [2003Gro]
( $\alpha$ Cu) $\leq 1084.87$	$cF4$ $Fm\bar{3}m$ Cu	$a = 361.48$	pure Cu at 25°C, [V-C] dissolves up to 19.7 at.% Al at 559°C [2003Gro]; dissolves up to 35.84 at.% Zn at 300°C [2003Leb]
( $\eta$ Zn) $\leq 419$	$hP2$ $P6_3/mmc$ Mg	$a = 266.46$ $c = 494.61$	pure Zn at 22°C, [V-C] dissolves up to 1.5 at.% Cu at 424°C [2003Leb]
$\theta$ , CuAl <sub>2</sub> $\leq 591$	$tI12$ $I4/mcm$ CuAl <sub>2</sub>	$a = 605.0$ $c = 487.0$	from 31.9 to 33.0 at.% Cu at 33.3 at.% Cu, [1985Mur]
$\eta_1$ , CuAl(h) 624-560	$o*32$	$a = 408.7$ $b = 1200$ $c = 863.5$	49.8 to 52.4 at.% Cu [V-C2, Mas2, 1985Mur] Pearson symbol: [1931Pre]
$\eta_2$ , CuAl(r) $\leq 561$	$mC20$ $C2/m$ CuAl(r)	$a = 1206.6$ $b = 410.5$ $c = 691.3$ $\beta = 55.04^\circ$	[1985Mur], from 49.8 to 52.3 at.% Cu
$\zeta_1$ , $\sim$ Cu <sub>47.8</sub> Al <sub>35.5</sub> (h) 590-530	$oF88 - 4.7$ $Fmm2$ Cu <sub>47.8</sub> Al <sub>35.5</sub>	$a = 812$ $b = 1419.85$ $c = 999.28$	55.2 to 59.8 at.% Cu, [Mas2, 1994Mur] structure: [2002Gul]
$\zeta_2$ , Cu <sub>11.5</sub> Al <sub>9</sub> (r) < 570	$oI24 - 3.5$ $Imm2$ Cu <sub>11.5</sub> Al <sub>9</sub>	$a = 409.72$ $b = 703.13$ $c = 997.93$	55.2 to 56.3 at.% Cu, [Mas2, 1985Mur] structure: [2002Gul]
$\epsilon_1$ , Cu <sub>100-x</sub> Al <sub>x</sub> 958-848	cubic ? -	-	$37.9 \leq x \leq 40.6$ [1985Mur]
$\epsilon_2$ , Cu <sub>1+x</sub> Al 850-560	$hP6$ $P6_3/mmc$ Ni <sub>2</sub> In	$a = 414.6$ $c = 506.3$	$0.22 \leq x \leq 0.57$ [1985Mur]
$\delta_1$ , Cu <sub>100-x</sub> Al <sub>x</sub>	$hR^*$ -	$a = 869.0$ $\alpha = 89.78^\circ$	$38.1 \leq x \leq 40.7$ [1985Mur]
$\gamma_0$ , Cu <sub>100-x</sub> Al <sub>x</sub> 1037-800	$cI52$ $\bar{I}43m$ Cu <sub>5</sub> Zn <sub>8</sub> -	-	$31 \leq x \leq 40.2$ [1985Mur]
$\gamma$ , Cu <sub>5</sub> (Cu <sub>x</sub> Zn <sub>2-2x</sub> Al <sub>x</sub> ) <sub>7</sub>	$cP52$ $P\bar{4}3m$ Cu <sub>9</sub> Al <sub>4</sub>	$a = 870.68$	Zn free 69.23 at.% Cu, [V-C2]
$\gamma$ , Cu <sub>9</sub> Al <sub>4</sub> < 890		$a = 886.9$	Al free [V-C2] Cu <sub>9</sub> Al <sub>4</sub> is ordered with Cu and Al on 2nd sites, $cP52$ -Cu <sub>9</sub> Al <sub>4</sub> type
$\gamma$ , Cu <sub>5</sub> Zn <sub>8</sub> < 835	$cI52$ $\bar{I}43m$ Cu <sub>5</sub> Zn <sub>8</sub>		

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\alpha_2$ , Cu <sub>100-x</sub> Al <sub>x</sub> ≤ 363°C	TiAl <sub>3</sub> -type long period super- lattice	$a = 366.6$ $c = 367.5$	$22 \leq x \leq 23.5$ at 77.9 at.% Cu, [1985Mur]
$\beta'$ , CuZn(r) ≤ 468	$cP2$ $Pm\bar{3}m$ CsCl	$a = 295.9$	at 49.5 at % Zn [V-C2], from 44.8 to 50.0 at.% Zn
$\delta$ , CuZn <sub>3</sub> 700-560	$hP3$ $P\bar{6}$ CuZn <sub>3</sub>	$a = 427.5$ $c = 259.0$	[V-C2], from 72.4 to 76.0 at.% Zn [1985Mur]
$\epsilon$ , $\approx$ CuZn <sub>4</sub> ≤ 598	$hP2$ $P6_3/mmc$ Mg	$a = 274.18$ $c = 429.39$	[V-C2], from 78 to 88.0 at.% Zn
$\beta$ , (Cu,Zn,Al) $\beta$ , CuZn(h) 903-454 $\beta$ , CuAl 1049-559	$cI2$ $Im\bar{3}m$ W	$a = 299.67$ $a = 285.64$ $a = 294.6$	[V-C2], from 36.1 to 55.8 at.% Zn at 672°C in two-phase field, [1985Mur] at 75.7 at.% Cu, 580°C [1985Mur] solid solubility range: 70.6 to 82.0 at.% Cu
* $\tau$ , $\approx$ Cu <sub>5</sub> Zn <sub>2</sub> Al <sub>3</sub> < 740	$\approx cP2$ CsCl	$a = 290.4$ $a = 293.2$	Cu <sub>40</sub> Zn <sub>7</sub> Al <sub>53</sub> [1942Koe] at Cu <sub>46</sub> Zn <sub>20</sub> Al <sub>34</sub> [1942Koe]
* $\tau'$ , $\approx$ Cu <sub>3</sub> Zn	$hR9$	$a = 867.6$ $\alpha = 27.41^\circ$	rhombohedral superstructure of 5 CsCl lattice [1942Koe], [1975Mur, 2000Dor]

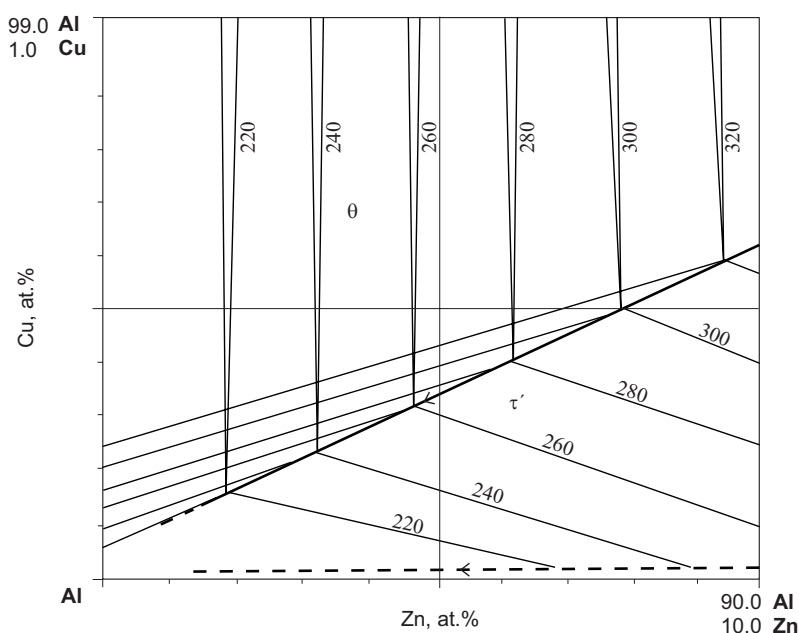
**Table 2:** Invariant Equilibria

Reaction	$T$ [°C]	Type	Phase	Composition (at.%)		
				Al	Cu	Zn
$L + \delta + \tau \rightleftharpoons \epsilon$	625	$P_2$	L	29.7	26.9	43.4
			$\delta$	26.3	45.4	28.3
			$\tau$	33.5	46.7	19.8
			$\epsilon$	27.9	44.1	28.0
$L + \epsilon_2 \rightleftharpoons \eta_1 + \tau$	620	$U_6$	L	62.6	35.2	2.2
			$\epsilon_2$	22.0	53.0	25.0
			$\eta$	25.5	51.4	23.1
			$\tau$	24.0	51.0	25.0
$L + \eta_1 \rightleftharpoons \theta + \tau$	580	$U_8$	L	65.9	31.6	2.5
			$\eta$	29.4	48.1	22.5
			$\theta$	47.0	32.5	20.5
			$\tau$	30.0	46.0	24.0
$\delta \rightleftharpoons \gamma_1 + \tau + \epsilon$	480	$E_2$	$\delta$	19.1	43.2	37.7
			$\gamma$	15.2	44.4	40.4
			$\tau$	26.2	48.0	25.8
			$\epsilon$	17.2	40.2	42.6
$L + \theta \rightleftharpoons (Al) + \tau$	422	$U_9$	L	44.5	11.3	44.2
			$\theta$	66.8	32.0	1.2
			(Al)	54.4	1.4	44.2
			$\tau$	52.1	39.0	8.9

Reaction	$T [^{\circ}\text{C}]$	Type	Phase	Composition (at.%)		
				Al	Cu	Zn
$\text{L} + \tau \rightleftharpoons (\text{Al}) + \varepsilon$	396	$\text{U}_{10}$	L	28.2	9.4	62.4
			$\tau$	50.4	39.2	10.4
			(Al)	42.0	1.5	56.5
			$\varepsilon$	11.2	22.0	66.8
$\text{L} \rightleftharpoons (\text{Al}) + \varepsilon + (\text{Zn})$	377	$\text{E}_3$	L	15.4	3.7	80.9
			(Al)	37.0	1.4	61.6
			$\varepsilon$	3.3	15.3	81.4
			(Zn)	3.1	2.9	94.0
$\tau + (\text{Al})'' \rightleftharpoons (\text{Al})' + \varepsilon$	288	$\text{U}_{11}$	$\tau$	59.2	35.7	5.1
			(Al)''	50.3	1.8	47.9
			(Al)'	80.5	1.4	18.1
			$\varepsilon$	2.8	16.6	80.6
$(\text{Al})'' + \varepsilon \rightleftharpoons (\text{Al})' + (\text{Zn})$	278	$\text{U}_{12}$	(Al)''	49.1	1.5	49.4
			$\varepsilon$	2.4	18.7	78.9
			(Al)'	83.4	0.8	15.8
			(Zn)	2.4	3.0	94.6
$(\text{Al})' + \varepsilon \rightleftharpoons \tau + (\text{Zn})$	268	$\text{U}_{13}$	(Al)'	43.3	0.8	55.9
			$\varepsilon$	0.7	17.5	81.8
			$\tau$	52.7	39.2	8.1
			(Zn)	1.9	1.7	96.4

**Table 3:** Saturation Concentrations of Al and Cu in (Zn) at Different Temperatures

Temperature [ $^{\circ}\text{C}$ ]	Al (at.%)	Al (mass%)	Cu (at.%)	Cu (mass%)
375	3.0	1.25	2.8	2.8
350	2.7	1.1	2.5	2.5
300	2.2	0.9	2.1	2.1
275	1.9	0.8	1.7	1.7
250	1.5 (0.9)	0.6 (0.4)	1.2 (0.9)	1.2 (0.9)

**Fig. 1:** Al-Cu-Zn. Solvus of the (Al) phase and three phase equilibrium (Al)+ $\theta$ + $\tau$  at different temperatures [ $^{\circ}\text{C}$ ]



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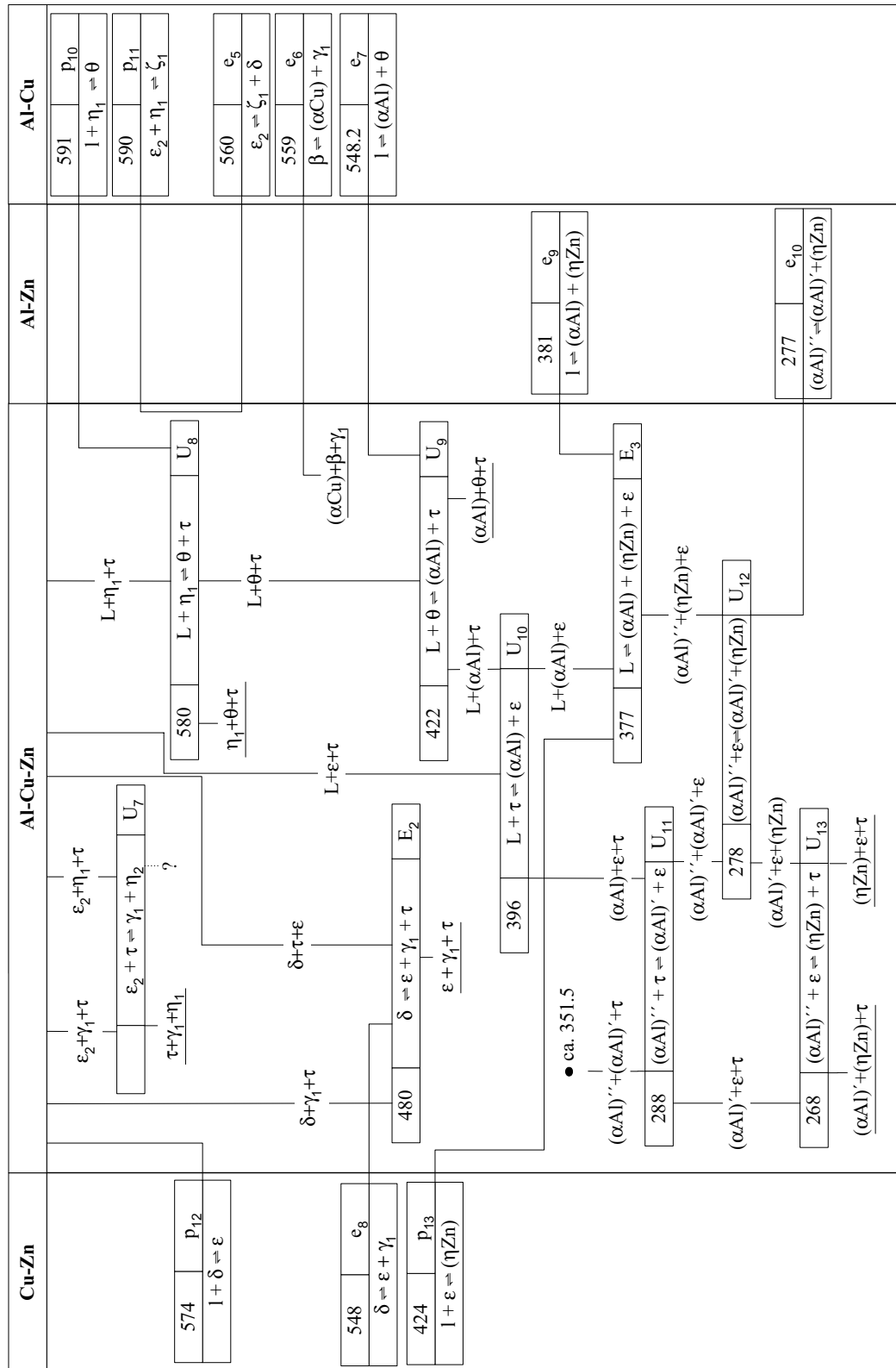
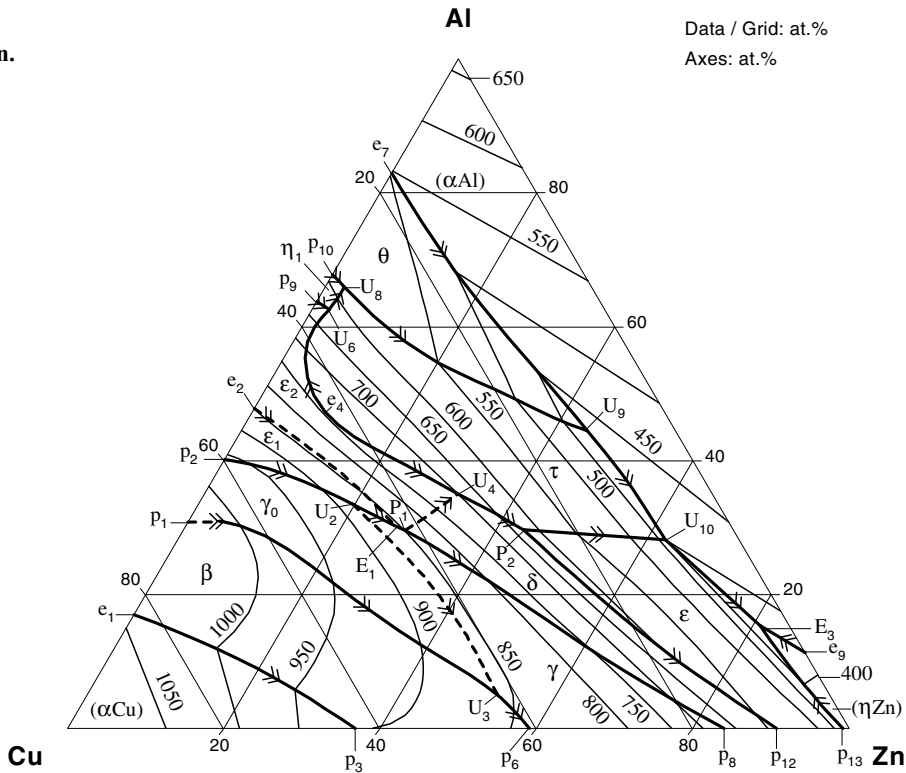
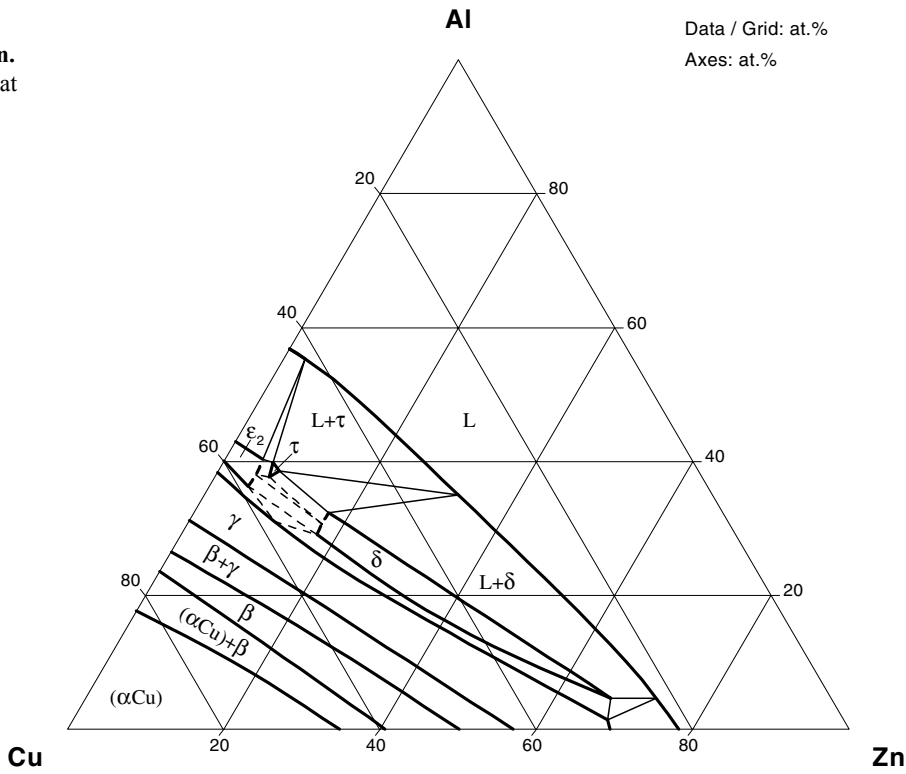


Fig. 2b: Al-Cu-Zn. Reaction scheme, part 2

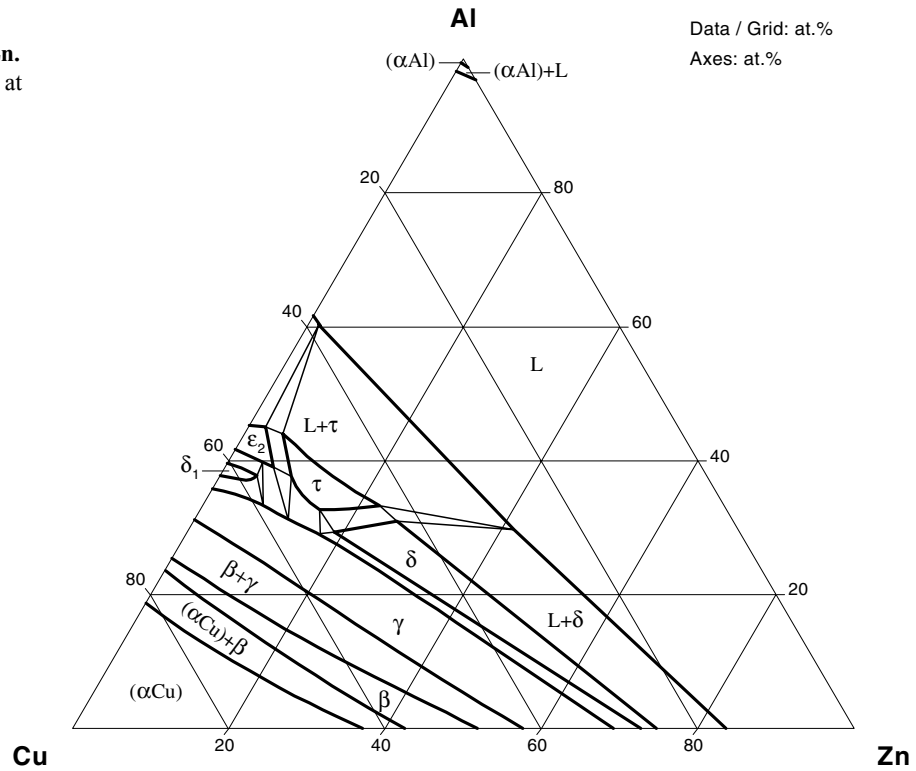
**Fig. 3: Al-Cu-Zn.**  
Liquidus surface



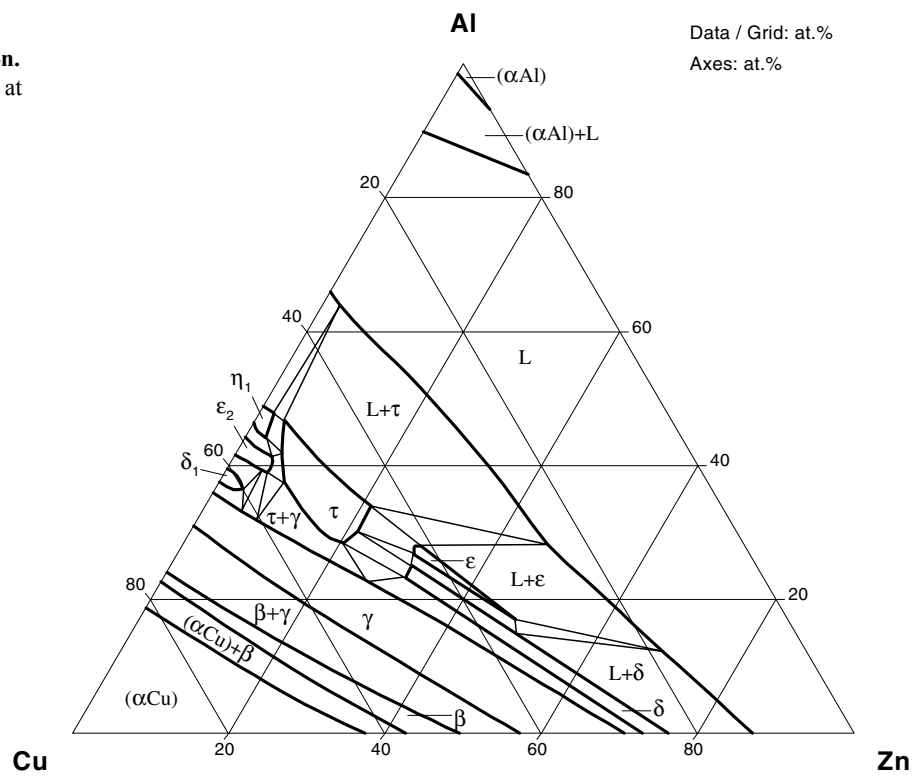
**Fig. 4: Al-Cu-Zn.**  
Isothermal section at  
700°C



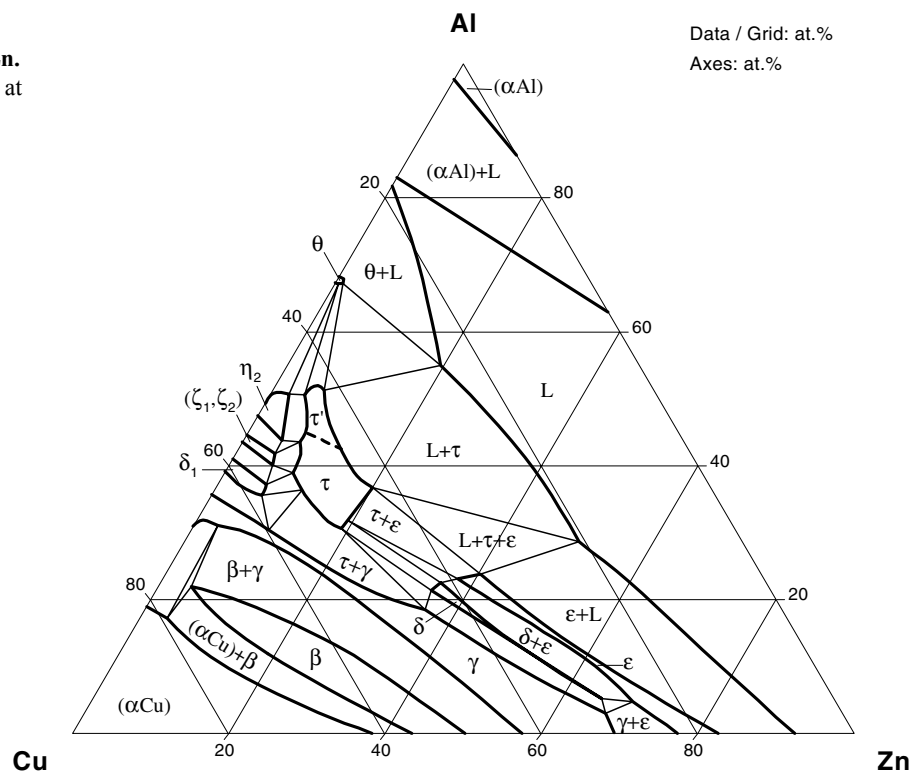
**Fig. 5: Al-Cu-Zn.**  
Isothermal section at  
650°C



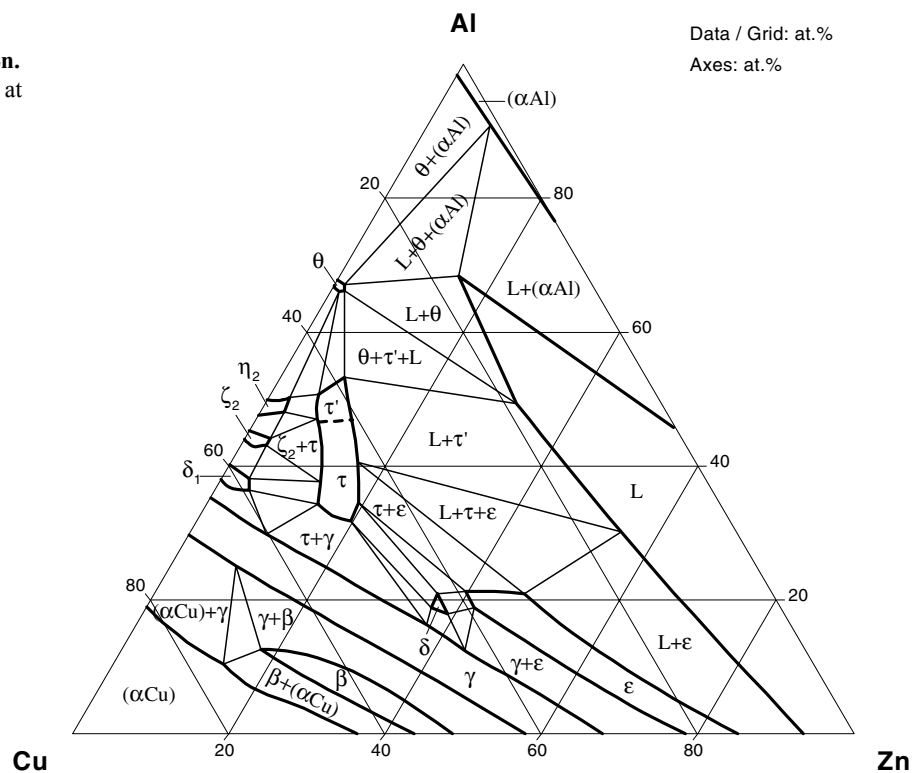
**Fig. 6: Al-Cu-Zn.**  
Isothermal section at  
600°C



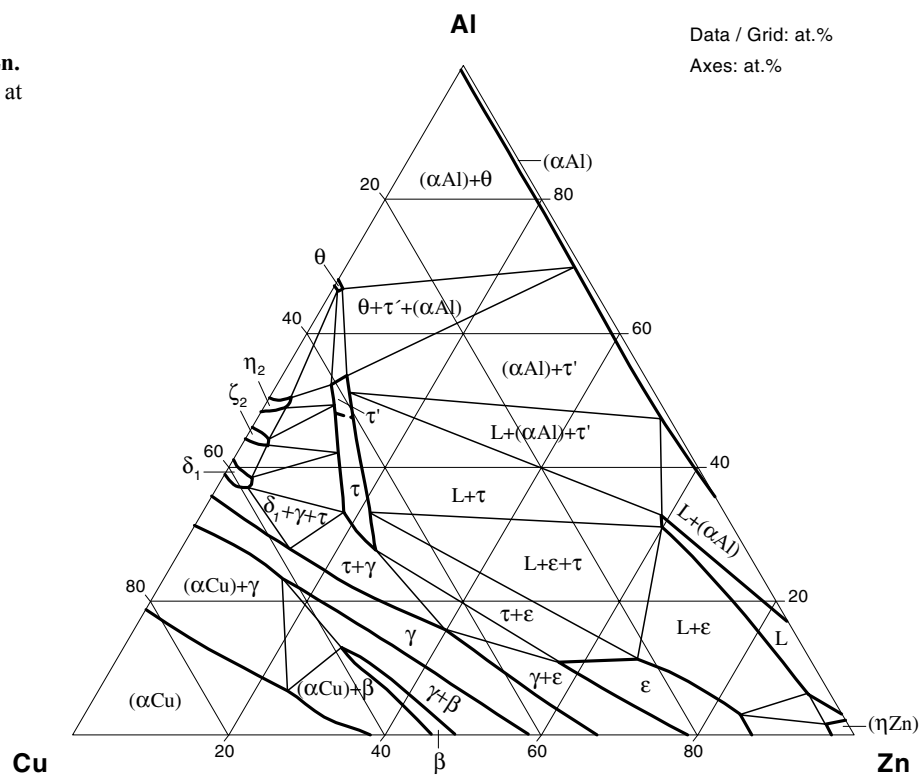
**Fig. 7: Al-Cu-Zn.**  
Isothermal section at  
550°C



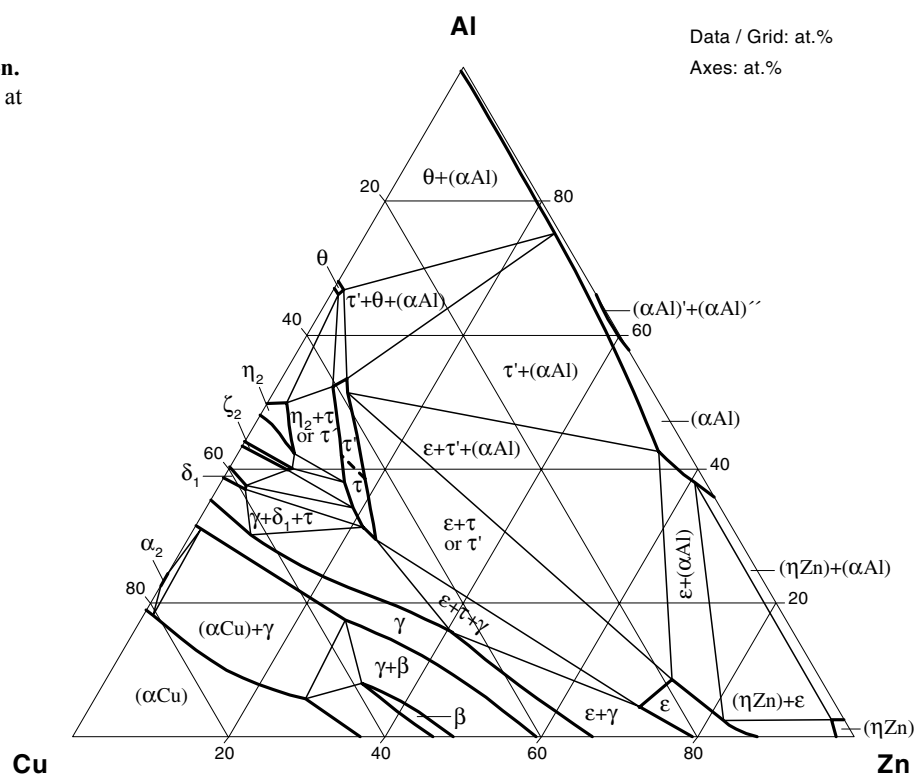
**Fig. 8: Al-Cu-Zn.**  
Isothermal section at  
500°C



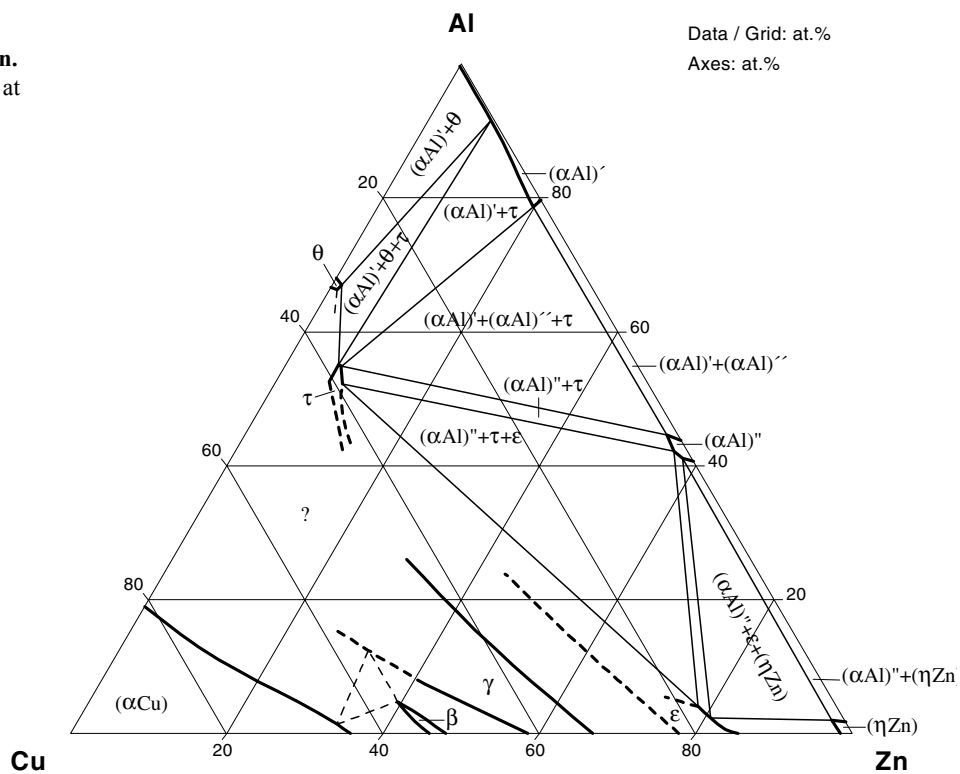
**Fig. 9: Al-Cu-Zn.**  
Isothermal section at  
400°C



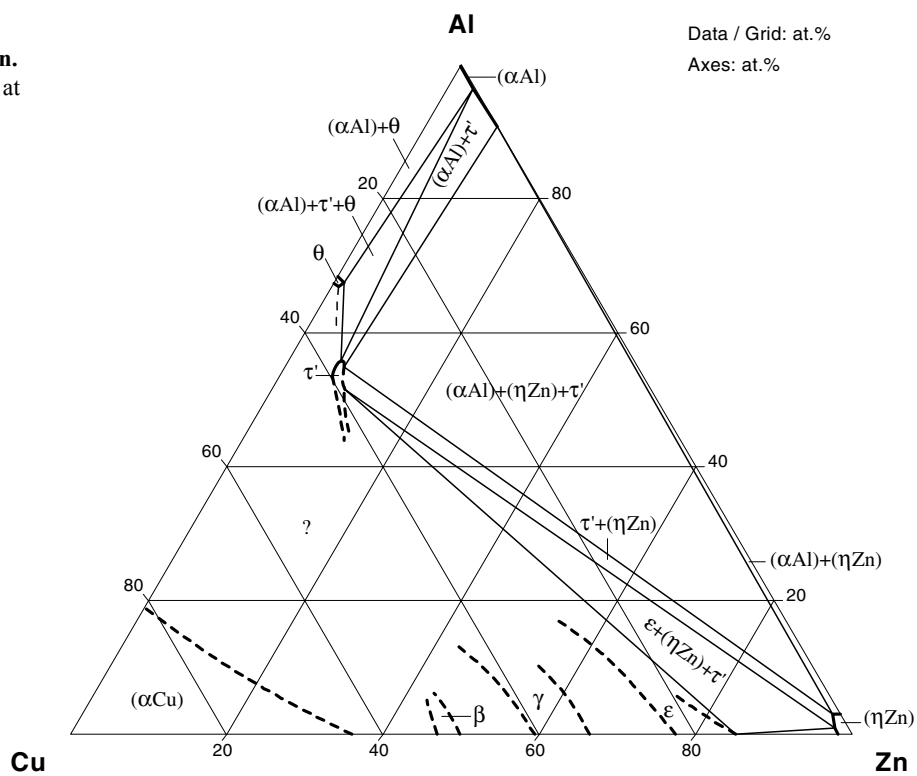
**Fig. 10: Al-Cu-Zn.**  
Isothermal section at  
350°C



**Fig. 11: Al-Cu-Zn.**  
Isothermal section at  
300°C



**Fig. 12: Al-Cu-Zn.**  
Isothermal section at  
240°C



**Fig. 13: Al-Cu-Zn.**  
Isothermal section at  
200°C

