Aluminium – Copper – Lithium

Matvei Zinkevich, Tamara Velikanova, Mikhail Turchanin, Zhenmin Du

Introduction

The experimental data for the Al-Cu-Li system are mostly concentrated in the Al rich corner. Table 1 summarizes experimental investigations pertaining to phase relations, structure, and thermodynamics reported in the literature. [1955Har] were the first to carry out a systematic study of phase equilibria in the Al-Cu-Li system. By means of X-ray and optical microscopy techniques designed to minimize the effects of oxidation they provided extensive data for the Al corner at 500 and, tentatively, at 350°C. In the composition range extending up to 60 mass% Cu and 20 mass% Li they identified for the first time a total of six ternary solid phases, designated as τ_B, τ_1, τ_2, R (in this assessment τ_3), Q (τ_4), and P (τ_5). The three ternary intermetallic compounds, τ_B, τ_1 and τ_2, were found to be in equilibrium with the Al rich solid solution (Al). The structure of τ_2, τ_3, τ_4, and τ_5 remained undetermined at that time. Subsequently, [1961Fri] studied the combined solubility of Cu and Li in (Al) at 200 and 500°C. Further experimental investigations of the equilibria in the ternary system were reported by [1960Mik, 1963Sha, 1965Boc, 1986Smi, 1986Rio, 1987Che, 1988Dor, 1989Dub, 1990Tak, 1991Che1]. [1960Mik] reported three vertical sections $CuAl_2$-LiAl, Al-Cu:Li = 4:1 (mass%), and Al-Cu:Li = 9:1 (mass%) but they did not observe the existence of τ_B. Several errors in the $CuAl_2$-LiAl section [1960Mik] were pointed out by [1988Zak]. Some inconsistencies were observed by [1988Riv] in the liquidus surface proposed by [1960Mik, 1963Sha]. Four vertical sections (at 4, 5 and 6 mass% Cu and 95 mass% Al) were reported by [1965Boc]. Two invariant reactions were proposed by [1977Dri] near the Al-Cu side. The phase equilibria in the ternary Al-Cu-Li system were reviewed subsequently by [1968Age, 1968Dri, 1969Wat, 1976Mon, 1977Dri, 1980Zak, 1987Flo, 1987Lav, 1988Riv, 1991Har, 1995Bod]. The critical evaluation by [1991Har] included reaction scheme, liquidus surface and isothermal section at 500°C in the Al rich region. Since then many papers were devoted to the Al-Cu-Li alloys. Solidus and solvus temperatures were metallographically determined for 4 alloy compositions by [1988Dor]: 1.96Li, 2.68Cu, ~95 mass% Al; 2.23Li, 2.76Cu, ~95 mass% Al; 2.40Li, 2.66Cu, ~95 mass% Al; 2.67Li, 2.83Cu, ~95 mass% Al. The homogeneity range of the (Al) ternary solid solution at 500°C proposed by [1988Dor] is larger than that suggested by [1976Mon]. A new experimental determination of the phase equilibria of the Al rich alloys was carried out by [1991Che1]. The primary phases, reaction sequences, and solidification temperatures were studied. In the calculations, τ_2 and τ_3 phases were treated as stoichiometric compounds. A liquidus projection was also calculated.

The thermodynamic properties of phases were studied by many researchers. The enthalpy of formation of compounds and liquid alloys as well as enthalpy of fusion of ternary compounds were studied calorimetrically by [1987Che, 1988Dub, 1989Dub, 2002Mos]. Thermodynamic properties of liquid alloys and phases in equilibrium were studied by [2002Mos] using electromotive force method. Low-temperature heat capacity of the τ_2 phase was investigated by [1988Wag, 1997Wan].

The Al rich part of the phase diagram was thermodynamically assessed by [1989Dub, 1991Che2, 1990Ans, 1992Sau, 1998Ans, 2002Mos] using the CALPHAD method. A detailed experimental analysis of the constitution and thermodynamics of the Al-Cu-Li system coupled with thermodynamic calculation of the equilibrium phase diagram, with emphasis on Al rich region, was carried out by [1988Dub, 1989Dub] allowing them to present a liquidus surface focusing on the τ_2 and τ_3 phases. Yet another thermodynamic calculation of the system in the Al rich corner was attempted by [1991Che2]. Values of the enthalpies of formation for the ternary intermetallic phases τ_B, τ_1, τ_2, and τ_3 were determined experimentally as -17 ± 1, -20.6 ± 1, -20.4 ± 1, -22.1 ± 1 kJ·mol^{-1} [1988Dub, 1989Dub]. The calculated values of enthalpy of formation of τ_B, τ_1, and τ_2 are –21, –20 and –17 kJ·mol^{-1}, respectively [1991Che2]. Unfortunately, probable misprints are responsible for the incorrect values (–27, –30 and –29 kJ·mol^{-1}, respectively) quoted by [1991Che2] for [1989Dub].

[1991Che2] did not differentiate between the τ_2 and τ_3 phases. This differs from the assessment of others, where these phases are modeled separately. A problem for [1989Dub, 1990Ans, 1991Che1, 1992Sau,

1998Ans] was the lack of thermodynamic data on the liquid phase. [2002Mos] used their own data for enthalpy of mixing of the liquid phase in the modeling of phase equilibria. The results of optimization by [1989Dub, 1990Ans, 1998Ans, 2002Mos] can be considered as a consequent development of models where the last one demonstrates good agreement with majority of experimental results on phase equilibria and thermodynamics. In the current assessment the results of [2002Mos] are taken as the basis for the evaluation of the phase equilibria.

A number of investigations of quasicrystalline τ_2 together with the related τ_3 phase were performed after 1985. The ternary phase τ_2 was unambiguously identified as an icosahedral quasicrystalline phase by [1986Dub] and considered as a stable quasicrystalline phase. The icosahedral quasicrystalline τ_2 phase can be obtained by rapid or slow cooling from the melt [1986Dub, 1986Sai, 1987Lan, 1987Mai, 1987Rao, 1988Par, 1989Kor, 1989She, 1993Deg]. Quasicrystal growth processes were studied by [1987Gay, 1987Lan, 1988She2, 1988Par]. Slowly solidified icosahedral τ_2 quasicrystals can grow as facetted dendrites with an apparent rhombic triacontahedral habit [1987Gay]. Quasicrystalline grains can grow along the 5-fold axis [1987Lan], and formation of a texture was observed in melt-spun quasicrystals with a 5-fold axis aligned perpendicular to the ribbon surface [1989Sug]. [1988Par] and [1993Deg] have grown centimeter-sized single-grained τ_2 quasicrystals using the Bridgman method. Easy nucleation of icosahedral particles combined with the slow kinetics of the $\tau_2 \rightleftharpoons \tau_3$ transformation is probably the reason for growth of large icosahedral crystals [1988She2]. The icosahedral quasicrystalline τ_2 phase can also be formed by solid-state reaction from the supersaturated (Al) solid solution [1985Sai2, 1986Cas1, 1986Cas2, 1987Cas1, 1991Lar]. DSC was used for studying the stability of the icosahedral quasicrystalline τ_2 phase [1987Che, 1988She2, 1991Lar] and of the τ_3 phase [1987Che, 1988She2]. Salient feature in the thermal behavior of icosahedral quasicrystalline τ_2 is the absence of exothermic transition characteristics of metastable phases [1987Che, 1988She2, 1991Lar]. The reversibility of the formation of icosahedral τ_2 on ageing at room temperature after its partial destruction during annealing at 400°C was observed by [1991Lar]. The results obtained by [1955Har, 1960Mik, 1963Sha, 1965Boc, 1987Che, 1988Dub, 1991Che1] show that the phase equilibria in the Al-Cu-Li system are complex and still need careful experimental work for a satisfactory interpretation. Some of these investigators found that the lithium content changed in the course of their experiments. [1960Mik] analyzed the chemical compositions of three alloys after solidification and found that the lithium loss varied from 10 to 23 mass%.

Binary Systems

Assessments of the Al-Cu system by [2004Gro], the Al-Li system by [2002Gro], and the Cu-Li system by [2006Boc] are accepted. They are based on [1994Mur, 1998Liu] for Al-Cu, [1982McA] for Al-Li and [1994Pel] for Cu-Li. The thermodynamic data set of the COST 507 action [1998Ans, 1991Sau] for the corresponding binary systems was used to calculate figures and the reaction scheme in the present assessment. The agreement between calculated and evaluated diagrams is very good. The only differences are minor shifts in the temperatures of invariant equilibria and the treatment of $\gamma_0 \rightarrow \gamma_1$ phase transition in the Al-Cu system (first order in [1998Ans] and second order in [2004Gro]). In addition, the ξ, δ, Li_3Al_2, Li_9Al_4, τ_B, τ_1, τ_2, and τ_3 phases are treated as stoichiometric, while η_1 and η_2 as well as Li_9Al_4(h) and Li_9Al_4(r) are not differentiated and called η and Li_9Al_4, respectively.

Solid Phases

The crystal data for solid phases are listed in Table 2. The cubic τ_B, $LiCu_4Al_{7.5}$ phase forms peritectically at about 550°C according to the experimental data of [1963Sha]: the value calculated in the present assessment is somewhat higher, P_3, 584°C (see section Invariant Equilibria and Table 3). The τ_B phase also crystallizes on ageing Al rich commercial alloys between room temperature and 350°C [1959Sil, 1973Sch1, 1991Lud]. The τ_1 phase, $LiCuAl_2$, is formed congruently at about 695°C [1963Sha, 1989Dub] (693°C after thermodynamic calculation). It also precipitates from aged alloys with a well-defined plate-shaped morphology [1955Har]. The hexagonal crystal structure of τ_1 was first proposed by [1955Har]. The existence of the τ_1 phase was reported without details by [1966Che]. The τ_1 phase formation was assumed to occur via direct nucleation and growth from the saturated (Al) solid solution following a stacking fault

mechanism [1972Nob]. This point of view was confirmed by [1987Cas2]. After some debates among [1988How, 1987Hua1, 1987Rad, 1992Hua], the τ_1 phase was confirmed to be of a hexagonal structure with space group *P6*/*mmm* [1987Hua1, 1988Vec3, 1990Sma]. High-resolution TEM examination and simulation [1987How, 1987Rad, 1992Hua] yielded results consistent with the hexagonal structure, though the exact atom positions were assigned slightly differently by [1987How, 1987Rad] compared to [1987Hua1]. Refinement of the hexagonal structure of $LiCuAl_2$ was carried out using single crystal X-ray diffraction [1990Sma]. Positron lifetime measurements were carried out during in-situ annealing of quenched samples of an alloy with composition 7.5Li-1.1Cu-91.4 (at.%) Al. Semicoherent and incoherent precipitation of the τ_1 phase was detected, but no quenched-in vacancies were found [1992Dlu]. The presence of the τ_1 phase in Al rich alloys can facilitate hydrogen entry and cause embrittlement of the alloys [1991Mel]. The structure of the τ_3 phase, Li_3CuAl_5 (R phase after [1955Har]) was first determined by [1963Che] and found to be based on the Frank-Kasper $Mg_{32}(Zn,Al)_{49}$ structure. Using X-ray and neutron diffraction, the atomic arrangement in the τ_3 (R) phase was redetermined [1988Aud1, 1988Gur, 1989Aud, 1990Gur]. The atom positions proposed by [1988Aud1, 1988Gur, 1990Gur, 1992Tam] are slightly different from [1963Che] but confirm the successive icosahedral and dodecahedral shells. The τ_3 phase, Li_3CuAl_5, is a bcc crystalline phase (space group $Im\bar{3}m$) with 162 atoms per unit cell (see Table 2) [1988Aud1, 1992Tam]. The origin is unoccupied. The body-centered sites are surrounded by successive atomic shells with almost icosahedral symmetry: a small Al, Cu icosahedron (r = 251.8 pm), a Li pentagonal dodecahedron (r = 453.2 pm) and a second Al,Cu icosahedron (r = 504.8 pm) [1992Tam]. The set of the last two shells forms a small triacontahedron. The next shells are an Al, Cu "pentakisdodecahedron" [1992Tam] (r = 668.6 pm), a second Li dodecahedron (r = 750.5 pm) and a Li icosahedron (r = 812.3 pm). The last two shells form a large triacontahedron. The τ_3 phase is therefore described as a bcc stacking of these large triacontahedra. Translational planar defects are characteristic of the microstructure of Li_3CuAl_5 crystals [1991Don, 1992Don]. When these defects have a high density, they become periodically organized what leads to pseudo-fivefold diffraction patterns [1992Don], which are used for identifying the icosahedral quasicrystalline τ_2 phase [1991Don]. The τ_3 phase can be therefore presented as an interlinking crystal in the whole family from large-parameter crystals to the quasicrystal τ_2. Imperfections in the τ_3 phase crystal structure were also analyzed by [1991Shi]. Intermediate states between the icosahedral quasicrystal τ_2 and the τ_3 phase were observed at the interface τ_2-τ_3 by TEM investigations [1993Don] on annealing and attributed to the chemical diffusion between τ_2 and τ_3. The defect network, randomly organized at low defect density in the τ_3 phase, becomes a periodic when the defect density increases. This complex organization suggests that diffusion rates are very low in the quasicrystalline τ_2 phase and the equilibrium state is difficult to reach. This can explain some inconsistencies in the TEM and X-ray results obtained by several authors [1993Nis]. A new rhombohedral approximant crystal is also suggested by [1993Don]. The close structural relationship between the icosahedral phase τ_2 and the cubic τ_3 phase was established by [1989Aud] and is also proved by the results obtained using either scanning electron microscopy [1986Aud], X-ray diffraction [1986Mar, 1987Dmo, 1987She, 1987Sma, 1988Aud1, 1988Els, 1988Gur, 1988She1, 1989She, 1991Boi, 1993Qiu, 1993Ara], high-resolution X-ray scattering experiments [1987Poo], X-ray absorption fine structure spectroscopy (XAFS) [1987Ma, 1987Ste], pulsed neutron scattering [1988She1, 1989She] or inelastic neutron scattering measurements [1991Gol, 1992Gol] as well as nuclear magnetic resonance measurements [1988Lee]. Both phases have compositions, which are very close [1987Che, 1989Aud, 1988Dub] (see Table 2). A comparison between high-resolution electron microscopy (HREM) image simulations on the τ_3 phase with experimental HREM images of the icosahedral τ_2 phase also showed a strong similarity in the local order arrangements between the two phases [1992Tam]. The structure of the icosahedral phase τ_2 has also been shown to be related not only to the cubic τ_3 phase but also to several stable intermetallic compounds $(Li,Mg)_{0.3}(Cu,Zn)_{0.1}Al_{0.6}$ with chemical compositions close to τ_2 and τ_3 [1989Aud]. Neutron diffraction data strongly suggest that short- and medium-range orders are almost the same in the τ_2 and τ_3 phases [1989Aud]. The Friauf polyhedron could be the only structural unit common to quasicrystalline and related crystalline Li-(Cu,Zn,Mg)-Al phases [1987Fru, 1989Aud, 1991LeB, 1991Leb, 1993Don]. Small changes in the composition or in the defect network of the periodic τ_3 phase can produce the τ_2 aperiodic network [1993Don]. The strong similarities, which exist between the structures of τ_2 and τ_3 (R after [1955Har, 1989Aud]) as well as the existence of intermediate states between

τ_2 and τ_3 structures [1991Don, 1992Don, 1993Don] are considered as support to the point of view that a unique symbol, τ_2(R), can be used for both τ_3 and τ_2 phases. The absence of exothermic thermal effect for the $\tau_2 \rightarrow \tau_3$ transition [1987Che, 1988She2, 1991Lar] and the fact that the values of the enthalpies of formation are almost the same for τ_2 and τ_3 [1988Dub, 1989Dub] can be attributed to very close compositions and very similar crystal structures of the compounds.
The TEM observation of microcrystals in association with the icosahedral quasicrystalline τ_2 phase caused some controversy about its stability and existence range [1987Bar, 1987Hua2, 1988Mic, 1988Sad, 1988Vec1, 1988Vec2, 1989Tos, 1989How, 1990Mic1, 1990How]. A tentative interpretation of the X-ray diffraction patterns of the icosahedral τ_2 phase with a tetragonal unit cell was proposed by [1988Ana]. X-ray precession and electron diffraction data indicated a perfect icosahedral symmetry [1987Den], while others revealed deviations from an icosahedral symmetry [1987Mai, 1988Yu, 1993Nis]. Comparison between the electron diffraction patterns of the as-quenched and the annealed τ_2 phase revealed a pronounced deviation from the perfect icosahedral symmetry after annealing [1987Yu]. Convergent beam electron diffraction of the τ_2 and τ_3 phases indicated that the quasicrystalline and crystalline structures seem to occur simultaneously [1988Las]. Structural models were developed for the icosahedral τ_2 phase. Most of them consider the structure as the three-dimensional cut of a six-dimensional crystal [1988Els, 1991Boi, 1991Sma, 1992Yam]. The icosahedral quasicrystalline τ_2 phase is also viewed as the result of competition between antisymmetric coupling of Friauf polyhedra forming prolate Penrose rhombohedra and symmetric coupling forming 5-fold rings of prolate rhombohedra. Antisymmetric couplings do not exist in the τ_3 crystalline phase [1987Fru]. They initiate multiple twinning, which produces an average icosahedral symmetry [1987Fru]. The atomic structure of a perfect icosahedral quasicrystal can also be achieved in a three-dimensional Penrose and the structure may be understood in terms of four zonohedra [1987Guy1, 1987Guy2, 1988Aud2]. The powder and single crystal neutron and X-ray diffraction data were obtained for the icosahedral quasicrystal τ_2 by [1991Boi] and used by [1994Elc] for refining the structure. Structure factors of the icosahedral τ_2 phase were determined by [1993Qiu], in good agreement with previous structural investigations and models [1988Els, 1991Boi].
Quantum structural diagrams successfully predict the existence of the τ_2 phase [1986Vil]. Using a molecular dynamics simulations, [1993Win] found that the structure of the icosahedral τ_2 phase may be stable. The same conclusion was reached by [1993Nie] who calculated the total energies of the τ_2 and τ_3 phases and compared them with fictitious ternary solid solutions and mixtures. However, the τ_2 phase was observed to transform to the τ_3 phase after an isothermal heat treatment at 400°C for 20 min [1992Yan] or during argon-ion bombardment [1988Sad]. A defect network and translation domains could be formed during the $\tau_2 \rightarrow \tau_3$ phase transformation [1991Shi].
The τ_4(Q) and τ_5(P) phases were additionally reported by [1955Har] in alloys annealed at 500 and 350°C. Only some X-ray lines but no compositions are given for them. The composition of τ_5 appears to be close to that of τ_B phase since the alloys in the <35 at.% Cu, <15 at.% Li range contained this phase together with τ_B: $\theta+\tau_B+\tau_5$ / $\tau_B+\tau_5/\tau_5+\tau_{B+}\tau_1$. The composition 30Li-30Cu-40Al (at.%) reported by [1970Ole] for τ_4 does not contradict with phase constituents of alloys near the τ_1+LiAl tie-line of the $\tau_1+\tau_3$+LiAl phase triangle [1955Har]. The ternary phases $LiCu_2Al$ (τ_6) and $Li_3Cu_3Al_4$ (τ_7) were reported in the only short publication by [1966Che]. Further investigation is needed to obtain a complete picture concerning a number of ternary compounds in the system and crystal structure of the new ternary phases. The data on an extension of solid solutions based on binary phases are also very scarce.

Quasibinary Systems

Two maxima of three phase equilibria, both quasibinary eutectics, e_2 and e_3: $L \rightleftharpoons \tau_1 + \varepsilon_2$ and $L \rightleftharpoons \tau_1$ + LiAl, respectively are found by calculation in the current assessment (see Table 3). The τ_1 - LiAl section (Fig. 1) is the only quasibinary system because τ_1 and LiAl are congruently melting phases. This section was never presented in experimental reports, it is calculated in the present assessment. The quasibinary peritectic $L + LiAl \rightleftharpoons \tau_3$ reported by [1991Har, 1995Bod] is not confirmed. The partial quasibinary system proposed by [1987Che, 1988Par] within the composition range Li_3CuAl_x where $4.5 < x < 10$ is not accepted because it does not follow the thermodynamic criteria for quasibinary systems.

Invariant Equilibria

The invariant reactions and the reaction scheme resulting from the thermodynamic calculation for solid-liquid phase equilibria are given in Table 3 and Fig. 2, respectively. Only the τ_B, τ_1, τ_2 and τ_3 ternary intermediate phases were involved in the calculation. There is good agreement between the calculated four phase invariant equilibria and experimental data published by [1965Boc, 1988Dub, 1989Dub] for the range of >50 at.% Al (reactions P_1, P_2, U_3, U_5, U_7, U_8, U_9, and E_1) as well as between the calculated and experimental temperatures of congruent melting of the τ_1 phase. Two maxima of three-phase invariant equilibria of the eutectic type (e_2, e_3) are found. Moreover, there is a good agreement between calculations and the experimental data of [1963Sha, 1977Dri, 1991Che1] for the above mentioned invariant reactions, on one hand, and of [1965Boc, 1988Dub, 1989Dub] for U_9 ($L + \theta \rightleftharpoons (Al) + \tau_B$), on the other hand, as well as between the calculations and experimental data of [1960Mik, 1963Sha, 1965Boc, 1977Dri, 1988Dub, 1989Dub, 1991Che1] for E_1 ($L \rightleftharpoons + (Al) + \tau_B + \tau_1$). However, the calculated temperatures for the reactions $L + \eta + \tau_1 \rightleftharpoons \tau_B$ (P_3, 584°C) and $L + \eta \rightleftharpoons \theta + \tau_B$ (U_6, 574°C) are markedly higher than ones reported by [1963Sha] (the only who investigated them): 550 and 542°C, respectively.

The liquid compositions for all the U-type transition reactions given by [1991Che1] in figure 7 of their work are inconsistent with the reactions, which are proposed there [1991Che1], because they are located inside the triangles formed by the compositions of solid phases participating in succeeding equilibria shown in figure 6 of [1991Che1]. Unfortunately, [1991Che1] did not report the numerical data on the composition of phases at the invariant equilibria. The temperatures reported by [1960Mik] are drastically different from those of other authors and cannot be accepted. The congruent melting of the τ_3 phase proposed by [1987Che, 1988Par, 1989Dub] is not confirmed by thermodynamic calculations. As it follows from the relative position of compositional points, which participate in the equilibrium, congruent melting of the τ_3 phase turns out to be impossible, even though the narrow homogeneity ranges of τ_2 and τ_3 phases are taken into account. It is worth noting that the composition of the τ_3 phase is very close to that of the liquid phase composition at P_1 (see Table 3). The calculated liquid phase compositions for P_1, P_2, U_5, P_3, U_6, U_7, U_8, U_9, and E_1 invariant equilibria and the data according to the critical evaluation of [1991Har, 1995Bod] based on the experimental data of [1960Mik, 1963Sha, 1965Boc, 1987Che, 1988Dub] as well as the calculated data of [1992Sau, 2002Mos] appear to be in satisfactory agreement, because the deviations are below 3 at.%. However, in some cases these differences cause the change of the proposed type of equilibria as one can see in the case of the reactions $L + LiAl \rightleftharpoons \tau_1 + \tau_3$ by [1991Har, 1995Bod] as well as $L + \tau_3 \rightleftharpoons LiAl + \tau_2$, $L + \eta \rightleftharpoons \tau_B + \tau_1$, and $L + \eta + \theta \rightleftharpoons \tau_B$ by [2002Mos] instead of P_1, P_2, P_3 and U_6, respectively, after the current assessment.

Both the τ_2 and τ_3 phases are considered in the current assessment as separate and stable phases according to [1988Dub, 1988Riv, 1989Dub, 1991Har, 1995Bod, 2002Mos]. In contrast to this point of view a continuous transition between the τ_2 and R (τ_3) structures was reported [1991Don, 1992Don, 1993Don] and the unique symbol, τ_2 (R), was proposed for designation of these phases.

The region of the phase diagram, where Al content is below 50 at.% has not been experimentally determined. The conclusion of [1960Mik] concerning the equilibria of the (Cu) solid solution with the phases LiAl, τ_1, and ε_2 can not be considered enough justified because it is based only on the investigation of nonequilibrated alloys using the DTA and microstructural methods. In addition, the results of [1960Mik] contradict with all other experimental data on phase relations in the ternary system and cannot be accepted. Phase equilibria in this composition range were calculated by only taking into account the data for boundary binary systems and thermodynamic data for the liquid at high Al content. Equilibria involving (Cu) reported by [1960Mik] were not confirmed by thermodynamic calculations.

The existence of four phase monotectic reactions (U_4 and E_2) is the most interesting result for this composition range of the system (<50 at.% Al). They arise from the stabilization of the metastable liquid-liquid miscibility gap from the binary Cu-Li system reported by [1994Pel, 2006Boc]. The stable ternary miscibility gap maximum according to the calculation (at ~960°C, ~30 at.% Cu and ~60 at.% Li) is markedly higher than that assumed in the binary Cu-Li. Certainly, in future analysis of this system, the ternary τ_4, τ_5 and possibly other phases should be considered. Also, it is desirable to take the ranges of homogeneity for the ternary solutions based on binary and ternary compounds into consideration.

Liquidus Surface

The liquidus surface calculated according to the thermodynamic description of [2002Mos] in the whole range of compositions is presented in Figs. 3 a, b. Additionally, the $\gamma_0 \rightarrow \gamma_1$ phase transition is shown (dashed line) since it is accepted to be of second-order in the Al-Cu system [2004Gro], but this feature is not modeled in [1998Ans, 2002Mos]. For the Al rich part of the system it is in satisfactory agreement with that given in critical evaluation of [1991Har, 1995Bod] based on the results obtained by [1963Sha, 1965Boc, 1988Dub, 1989Dub]. The Al rich, Cu rich and Li rich regions of the liquidus projection are shown in Figs. 3 c, d, e and f.

Isothermal Sections

The calculated partial isothermal sections at Al content 50 to 100 at.% are given in Figs. 4 to 8. The homogeneity range of the (Al) solid solution at 350°C according to the current assessment is shown in Fig. 4. The calculation is in good agreement with the experimental data for 350°C. Isothermal section at 400°C is given in Fig. 5 and shows good compliance with that of [1989Dub]. The isothermal section of the Al corner at 500°C according to the current assessment (Fig. 6) agrees well with that given in the critical evaluations of [1988Riv, 1991Har, 1995Bod] mainly based on [1955Har] and with the experimental ones determined by [1989Dub]. The homogeneity range of the (Al) solid solution agrees fairly well with that of [1961Fri], but initial slopes of the (Al) phase boundaries after [1961Fri] contradict van't Hoff relation, so that these data cannot be accepted. For τ_2 and τ_3, the compositions determined by [1988Dub] were selected, which agree with those given by [1987Che] and [1955Har] within the given error of ± 3%.
It should be noted that there is a significant temperature dependence of the homogeneity range of the (Al) solid solution, and a wide range of coexistence of the τ_1 and τ_2 phases with the (Al) phase. The phase relations at 555 and 615°C are shown in Figs. 7, 8 according to the current calculation. The τ_2 phase is predicted to be the predominant phase in equilibrium with the (Al) matrix in the ternary Al rich alloys annealed below 500°C. The τ_2 phase is expected to precipitate together with the τ_1 phase in alloys located on the Cu rich side of the (Al) + τ_2 field. The LiAl compound should precipitate with τ_2 in the ternary alloys located between the Li rich side of the (Al) + τ_2 domain and the Al-Li side. Despite the difficulty in achieving thermodynamic equilibrium at the lower temperatures (*e.g.* below 400°C), this trend appears to be in good qualitative agreement with the observed equilibrium precipitation in extensively overaged alloys [1986Cas2, 1986Cas3, 1986Tos, 1989Dub].

Temperature – Composition Sections

Ten temperature-composition sections studied experimentally are reported: $CuAl_2$-LiAl, Al-(Cu:Li = 4:1, mass%) and Al-(Cu:Li = 9:1, mass%) by [1960Mik]; $CuAl_2$-τ_B/τ_B-τ_1 and τ_1-Al by [1963Sha]; at 95 Al mass% and at 4, 5 and 6 Li (mass%) by [1965Boc]; and Al-τ_2 by [1988Dub]. All of them were revised in the current assessment by computation using the CALPHAD method. The results are given in Figs. 9 to 18. Additionally, the calculated vertical section Al-67Li33Cu (at.%) and one through the critical points of the miscibility gap in the liquid are given in Figs. 19, 20a, 20b.
There is a good agreement between the experimental data of [1965Boc] and calculated sections along the same composition lines at 95 mass% Al, 4, 5 and 6 mass% Li, which are given in Figs. 9 to 12, respectively. The significant temperature dependence of the (Al) + LiAl + τ_2 / (Al) + LiAl phase boundary according to the calculation shown in Fig. 9 correlates well with the significant temperature dependence of the (Al) / (Al) + LiAl boundary in the Al-Li binary system.
The phase regions and the temperature of the isotherms corresponding to the invariant equilibria E_1 and P_3 shown in the section $CuAl_2$-τ_B / τ_B-τ_1 and Al-τ_1 by [1963Sha], generally, are in agreement with the calculated vertical sections $CuAl_2$-τ_1 and τ_1-Al given in Figs. 13, 14, respectively. The details are not discussed here, because the compositions of the alloys under investigation in [1963Sha] do not correspond to the claimed sections. They were shifted from the nominal composition to the Al corner according to the chemical analysis data after [1963Sha]. An interpretation of the phase relations in the vertical sections $CuAl_2$-LiAl, Al-(Cu:Li = 4:1, mass%) and Al-(Cu:Li = 9:1, mass%) by [1960Mik] cannot be accepted.

These sections are based only on the investigation of as-cast alloys using DTA and microscopical methods. The calculated ones are given in Figs. 15 to 17 along the same composition lines. Experimental data on liquidus for alloys along the section Al-τ_2 reported by [1988Dub] agree with the calculated diagram given in Fig. 18. Only preliminary picture of the phase relations at lower temperatures are reported by [1988Dub]. The congruent melting of τ_1 and incongruent melting of τ_2 and τ_3 phases as well as the dome of the liquid phase immiscibility near the Cu-Li edge of the Al-Cu-Li composition triangle are exhibited by the calculated vertical section Al-67Li33Cu (at.%) in Fig. 19. Vertical sections through the critical points of the miscibility gap in the vicinity of c_1 and c_2 are given in Figs. 20a and 20b, respectively.

Thermodynamics

The enthalpies of fusion for the τ_2 and τ_3 phases were measured by differential scanning calorimetry (DSC) [1987Che]. The values were reported to be same and equal to $\Delta_m H = 13.4$ kJ·mol^{-1}. This is perhaps due to the compositional and structural similarity between τ_2 and τ_3. [1988Dub, 1989Dub] determined the enthalpies of formation of τ_B, τ_1, τ_2 and τ_3 phases by means of solution calorimetry in liquid aluminium. The samples consisted of nearly single phases of the compounds and were annealed for 72 h at 500°C. The enthalpy of formation of phases at 25°C are $\Delta_f H°(\tau_B) = -17 \pm 1$ kJ·mol^{-1}, $\Delta_f H°(\tau_1) = -20.6 \pm 1.0$ kJ·mol^{-1}, $\Delta_f H°(\tau_2) = -20.4 \pm 1.0$ kJ·mol^{-1}and $\Delta_f H°(\tau_3) = -22.0 \pm 1.0$ kJ·mol^{-1}. Electromotive force and calorimetric studies of liquid and solid alloys were performed by [2002Mos]. Electromotive force studies were made for four sets of alloys at the following temperatures and compositions: T = 888 K (615°C), $x_{Al}/x_{Cu} = 9$, $0.001 \le x_{Li} \le 0.639$; T = 888 K (615°C), $x_{Al}/x_{Cu} = 4$, $0.013 \le x_{Li} \le 0.815$; T = 828 K (555°C), $x_{Al}/x_{Cu} = 7/3$, $0.0001 \le x_{Li} \le 0.5$; T = 778 K (505°C), $x_{Al}/x_{Cu} = 7/3$, $0.0032 \le x_{Li} \le 0.069$. Drop calorimetric studies were carried out to determine mixing enthalpies for liquid alloys. At 986 K (713°C), copper was dropped into the Al-Li bath with $x_{Al}/x_{Li} = 4$ to obtain alloys with $0.02 \le x_{Cu} \le 0.285$, and, at 945 K (672°C), lithium was dropped into an Al-Cu bath with $x_{Al}/x_{Li} = 6.07$ to obtain alloys with $0.023 \le x_{Li} \le 0.265$.

The thermodynamic information obtained by [1987Che, 1988Dub, 1989Dub, 2002Mos] along with the information on the phase equilibria updated by [1987Che] were combined to calculate the isothermal sections at 828 (555°C) and 888 (615°C) K in aluminium rich corner of the Al-Cu-Li phase diagram [2002Mos]. The optimized parameters of constituent binary Al-Li, Al-Cu, and Cu-Li systems were taken from [1998Ans]. For pure aluminium, copper and lithium the thermodynamic parameters from COST 507 database [1991Sau] were used. The τ_4 and τ_5 phase were not considered in the calculation as well as lithium solubility in the θ phase. Excess Gibbs energy of the liquid phase was described by equation [2002Mos]

$G^{ex} = x_{Al}x_{Cu}(-66622 + 8.1T + (x_{Al} - x_{Cu})(46800 - 90.8T + 10T\ln T) + (x_{Al} - x_{Cu})^2(-2812))$
$+ x_{Al}x_{Li}(-41500 + 20.96T + (x_{Al} - x_{Li})(10000 - 5.8T) + (x_{Al} - x_{Li})^2(15902 - 9.386T) - 250(x_{Al} - x_{Li})^3) +$
$x_{Cu}x_{Li}(66000 - 44.723T) + x_{Al}x_{Cu}x_{Li}\,(x_{Al}\,(-235832 + 169.7897T)$
$-163397.43\,x_{Cu} + x_{Li}(-264994.13 + 186.6438T))$ J·mol^{-1}.

According to this model wide range of immiscibility of liquid alloys can be predicted near Cu-Li side of the diagram. The dome of the miscibility gap has a flat maximum at ~960°C and ~30 at.% Cu, ~60 at.% Li. Gibbs energy of formation of ternary phases was described as:

$\Delta_f G°(\tau_B) = -18924.73 + 2.93494T$ J·mol^{-1},
$\Delta_f G°(\tau_1) = -22354.21 + 3.33970T$ J·mol^{-1},
$\Delta_f G°(\tau_2) = -18637.75 + 3.94024T$ J·mol^{-1},
$\Delta_f G°(\tau_3) = -19442.97 + 4.24074T$ J·mol^{-1}.

No ternary parameters were used for (Al) solid solution. Good agreement between majority of electrochemical and calorimetric results and the optimized thermodynamic parameters were observed. However, for alloys with $x_{Al}/x_{Cu} = 7/3$ differences between experimental [2002Mos] and calculated values were observed in one-, two- and three phase fields.

The low temperature heat capacity of rapidly quenched, annealed and single crystal samples of the τ_2 phase was measured in the temperature range 0.7-10 K using the thermal relaxation method [1988Wag]. In [1997Wan], the low temperature heat capacity of the τ_2 phase was investigated using an AC calorimetric method in temperature range 1-6 K for as-cast and annealed samples. It was found that preparation methods could greatly affect the electronic and vibrational properties.

Notes on Materials Properties and Applications

Al-Cu-Li alloys offer a combination of high elastic modulus, low density and high strength, which make them attractive for aerospace applications. The development of such alloys, which are weight saving in the aerospace structures was reviewed, including ingot metallurgy, rapid solidification, physical metallurgy and mechanical properties [1987Lav].

A summary of main and recent investigations of the properties of Al-Cu-Li alloys is given in Table 4. Aluminium alloys have undergone a series of developments for aircraft and aerospace applications since the 1970s [1960Ter, 1973Sch1, 1973Sch2, 1976Shc]. The demand for high specific strength without prior cold stretching, a very strong and rapid natural aging capability, good fracture toughness at room and cryogenic temperature, good weldability, and stress-corrosion-cracking resistance led to the further development of Al-Cu-Li-based alloys since the late 1980s [1991Bal, 1992Flo, 1995Yam, 1997Gil, 1998Rad, 2000Cso, 2000Dav, 2001Dut, 2002Gab, 2003Fra, 2003Sal]. Depending on composition and aging treatment, the high-strength is due to one or more of three different precipitates: δ'-$LiAl_3$, θ'- $CuAl_2$, τ_1-$LiCuAl_2$ and Guinier-Preston (GP) zones [1976Shc, 1993Sta, 1993Yu, 1995Yam, 2003Fra].

The precipitation behaviour of aged 1.6Li-3.2Cu-95.2Al (mass%) and 2.4Li-3.2Cu.94.4Al (mass%) was investigated using conventional TEM, high resolution transmission electron microscopy (HREM) and high angle annular detector dark-field-scanning transmission electron microscopy (HAADF-STEM) [2003Yos2, 2003Yos1]. The addition of small amounts of Zn, 0.50 mass%, to Al-Cu-Li alloys was shown to have a significant effect on their corrosion resistance or environmental properties [2002Gab]. A study was made on how additions of In, Mg and Si and impurities Na and K affect the microstructure and related mechanical properties of an Al-Cu-Li alloy [1997Gil]. The stress-corrosion cracking susceptibility of 2.05Li-2.15Cu-95.8Al alloy in 0.5 M NaCl solution was measured [1991Bal]. A theoretical model describing the evolution of the hardness profiles in the heat-affected zones of the Al-Cu-Li 2095 alloy was established [1998Rad]. The effect of quenching rate on the microstructure and mechanical properties of the Al-Cu-Li alloy AF/C 458 (1.8Li.2.7Cu-95.5Al, mass%) was investigated [2000Cso], and the microstructural features of AF/C 458 alloy were characterized to determined the average size, distribution, number density, spacing and volume fraction of the intermetallic strengthening precipitates δ′-$LiAl_3$ and τ_1-$LiCuAl_2$ [2003Fra]. The kinetics and mechanism of decomposition process of an 3.6Li-2.0Cu-94.4Al alloy, whose melt spun ribbons were cast at a linear rate of 10-20 $m \cdot s^{-1}$ and aged at 200°C, were analysed [2001Dut].

The electronic properties of icosahedral Al-Cu-Li quasicrystals were studied experimentally and the role of the interaction effect between the Fermi surface and Jones zone [1988Wag, 1992Hip, 1991Miz, 1993Fuj] were shown. The icosahedral τ_2 phase and the Frank-Kasper R phase (τ_3) show similar electronic, vibrational and transport properties [1988Wag]. The electronic properties of the R (τ_3) and τ_2 phases have also been studied by nuclear magnetic resonance (NMR) [1992Hip]. Low values of the density of states at the Fermi level were observed for the R (τ_3) phase as well as for the icosahedral τ_2 phase. The existence of a pseudogap at the Fermi level is therefore not a consequence of the quasiperiodicity [1992Hip]. The electronic specific heat coefficient was also measured for the icosahedral quasicrystalline τ_2 phase and the corresponding Frank-Kasper R (τ_3) phase [1991Miz]. The electronic structure near the Fermi level is essentially determined by the local atomic structure, which turns to be similar between the τ_2 phase and the corresponding Frank-Kasper R (τ_3) phase [1991Miz]. Low values of the electronic term in the expression of the specific heat (from $7.0 \cdot 10^{-6}$ to $1.5 \cdot 10^{-5}$ $J \cdot g^{-1} \cdot K^{-2}$) were found in melt-spun icosahedral τ_2 and in the R (τ_3) phase [1988Wag]. The specific heat of single-grained-icosahedral τ_2 phase was measured at low-temperature between 0.25 and 2.7 K [1987Jin], 4 and 80 K [1988Wan], 0.8 to 10 K [1988Bru] and between 1.5 and 6 K [1989Kim], as well as the electrical resistivity [1987Jin, 1989Kim] and the magnetoresistance at 1.4, 4.2 and 10 K [1988Bru, 1989Kim].

The understanding of the mechanical properties of the Al-Cu-Li alloys in the Al-Li rich part necessitates the identification of the GP zones and/or transition phases formed during ageing treatment [1984Bau, 1984Gil, 1984San]. The formation of GP zones on ageing is accompanied by a substantial rise of the electrical resistivity and strength properties, whilst ductility remains at a reasonable level [1991Kay].

Miscellaneous

The stable τ_1 phase was observed to be formed in 9.8Li-0.8Cu-89.4Al (at.%) alloy aged at 190°C for times varying between 10 min and 8 d. Other phases were also formed, which remained unidentified [1985Sai1]. Precipitation of τ_1 has also been reported to occur heterogeneously either at GP zones in 1.5Li-3.5Cu-95.0Al (mass%) alloys, or at matrix dislocations in 2.0Li-2.5Cu-95.5Al (mass%) alloys [1972Nob]. The spinodal decomposition of Al rich alloys (2.5Li-0.02Cu-97.48Al, 2.4Li-2.5Cu-95.1Al, 3.0Li-1.0Cu.96.0Al (mass%)) was investigated by high resolution transmission electron microscopy and by X-ray diffraction in quenched alloys aged for 168 h at room temperature [1989Rad]. Al rich δ'-$LiAl_3$ precipitates ($L1_2$ structure) were observed to develop in modulated order/disorder regions of varying Li content. A critical assessment on the solid-state transformations in Al-Cu-Li alloys was presented by [1987Flo].

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Table 1: Investigations of the Al-Cu-Li Phase Relations, Structure and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1955Har]	Melting in aluminized graphite crucible; annealing, subsequently quenching in paraffin, optical microscopy and X-ray powder diffraction	500, 350°C, 0 to 60 mass% Cu, 0 to 20 mass% Li
[1961Fri]	Microstructure investigation, hardness measurements	200, 500°C, 0 to 7 mass% Cu, 0 to 3 mass% Li
[1960Mik]	Microstructural, thermal and wet chemical analysis	Eighteen sections at constant atomic ratios Cu:Li of 1:3, 1:2, 1:1 etc. As-cast and cooled after DTA alloys
[1963Sha]	Microstructural and thermal analysis, powder X-ray diffraction	As-cast and cooled after DTA alloys (6 °C/min), 3.0 to 32.8 at.% Cu, 3.0 to 25 at.% Li
[1965Boc]	Microstructural, thermal and wet chemical analysis	400°C to liquidus, 0 to 6 mass% Cu, 0.25 to 6 mass% Li
[1972Nob]	Solution treatment followed by quenching and aging. Powder X-ray diffraction	Al - 3.5 (1.45) mass% (at.%) Cu -1.5 (5.70) mass% (at.%) Li; Al - 2.5 (1.03) mass% (at.%) Cu -2.0 (7.45) mass% (at.%) Li
[1973Sch1] [1973Sch2]	Solution treatment followed by quenching and aging. Powder X-ray diffraction, TEM	4.17 (1.78) mass% (at.%) Cu, 1.01 (3.94) mass% (at.%) Li
[1986Aud]	TEM	Al rich part of the system; τ_2-τ_3 phases in unannealed samples
[1986Dub]	TEM, HREM, SEM, X-ray diffraction	As-cast alloys of composition close to Al_6CuLi_3
[1986Mar]	Powder X-ray diffraction, TEM, SEM	τ_2, τ_3 phases
[1987Che]	Quantitative DTA, powder X-ray diffraction	Al_xLi_3Cu ($4.8 \leq x \leq 6.1$)
[1987Dmo]	X-ray diffraction	τ_2 and τ_3 phases
[1987Dub]	TEM, HREM, SEM, X-ray diffraction	As-cast alloys of composition close to τ_2
[1987Hua1]	Copper single roller melt-quenching technique, TEM, powder X-ray diffraction, electrical resistivity at RT to 600°C	Al-25.8 -18.6Li (mass%)
[1987Poo]	High-resolution X-ray scattering experiment	350°C, τ_2, τ_3 phases
[1987Rao]	Powder X-ray diffraction, SEM, EPMA	Al-25.1Cu-6.9Li (mass%) Al-27.9Cu-6.1Li (mass%) Al-27.5Cu-7.2Li (mass%)
[1987She]	Synchrotron X-ray powder diffraction	350°C, $Li_{33.7}Cu_{10.2}Al_{56.1}$
[1987Sma]	Single crystal X-ray diffraction	As-grown alloy Al_6CuLi_3
[1987Ste] [1987Ma]	X-ray absorption fine structure (XAFS) spectroscopy	τ_2 phase

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1988Aud1] [1988Aud2]	Single crystal X-ray and neutron diffraction, SEM	τ_3 (Al_5CuLi_3) phase
[1988Dor]	Commercial alloys homogenized, heat-treated subsequently quenched, metallography	500 to 600°C, 1.96 to 2.67 Li mass%; 2.66 to 2.83 Cu mass%; melting, solvus
[1988Dub]	Thermal analysis, differential scanning calorimetry, solution calorimetry	> 50 at.% Al, $T \geq$ 500°C in the vicinity of the ternary compounds τ_2 and τ_3, Al-τ_2 section
[1988Els]	Single crystal X-ray diffraction	τ_2 phase
[1988Vec1]	Optical microscopy, EPMA, (wavelength-dispersive X-ray spectrometry), TEM	500°C, Al-26.9Cu-4.72 Li (mass%); 470°C, Al-24.1Cu-9.06Li (mass%), as cast alloys
[1988Vec3]	Single crystal, TEM, convergent beam electron diffraction, EPMA	500°C, 49.53Al-27.09Cu-23.42Li (at.%), τ_1 phase
[1988Wag]	Thermal relaxation method	0.7-10 K, τ_2 phase
[1988Yu]	X-ray and electron diffraction	As-cast and as-quenched Al_6CuLi_3
[1989Dub]	Thermal analysis, differential scanning calorimetry, solution calorimetry in liquid aluminium, double weighting technique in air and silicone oil. Thermodynamic modeling	300 to 600°C, Al rich corner of the system, liquidus, isothermal sections at 300, 400, 500, 600 and 750°C
[1990Ans]	Thermodynamic modeling	0 to 60 Cu, 0 to 12 Li mass%; liquidus surface
[1990Yan]	Single crystal X-ray diffraction	τ_1 phase
[1991Boi]	Powder and single crystal neutron and X-ray diffraction	τ_2 phase
[1991Che1] [1991Che2]	Optical microscopy, electron probe microanalysis, X-ray diffraction, scanning electron microscopy, differential thermal and chemical analysis. Thermodynamic modeling.	0 to 50 Cu, 0 to 50 Li at.%; Cu-Li spinodal; isothermal section at 500°C, liquidus surface
[1991Mat]	Powder X-ray diffraction (synchrotron radiation), TEM, inverse photoemission measurement	τ_2, τ_3 phase
[1992Sau]	Thermodynamic modeling	
[1992Tam]	HREM	Al_5CuLi_3, Al_6CuLi_3
[1993Don]	TEM, X-ray diffraction	Al_6Li_3Cu - Al_5Li_3Cu interface
[1997Wan]	AC calorimetric method	1 ≤ T ≤ 6 K, as-cast and annealed samples of τ_2 phase
[1998Ans]	Thermodynamic assessment	

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[2002Kon]	HREM	τ_1, τ_3 phases
[2002Mos]	Electromotive force method with salt electrolyte, drop, calorimetry, thermodynamic assessment	T = 888 K, x_{Al}/x_{Cu} = 9, 0.1 ≤ Li at.% ≤ 63.9; T = 888 K, x_{Al}/x_{Cu} = 4, 1.3≤ Li at.% ≤ 81.5; T = 828 K, x_{Al}/x_{Cu} = 7/3, 0.01≤ Li at.% ≤ 50; T = 778 K, x_{Al}/x_{Cu} = 7/3, 0.32≤ Li ≤ 6.9 (at.%); T = 986 K, x_{Al}/x_{Li} = 4, 2 ≤ Cu ≤ 28.5 (at.%); T = 945 K, x_{Al}/x_{Cu} = 6.07, 2.3≤ Li ≤26.5 (at.%)

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Al) < 660.452	*cF*4 $Fm\bar{3}m$ Cu	a = 404.96	pure Al [Mas2], lattice parameters at 25°C [V-C2], dissolves up to 2.48 at.% Cu at 548.2°C and 14 at.% Li at 596°C
(Cu) < 1084.62	*cF*4 $Fm\bar{3}m$ Cu	a = 361.46	pure Cu [Mas2], lattice parameters at 25°C [V-C2], dissolves 19.7 at.% Al at 363°C and 22 at.% Li at 180°C [Mas2]
(βLi) < 180.6	*cI*2 $Im\bar{3}m$ W	a = 350.96	pure Li [Mas2], lattice parameters at 25°C [V-C], practically no solubility for Al and Cu
β, Cu_3Al(h)	*cI*2 $Im\bar{3}m$ W	a = 295.4	70.6 to 82 at.% Cu [2004Gro] at 672°C in β + (Cu) alloy
γ_0, $Cu_{1-x}Al_x$ $Cu_{\sim 2}Al$ 1037 - 800	*cI*52 $I\bar{4}3m$ Cu_5Zn_8	-	0.31 ≤ x ≤ 0.402 [Mas2], 0.32 ≤ x ≤ 0.38 [2004Gro]
γ_1, Cu_9Al_4 < 890	*cP*52 $P\bar{4}3m$ Cu_9Al_4	 a = 870.23 a = 870.68	62 to 68 at.% Cu [2004Gro]; powder and single crystal [2004Gro] from single crystal [2004Gro]
δ, $Cu_{1-x}Al_x$ < 686	*hR** $R\bar{3}m$	 a = 1226 c = 1511	0.381 ≤ x ≤ 0.407 [2004Gro] 59.3 to 61.9 at.% Cu at x = 38.9 [2004Gro]
ε_1, $Cu_{1-x}Al_x$ 958 - 848	*c***	-	0.379 ≤ x ≤ 0.406 59.4 to 62.1 at.% Cu [2004Gro]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ε_2, $Cu_{2-x}Al$ 850 - 560	*hP*6 $P6_3/mmc$ Ni_2In	a = 414.6 c = 506.3	$0.47 \le x \le 0.78$; 55.0 to 61.1 at.% Cu [2004Gro]
η, CuAl(h) 624 - 560	*o**32	a = 408.7 b = 1200 c = 863.5	49.8 to 52.4 at.% Cu [2004Gro]
θ, $CuAl_2$ < 591	*tI*12 $I4/mcm$ $CuAl_2$	a = 606.7 c = 487.7	31.9 to 33.0 at.% Cu [2004Gro]
Li_9Al_4 347 - 275	*mC*26 $C2/m$ Li_9Al_4	a = 1915.51 b = 542.88 c = 449.88 β = 107.671°	[2002Gro]
Li_3Al_2	*hR*15 $R\bar{3}m$ Li_3Al_2	a = 450.8 c = 1426	[2002Gro]
LiAl	*cF*16 $Fm\bar{3}m$ NaTl	a = 637	at 50 at.% Li, 45 to 55 at.% Li [2002Gro]
* τ_B, $LiCu_4Al_{7.5}$ < 550	*cF*12 $Fm\bar{3}m$ CaF_2	a = 583 a = 583.28	[1955Har] 60.0 Al, 32.0 Cu, 8 Li (at.%) [1989Dub] ρ_{exp} ~ 3.9 g·cm^{-3} [1989Dub, 1991Lud]
* τ_1, $LiCuAl_2$ < 695	*hP*12 $P6/mmm$ $LiCuAl_2$	a = 496 c = 935 a = 496 c = 934.5 a = 497 c = 930 a = 497 c = 935 a = 495.3 c = 932.7	$Al_{1.96}Cu_{1.08}Li_{0.96}$ [1955Har,1963Sha] [1987Hua1] [1988Vec3] 50.0 Al, 25.0 Cu, 25 Li (at.%) [1989Dub] ρ_{exp} ~ 3.8 g·cm^{-3} [1989Dub] [1990Sma]
* τ_2, Li_3CuAl_6	quasicrystal	a = 505 τ^{3n}	τ = gold number = $(1 + 5^{1/2})/2$, n any integer, point group only m [1989Aud, 1991Leb] 56.0Al-10.8Cu-32.2Li (at.%) [1988Dub] ρ_{exp} = 2.47 g·cm^{-3} [1988Dub, 1989Dub]
* τ_3 < 635 Li_3CuAl_5	*cI*162 $Im\bar{3}m$ $Mg_{32}(Zn,Al)_{49}$	a = 1391.4 a = 1390.56	[1955Har,1963Che], 56.4Al-11.6Cu-32.0Li (at.%) [1989Aud] 54.5Al-11.4Cu-34.1Li (at.%) [1987Che] 56.0Al-12.0Cu-32.0Li (at.%) [1988Dub] ρ_{exp} = 2.46 g·cm^{-3} [1988Dub,1989Dub] [1986Dub, 1989Aud, 1991Boi, 1993Don]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_4	-	-	designated Q in [1955Har] 40 Al, 30Cu, 30 Li (at.%) [1970Ole]
* τ_5	-	-	designated P in [1955Har]

Table 3: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Al	Cu	Li
L′, L′′, (Cu)	~ 850	c_1, critical point	L′, L′′ (Cu)	~1.5 ~1.5	~50.5 ~90	~48 ~8.5
L + ε_1 ⇌ γ_1 + ε_2	836	D_1(U)	L ε_1 γ_1 ε_2	44.8 39.8 36.4 41.9	52.0 60.2 63.5 58.0	3.1 0 0 0
L ⇌ τ_1	693	congruent	L, τ_1	50.0	25.0	25.0
L + β ⇌ γ_1 + (Cu)	657	U_1	L β γ_1 (Cu)	24.2 24.4 31.0 21.7	50.1 75.6 69.0 75.8	25.7 0 0 2.5
L ⇌ τ_1 + ε_2	655	e_2 (max)	L τ_1 ε_2	46.6 50.0 46.0	37.6 25.0 54.0	15.8 25.0 0
L + ε_2 ⇌ τ_1 + γ_1	654	U_2	L ε_2 τ_1 γ_1	44.8 43.2 50.0 37.5	38.1 56.8 25.0 62.5	17.1 0 25.0 0
L ⇌ τ_1 + LiAl	649	e_3 (max)	L τ_1 LiAl	50.0 50.0 50.0	11.0 25.0 0	39.0 25.0 50.0
L + LiAl + τ_1 ⇌ τ_3	638	P_1	L LiAl τ_1 τ_3	56.4 51.5 50.0 55.0	10.9 0 25.0 11.7	32.7 48.4 25.0 33.3
L + LiAl + τ_3 ⇌ τ_2	618	P_2	L LiAl τ_3 τ_2	63.2 52.6 55.0 57.0	8.5 0 11.7 11.0	28.3 47.4 33.3 32.0
L + τ_3 ⇌ τ_1 + τ_2	614	U_3	L τ_3 τ_1 τ_2	63.8 55.0 50.0 57.0	12.1 11.7 25.0 11.0	24.1 33.3 25.0 32.0

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Al	Cu	Li
L' + (Cu) ⇌ L" + γ_1	600	U_4	L'	23.3	42.2	34.5
			L"	3.2	1.0	95.8
			(Cu)	21.1	75.4	3.5
			γ_1	31.0	69.0	0
L + ε_2 ⇌ η + τ_1	597	U_5	L	59.9	31.9	8.1
			ε_2	45.8	54.2	0
			η	49.0	51.0	0
			τ_1	50.0	25.0	25.0
L + η + τ_1 ⇌ τ_B	584	P_3	L	61.8	30.7	7.5
			η	49.2	50.8	0
			τ_1	50.0	25.0	25.0
			τ_B	60.0	32.0	8.0
L + η ⇌ θ + τ_B	574	U_6	L	65.7	29.8	4.5
			η	49.5	50.5	0
			θ	67.0	32.9	0
			τ_B	60.0	32.0	8.0
L + LiAl ⇌ (Al) + τ_2	564	U_7	L	72.9	5.2	21.9
			LiAl	53.7	0	46.3
			(Al)	85.6	0.3	14.1
			τ_2	57.0	11.0	32.0
L + τ_2 ⇌ (Al) + τ_1	540	U_8	L	74.0	11.9	14.1
			τ_2	57.0	11.0	32.0
			τ_1	50.0	25.0	25.0
			(Al)	90.1	1.0	8.9
L + θ ⇌ (Al) + τ_B	524	U_9	L	76.2	17.6	6.2
			θ	67.9	32.1	0
			(Al)	94.6	2.2	3.2
			τ_B	60.0	32.0	8.0
L ⇌ (Al) + τ_B + τ_1	522	E_1	L	75.0	16.7	8.3
			τ_B	60.0	32.0	8.0
			τ_1	50.0	25.0	25.0
			(Al)	93.5	1.9	4.6
L + LiAl ⇌ τ_1 + Li_3Al_2	512	U_{10}	L	25.6	3.2	71.2
			LiAl	44.6	0	55.4
			τ_1	50.0	25.0	25.0
			Li_3Al_2	40.0	0	60.0
L′, L′′, τ_1	~ 500	c_2, critical point	L′, L′′	~25	~10	~65
			τ_1	50.0	25.0	25.0
L' ⇌ L" + γ_1 + τ_1	489	E_2	L'	26.7	15.0	58.3
			L"	19.0	3.8	77.2
			γ_1	33.7	66.3	0
			τ_1	50.0	25.0	25.0

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Al	Cu	Li
$L + Li_3Al_2 \rightleftharpoons \tau_1 + Li_9Al_4$	334	D_2(U)	L	~8.8	close to 0	~91.2
			τ_1	50.0	25.0	25.0
			Li_3Al_2	40.0	0	60.0
			Li_9Al_4	30.8	0	69.2
$L + \tau_1 \rightleftharpoons Li_9Al_4 + \gamma_1$	313	U_{11}	L	~7.2	close to 0	~92.8
			τ_1	50.0	25.0	25.0
			Li_9Al_4	30.8	0	69.2
			γ_1	32.5	67.5	0
$L + (Cu) \rightleftharpoons \gamma_1 + (Li)$	180	D_3(U)	L	close to 0	close to 0	~100
			(Cu)	15.7	83.0	1.3
			γ_1	30.7	69.2	0
			(Li)	0	0	100
$L \rightleftharpoons \gamma_1 + Li_9Al_4 + (Li)$	175	D_4(E)	L	~1.1	close to 0	~98.9
			γ_1	31.0	69.0	0
			Li_9Al_4	30.8	0	69.2
			(Li)	0	0	100

Table 4: Investigations of the Al-Cu-Li Materials Properties

Reference	Method/Experimental Technique	Type of Property	Comments
[1959Sil]	Powder X-ray diffraction	Phase transformation	Ageing of supersaturated (Al) solid solutions
[1960Ter]	Tensile Measurement	Mechanical	0-1.5 mass% Li, 4.5 mass% Cu
[1973Sch1] [1973Sch2]	X-ray, TEM (transmission electron microscope)	Precipitation kinetics	Al alloy 2020 Aged at 165-275°C
[1976Shc]	Hardness measurement, TEM-EDP (electron diffraction patterns)	Mechanical	Al alloy VAD23
[1984San]	TEM, SEM (scanning electron microscope), Tensile measurement	Mechanical	Al-4Cu-2Li-0.2Zr Al-2.5Cu-2.5Li-0.2Zr Al-1.5Cu-3Li-0.5Mn
[1987Jin]	Specific heat capacity and electrical resistivity measurements	Physical	0.25 to 2.7 K, Al_6CuLi_3 from as-cast alloys of similar composition; $\tau_2+\tau_3$+(Al)
[1987Lav]	Review	Physical and mechanical	78 references
[1988Bru]	Specific heat capacity and electrical resistivity measurements	Physical	0.8 to 10 K, τ_2
[1988Lee]	Powder X-ray diffraction, nuclear magnetic resonance (NMR) spectroscopy	Physical	As-cast and melt-spun ribbons of composition near Al_6CuLi_3: 30 to 34 at.% Li; 9.6 to 13 at.% Cu
[1988She2]	Powder X-ray diffraction, TEM, DSC	Physical	Rapidly solidified $Li_xCu_{1.0}Al_{5.5}$, x = 3.0, 3.25, 3.4, 3.5, 3.7

Reference	Method/Experimental Technique	Type of Property	Comments
[1988Wan]	Powder X-ray diffraction, specific heat capacity measurement	Physical	0.5 to 10 K, quasi-crystalline (τ_2) dendrites and quasi-crystal of planar grow casting
[1989Kim]	Low-temperature specific heat (1.5 K to 6 K), electrical resistivity (1 K to RT), magnetoresistance (1.4, 4.2, 10 K)	Physical	Single crystal ~Li_4CuAl_6
[1991Bal]	Constant elongation rate technique	Physical, stress corrosion cracking susceptibility	2.05 mass% Li 2.15 mass% Cu
[1991Kay]	TEM, SEM, electrical resistivity, mechanical properties	Physical	(Al) supersaturated solid solutions
[1991Miz]	Single-roll spinning wheel apparatus, powder X-ray diffraction, DSC	Electronic, specific heat coefficient	τ_3 phase
[1992Flo]	SAXS (small-angle X-ray scattering)	Physical	8.49 at.% Li, 0.51 at.% Cu
[1992Gol]	Inelastic-neutron-scattering measurements	Physical Mechanical	τ_2 and τ_3 single crystals
[1992Hip]	Powder X-ray diffraction, pulsed nuclear, magnetic, resonance (NMR) spectroscopy	Density of states at the Fermi level	$Al_{57}Cu_{10.8}Li_{32.2}$, $Al_{56}Cu_{12}Li_{32}$
[1992Poo]	Review	Electronic	Quasicrystals
[1993Fuj]	Electronic structure modeling	Density of states	τ_2, τ_3 phases
[1993Sta]	TEM	Physical	Quasicrystalline τ_2
[1993Yu]	TEM, HREM (high resolution transmission electron microscopy) HAADF-STEM (high angle annular detector dark-field-scanning transmission electron microscopy)	Physical	Quasicrystals
[1995Yam]	Electrical resistivity and micro-Vickers measurements, TEM	Electronic Mechanical	Heat-treated at 823 K and aged at 303 to 473 K, alloys; Al-2.1Li-0.7Cu (mass%); Al-1.7Li-2.0Cu (mass%); Al-1.5Li-2.5Cu (mass%)
[1995Yam]	Resistivity, microhardness, TEM	Physical, Mechanical	1.5-2.1Li; 0.7-2.5Cu (mass%)
[1997Gil]	TEM	Mechanical, Physical	Al alloys 2020, 2090
[1997Sem]	Compressing measurement	Mechanical	Quasicrystalline Li_3CuAl_6, 300-773K, 22-225 MPa
[1997Wan]	ac calorimetric method	Physical, C_p	Quasicrystalline Al_6Li_3Cu, 1-6 K

Reference	Method/Experimental Technique	Type of Property	Comments
[1997Yu]	TEM, electron diffraction contrast analysis	Structure defects	Quasicrystalline Al_6Li_3Cu
[1998Rad]	Theoretical model	Mechanical, hardness	Al alloy 2095
[2000Cso]	TEM, SEM, microhardness and tensile testing	Mechanical, microhardness	Al alloys AF/C 458, 489
[2000Dav]	Tensile testing, DSC	Mechanical, Elongation	alloy I: 1.7 mass% Li alloy II: 1.5 mass% Li
[2001Dut]	Microhardness, X-ray, XSAS, TEM	Mechanical	Al-2.0Cu-3.6Li (mass%)
[2002Ber]	Velocity of sound measurement	Physical	Al_5Li_3Cu, Al_6Li_3Cu, 0-16 K
[2002Dav]	TEM, X-ray, DSC, tensile testing	Physical, Mechanical	Al alloys 2024, 2219
[2002Gab]	TEM, EDS (energy-dispersive spectrometer)	Precipitation	τ_1-Al_2LiCu, AF/C 458
[2003Fra]	Hardness measurement, TEM	Mechanical	AF/C 458
[2003Sal]	ECAE (equal-channel angular extrusion), TEM, EDS, hardness measurement	Mechanical, Elongation, Rockwell hardness	Al alloys 2095, 2195, 9095
[2003Yos2] [2003Yos1]	TEM, HREM, HAADF-STEM	Precipitation	3.2 Cu-1.6 Li, mass% 3.2 Cu-2.4 Li, mass%

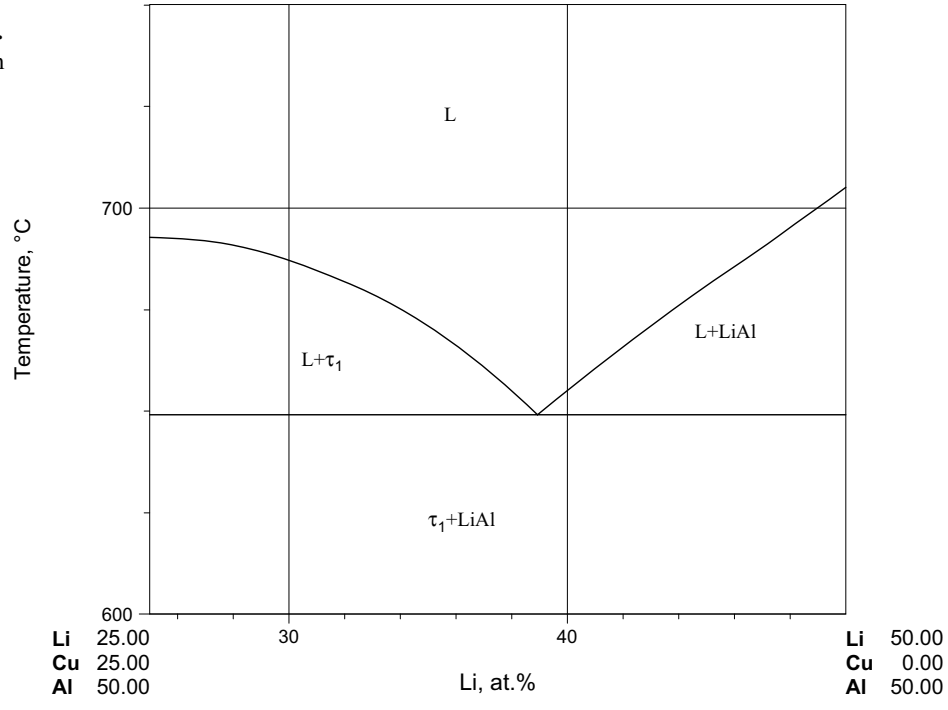


Fig. 1: Al-Cu-Li. Quasibinary section LiAl - τ_1

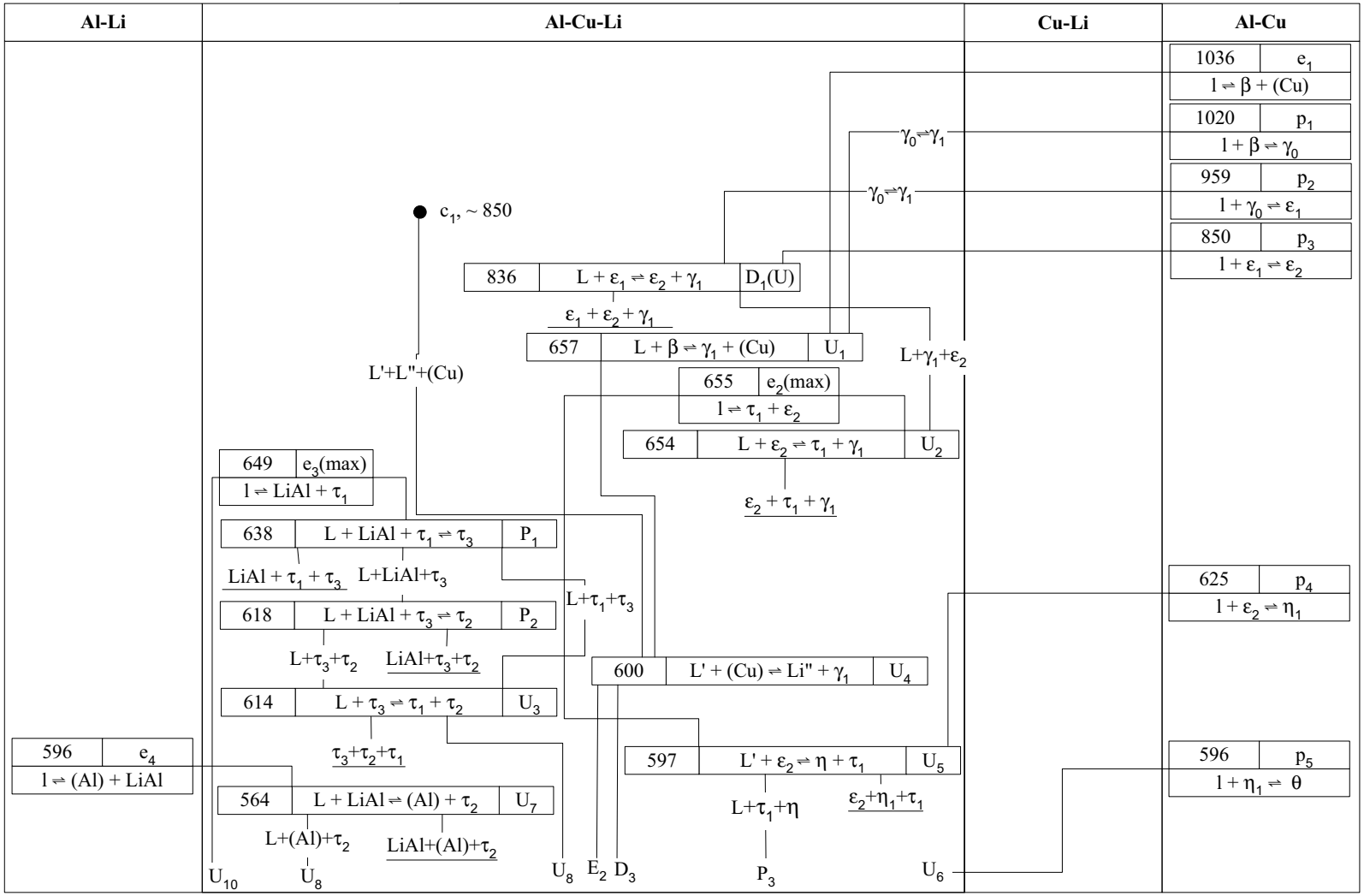
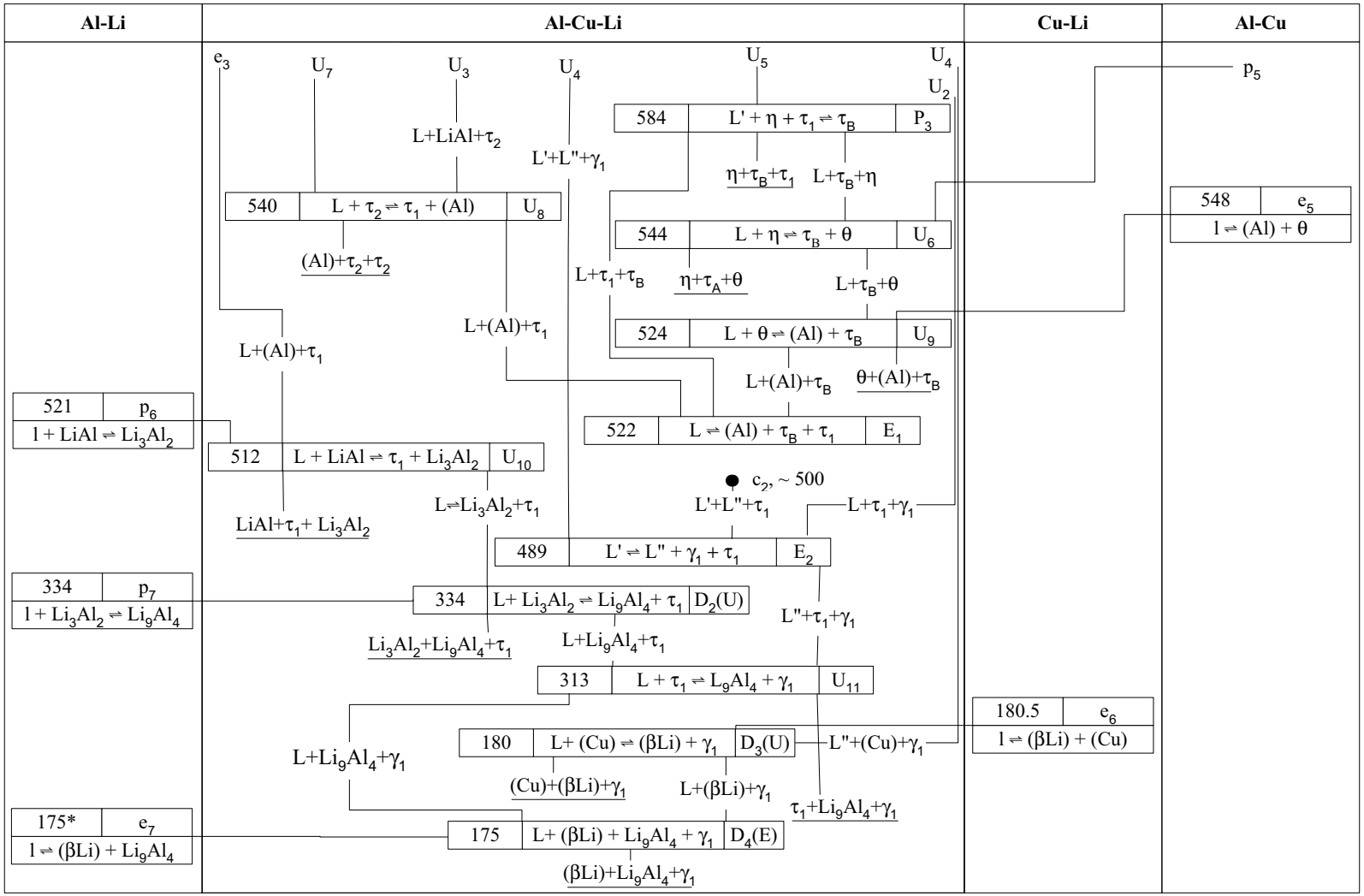


Fig. 2a: Al-Cu-Li. Reaction scheme, part 1



*e_7 : 175° C - calculated (180°C - experimental)

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

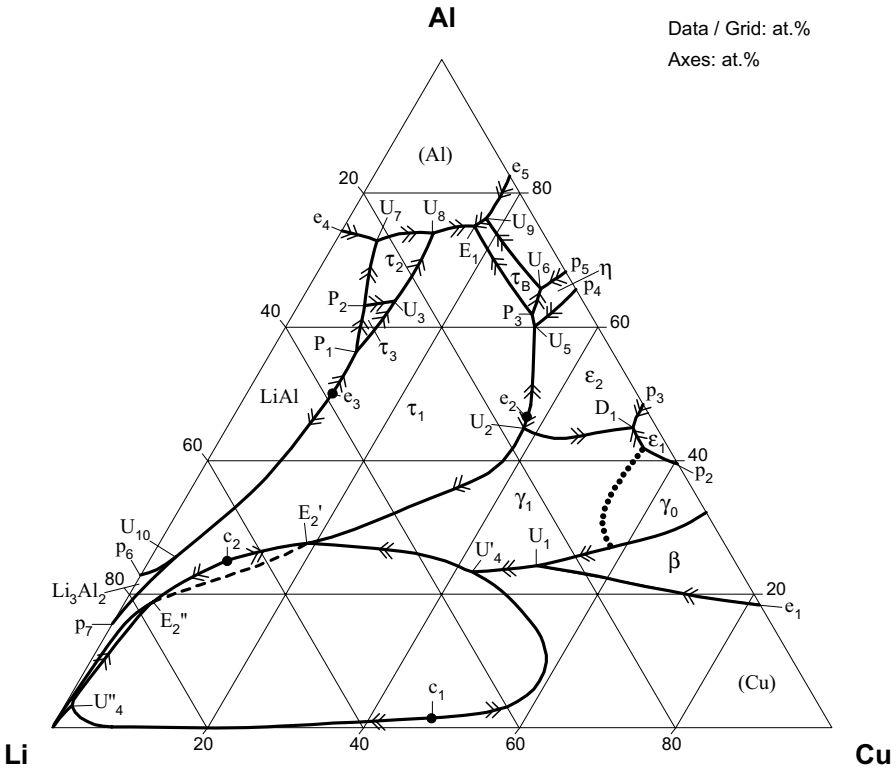


Fig. 3a: Al-Cu-Li. Liquidus surface projection

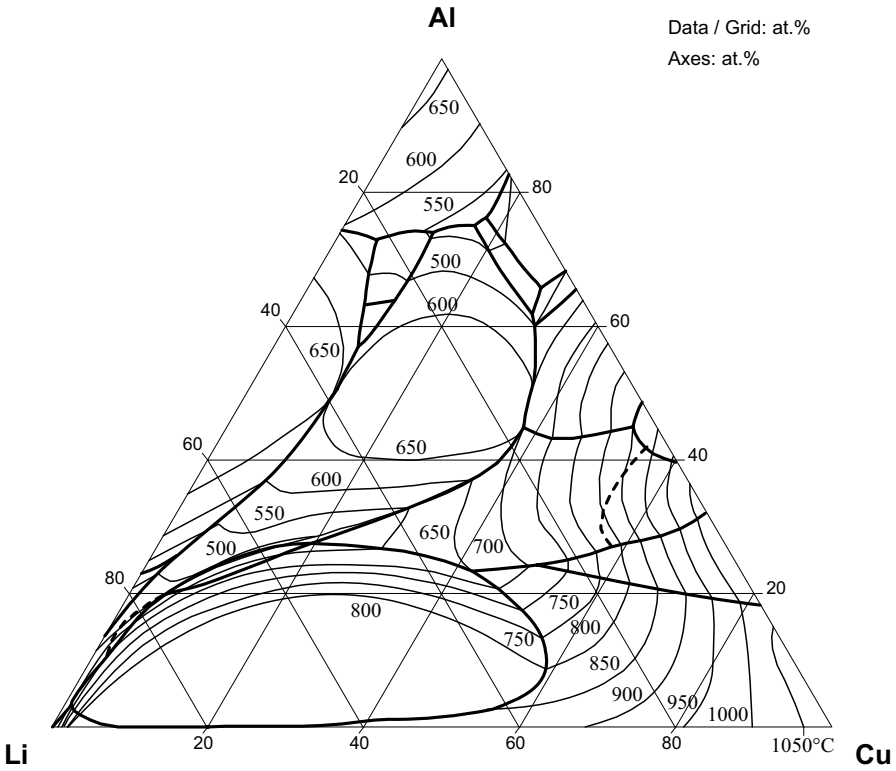


Fig. 3b: Al-Cu-Li. Liquidus isotherms projection

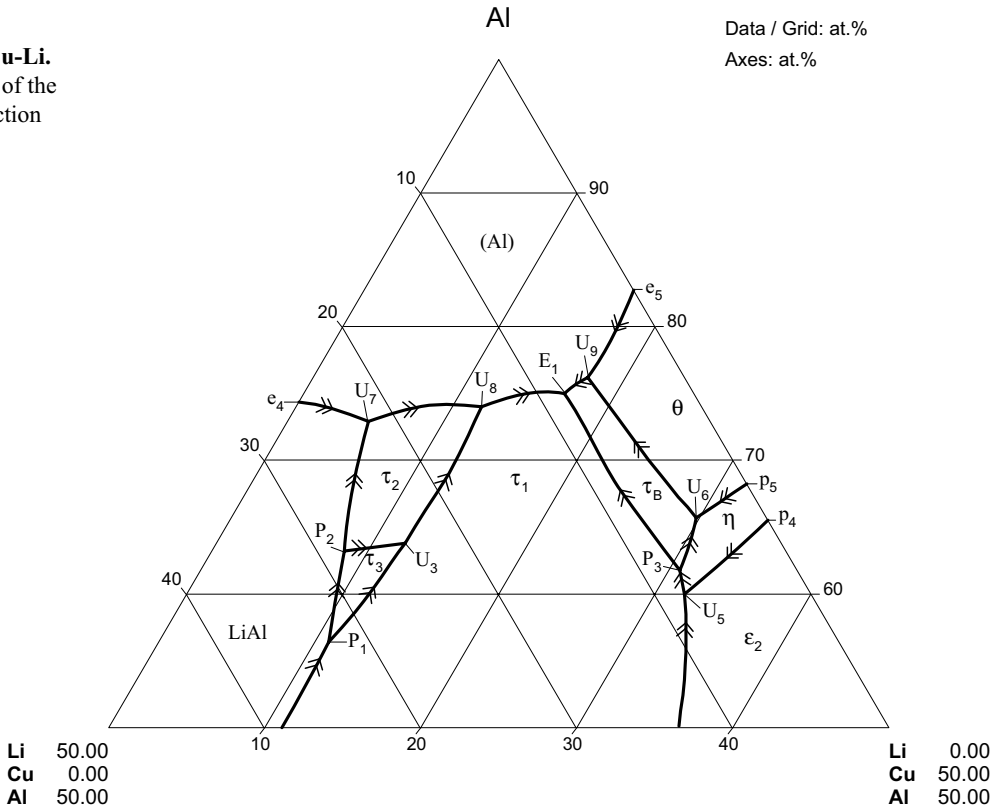


Fig. 3c: Al-Cu-Li.
Al rich region of the liquidus projection

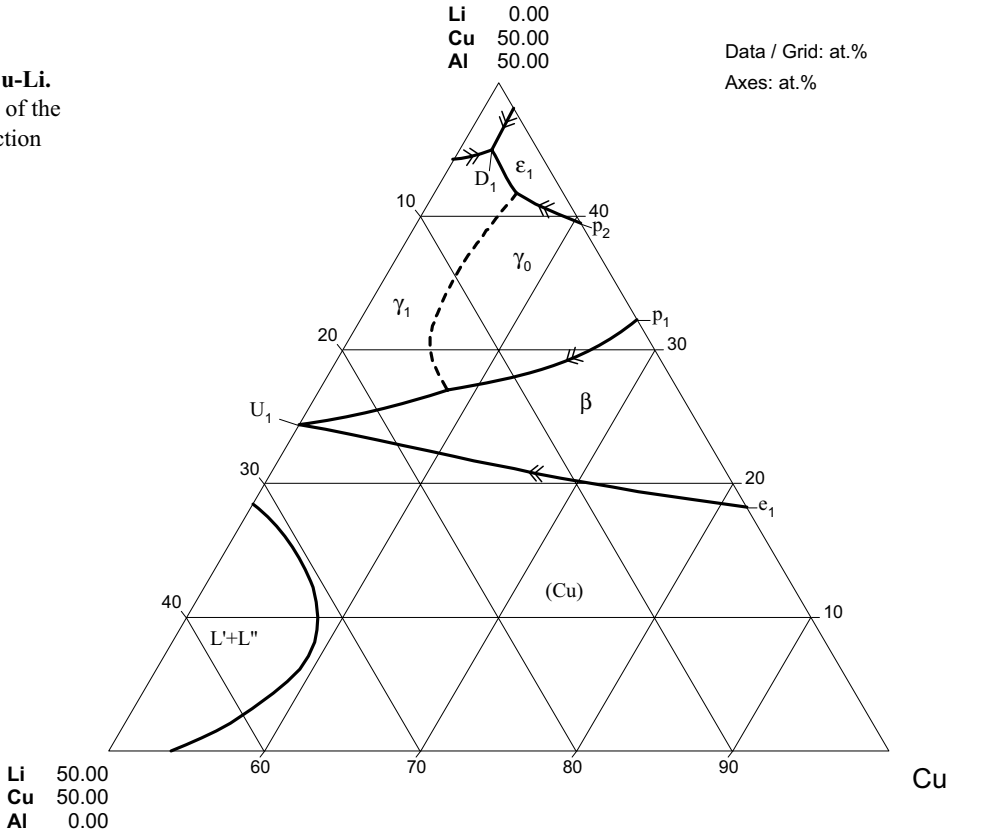


Fig. 3d: Al-Cu-Li.
Cu rich region of the liquidus projection

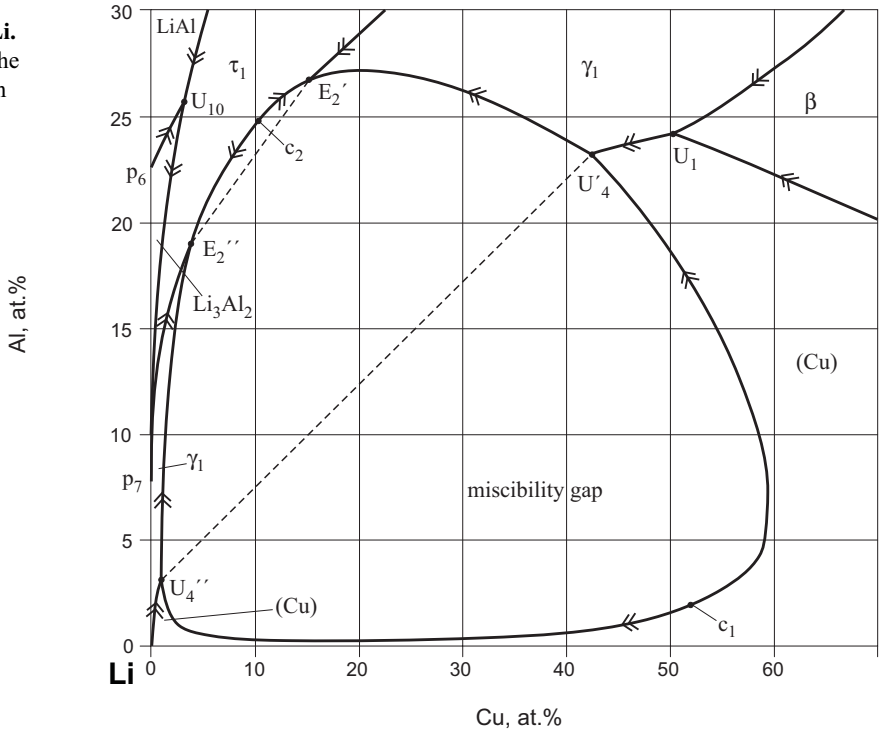


Fig. 3e: Al-Cu-Li. Li rich region of the liquidus projection

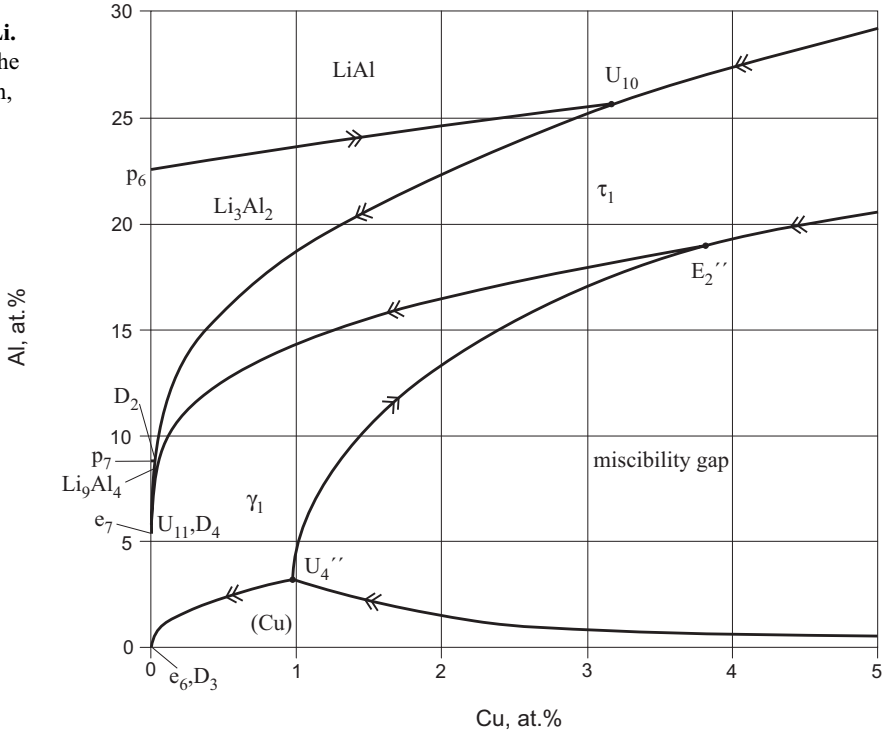


Fig. 3f: Al-Cu-Li. Li rich region of the liquidus projection, fragment near the Al-Li side

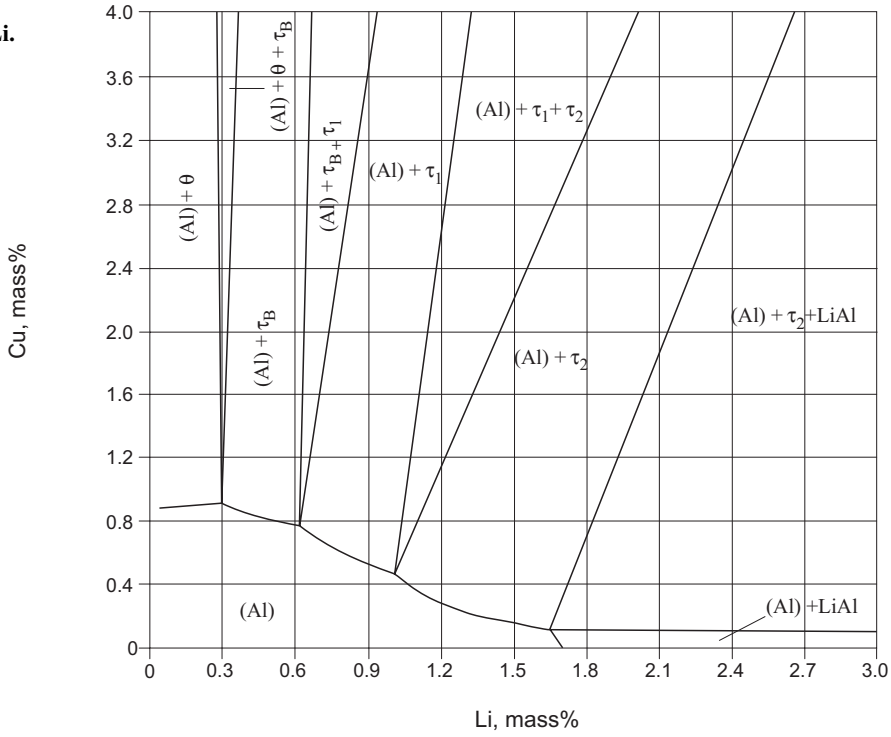


Fig. 4: Al-Cu-Li. Partial isothermal section at 350°C

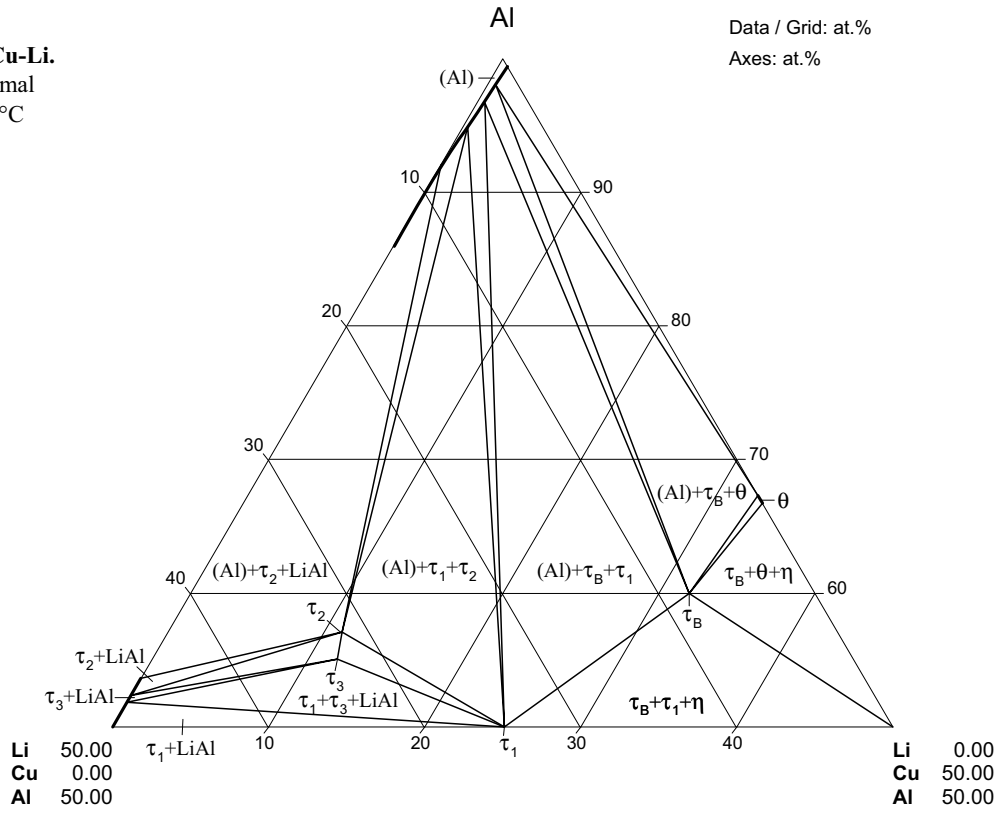


Fig. 5: Al-Cu-Li. Partial isothermal section at 400°C

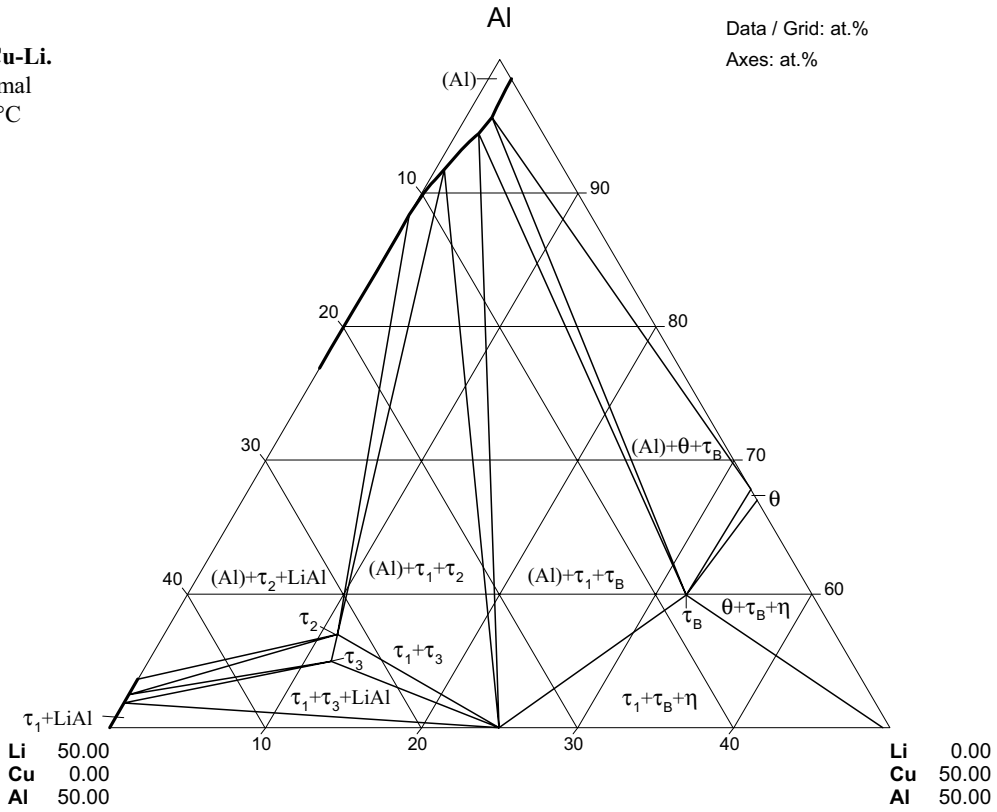


Fig. 6: Al-Cu-Li. Partial isothermal section at 500°C

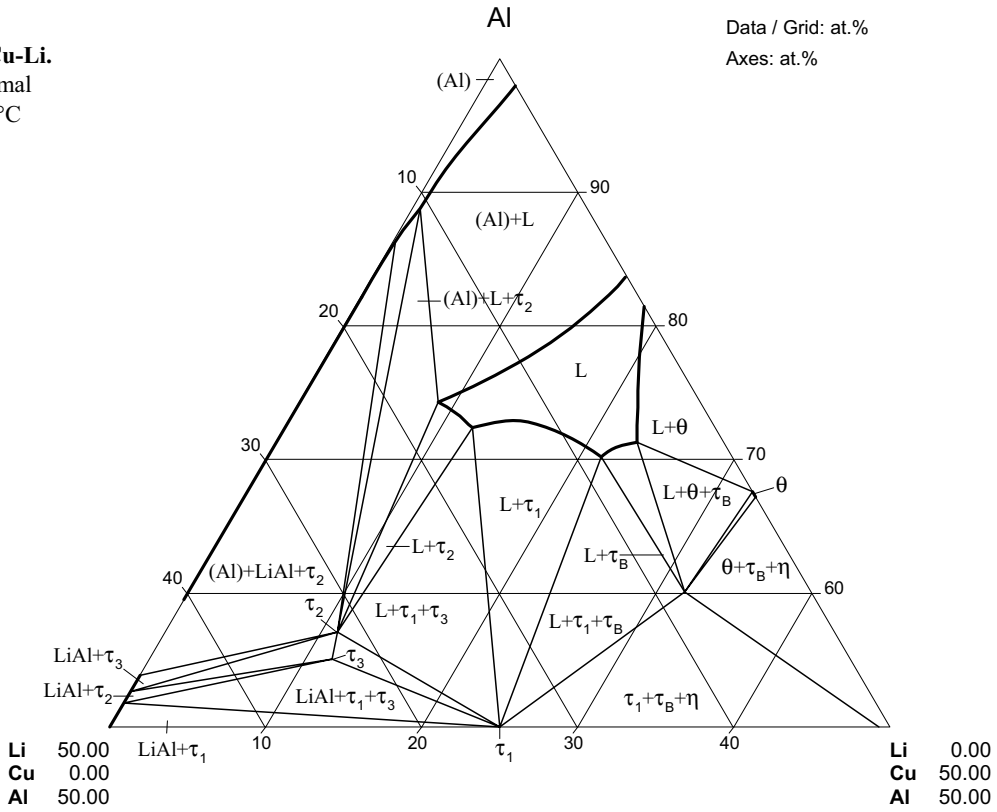


Fig. 7: Al-Cu-Li. Partial isothermal section at 555°C

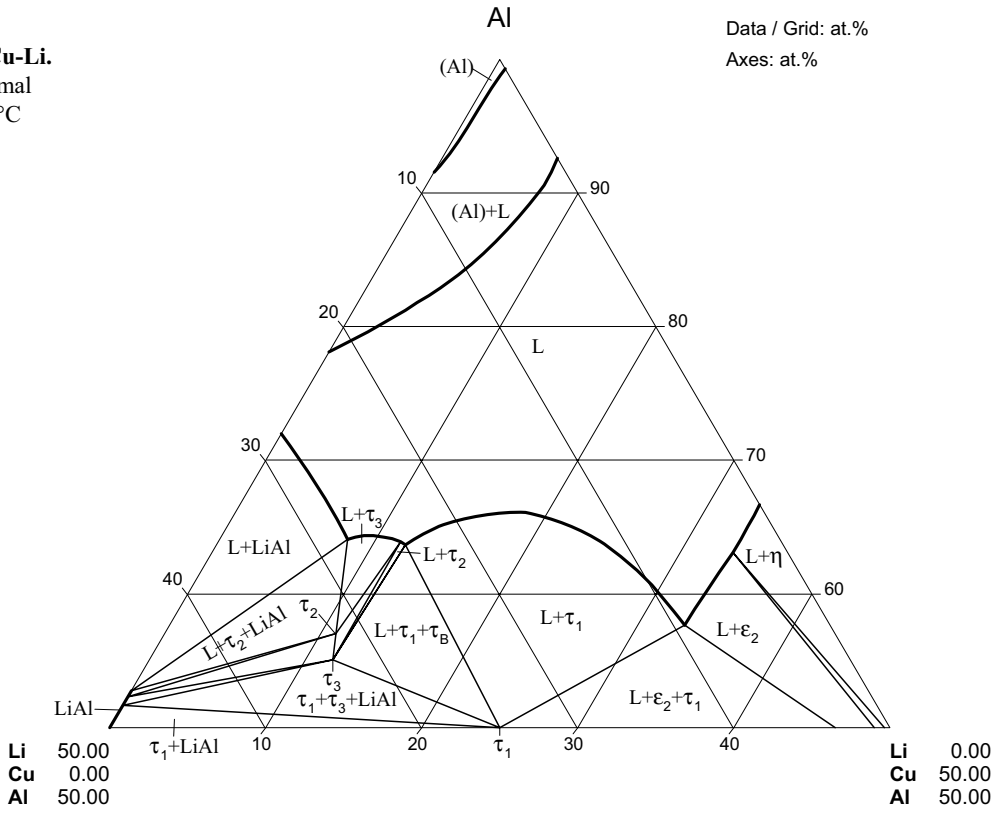


Fig. 8: Al-Cu-Li. Partial isothermal section at 615°C

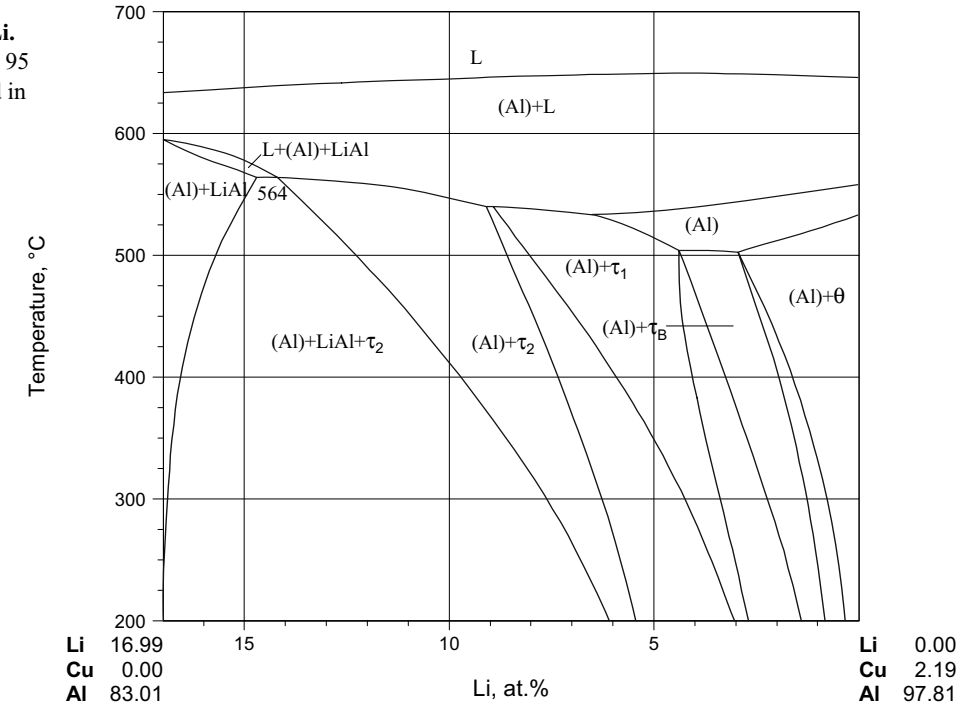


Fig. 9: Al-Cu-Li. Vertical section at 95 mass% Al, plotted in at.%

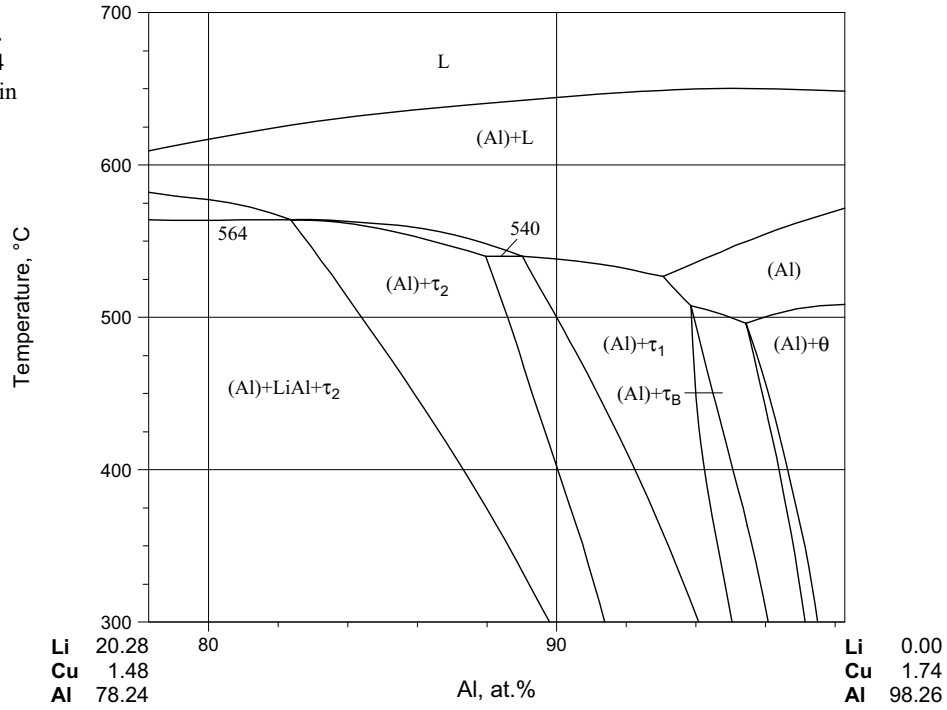


Fig. 10: Al-Cu-Li. Vertical section at 4 mass% Cu, plotted in at.%

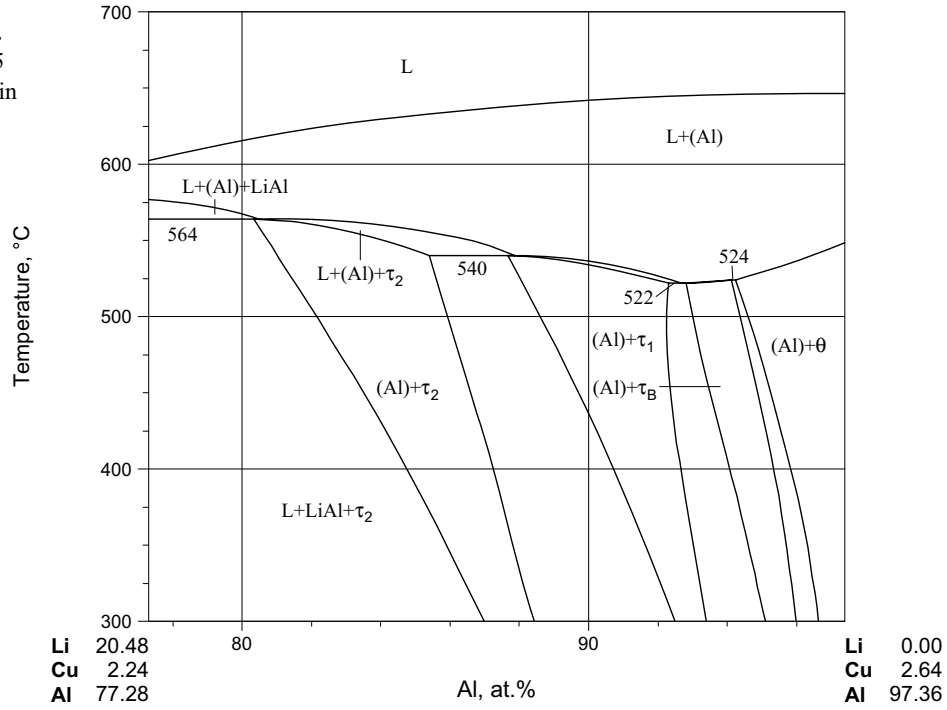


Fig. 11: Al-Cu-Li. Vertical section at 5 mass% Cu, plotted in at.%

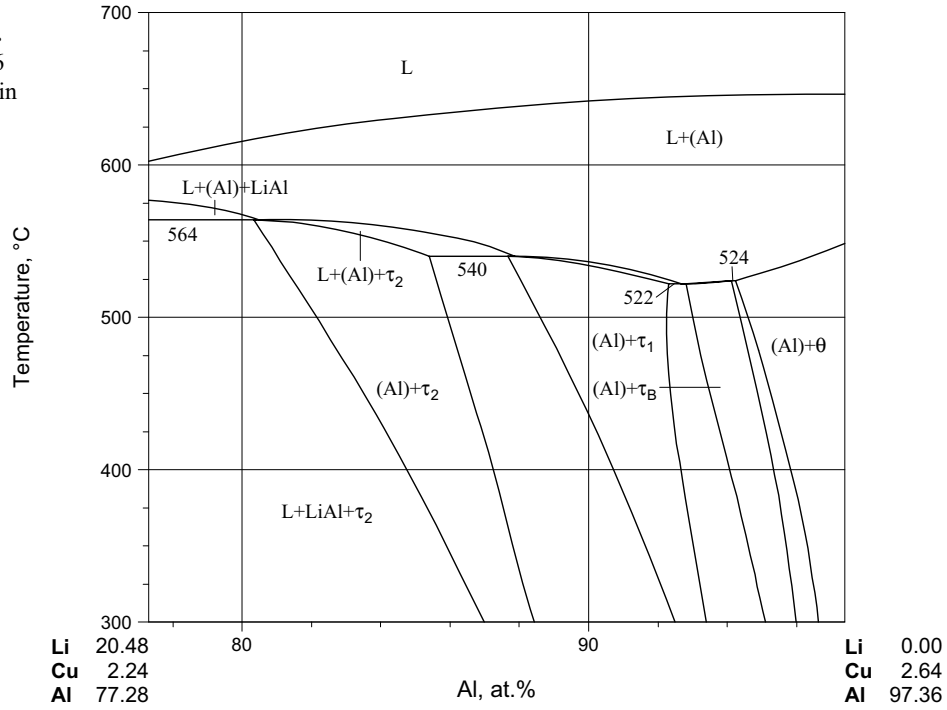


Fig. 12: Al-Cu-Li. Vertical section at 6 mass% Cu, plotted in at.%

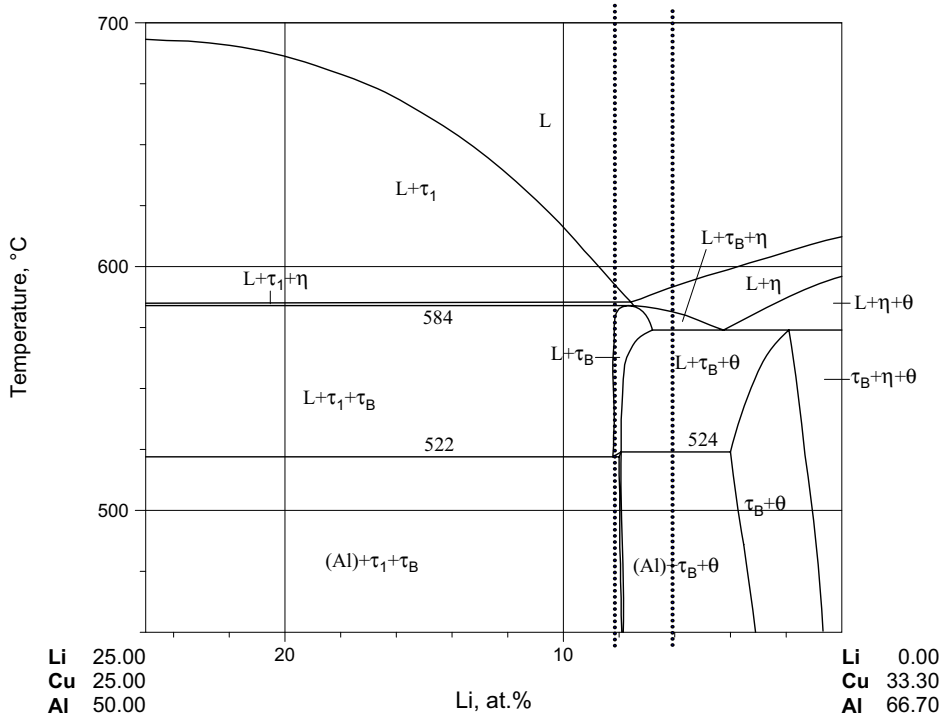


Fig. 13a: Al-Cu-Li. Vertical section $CuAl_2$ - τ_1

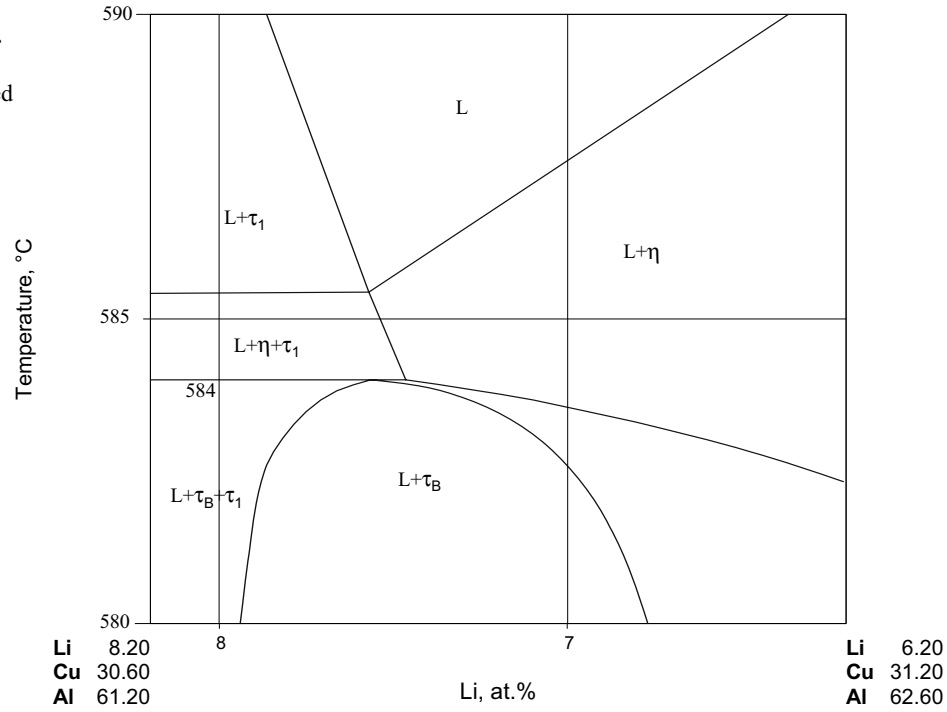


Fig. 13b: Al-Cu-Li. Vertical section $CuAl_2$ - τ_1. Enlarged part separated by dotted lines in Fig. 13a

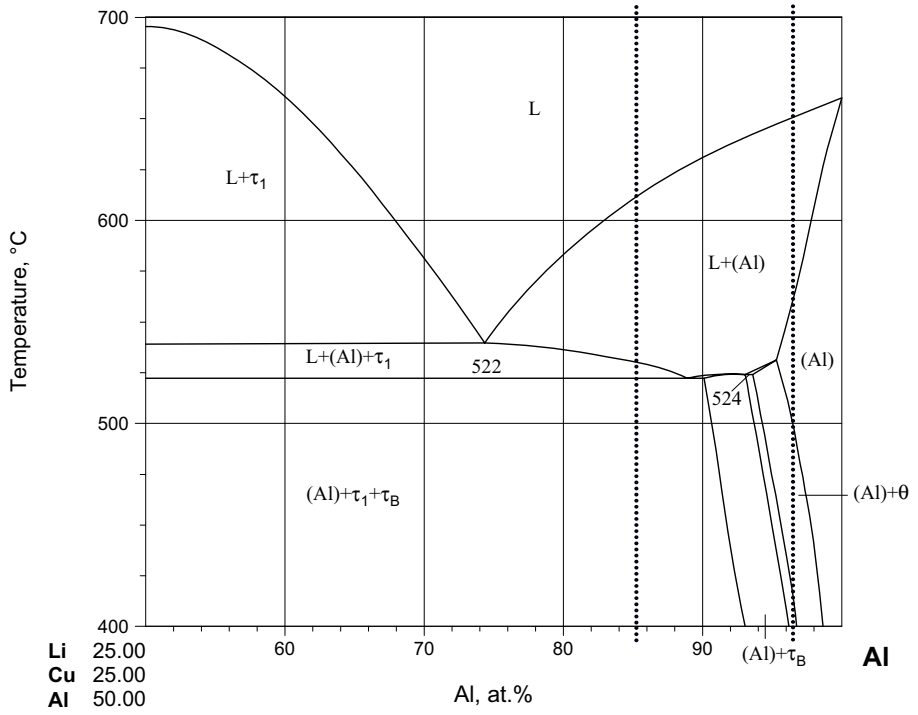


Fig. 14a: Al-Cu-Li. Vertical section τ_1 - Al

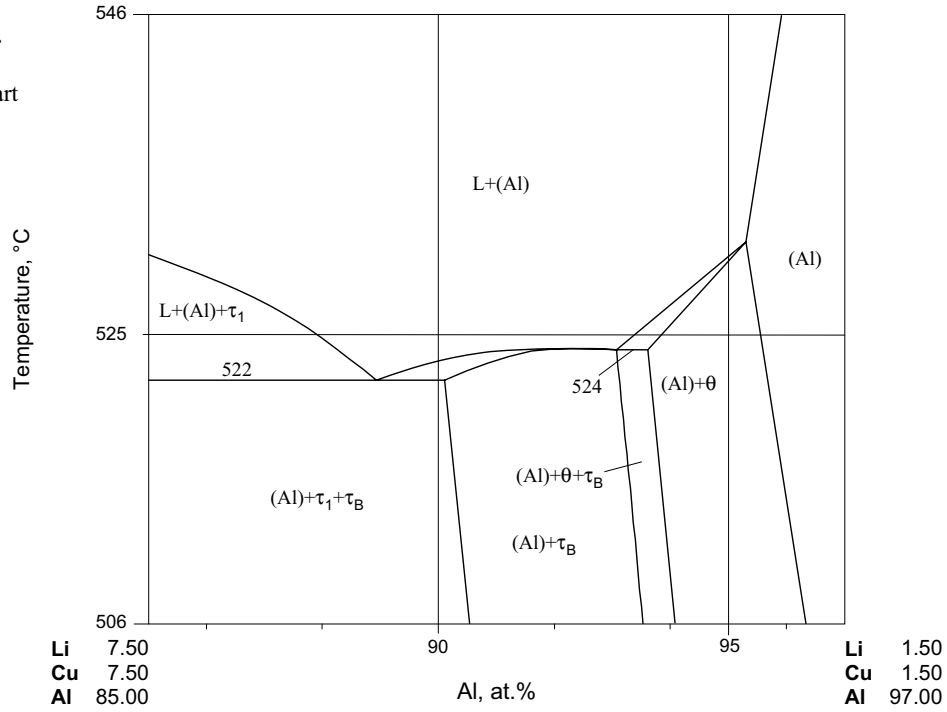


Fig. 14b: Al-Cu-Li. Vertical section τ_1 - Al. Enlarged part separated by dotted lines in Fig. 14a

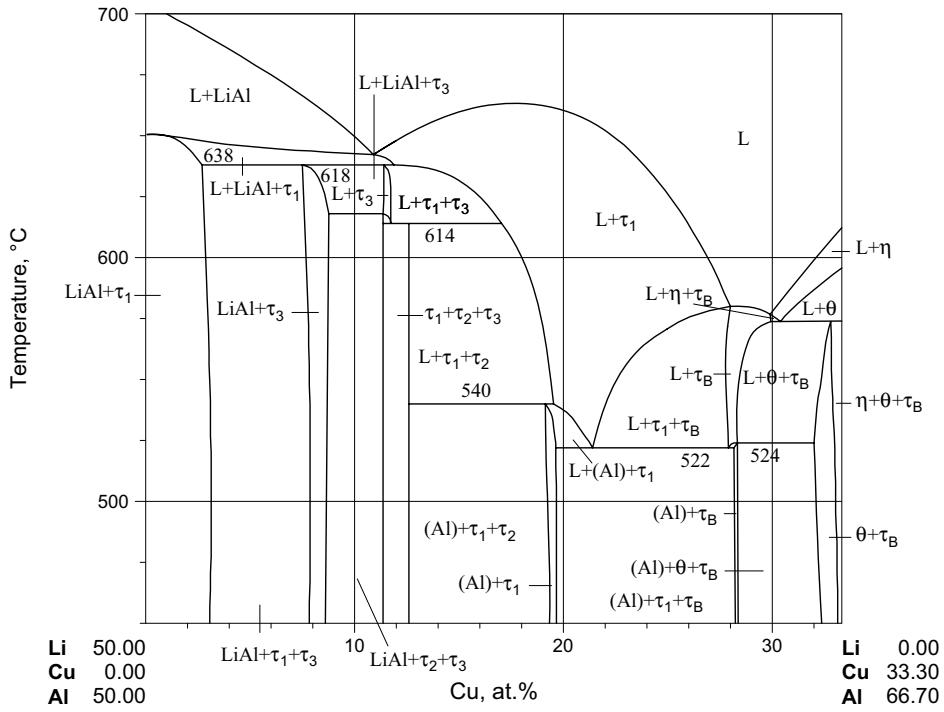


Fig. 15: Al-Cu-Li. Vertical section $CuAl_2$ - LiAl

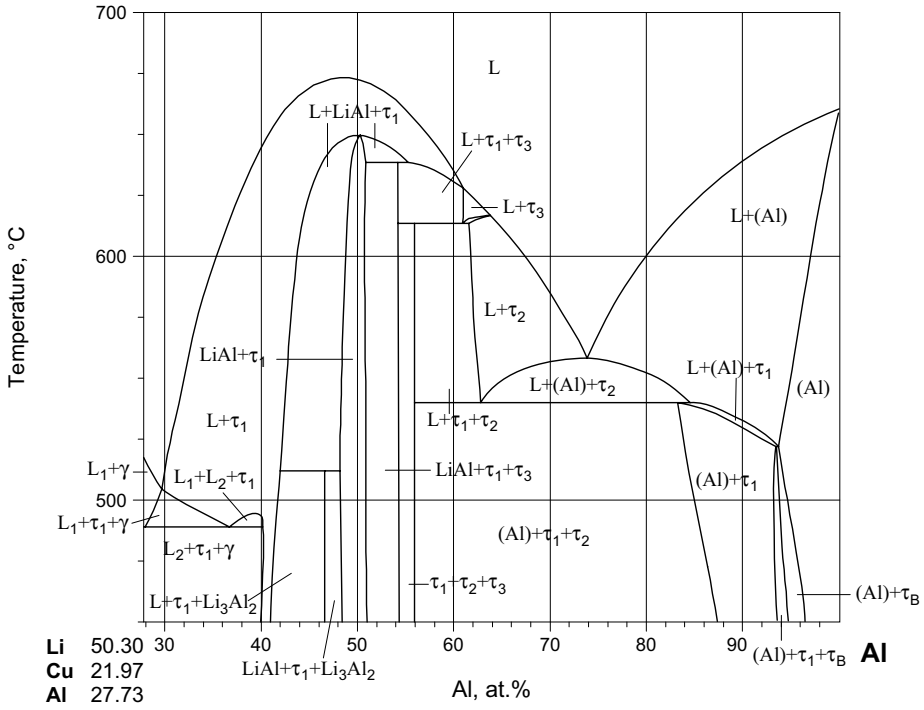


Fig. 16: Al-Cu-Li. Vertical section Al - (Cu:Li = 4:1, mass%), plotted in at.%

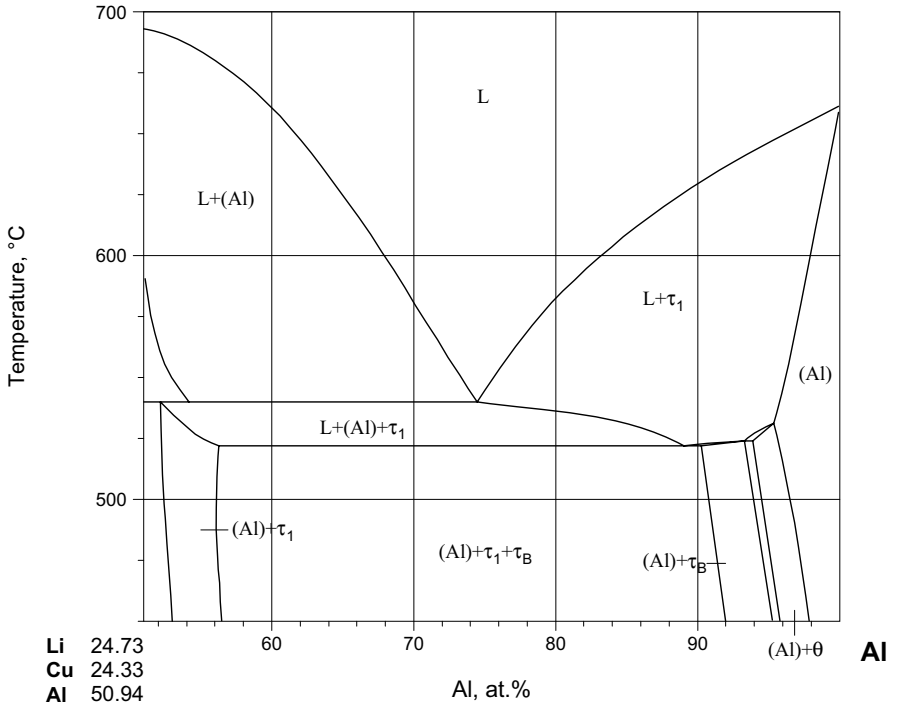


Fig. 17: Al-Cu-Li. Vertical section Al - (Cu:Li = 9:1, mass%), plotted in at.%

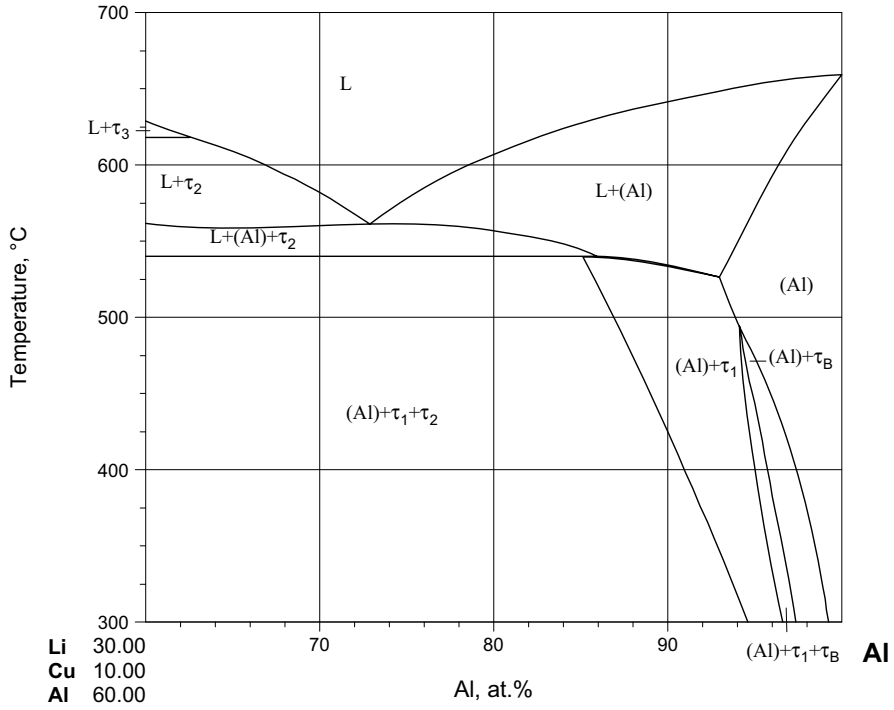


Fig. 18: Al-Cu-Li.
Vertical section
Al - τ_2

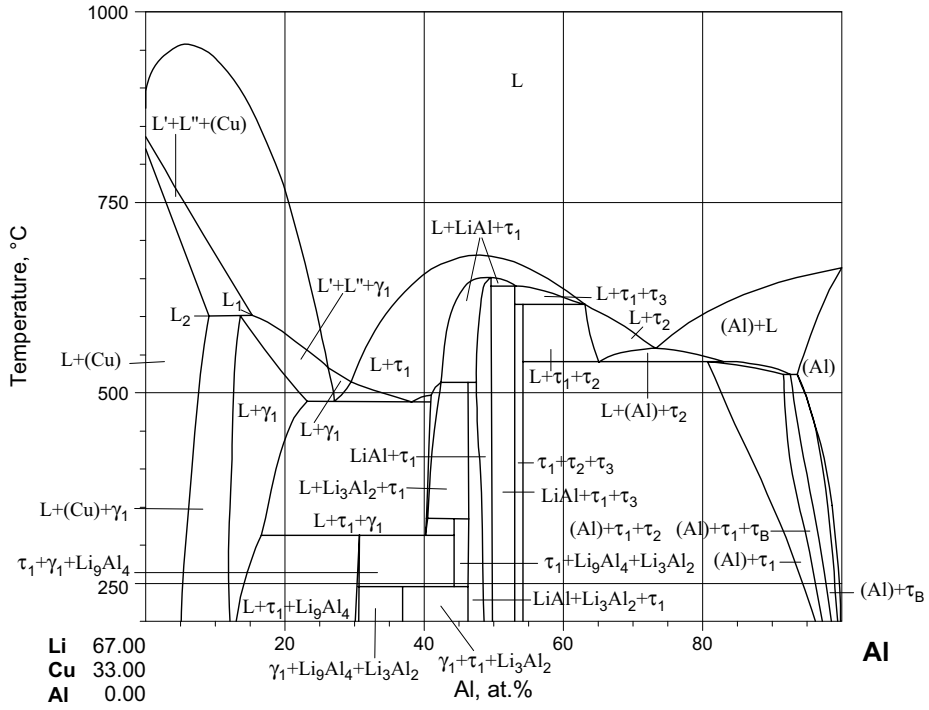


Fig. 19: Al-Cu-Li.
Vertical section
67Li33Cu - Al

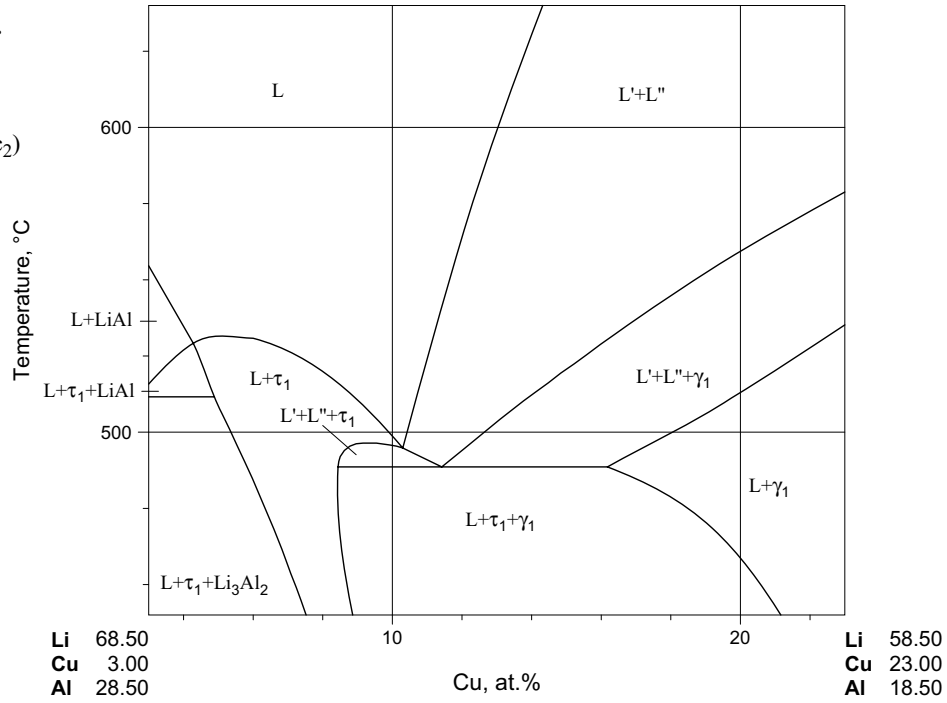


Fig. 20a: Al-Cu-Li. Vertical section through the critical points on the miscibility gap (c_1-c_2) in the vicinity of c_2 point

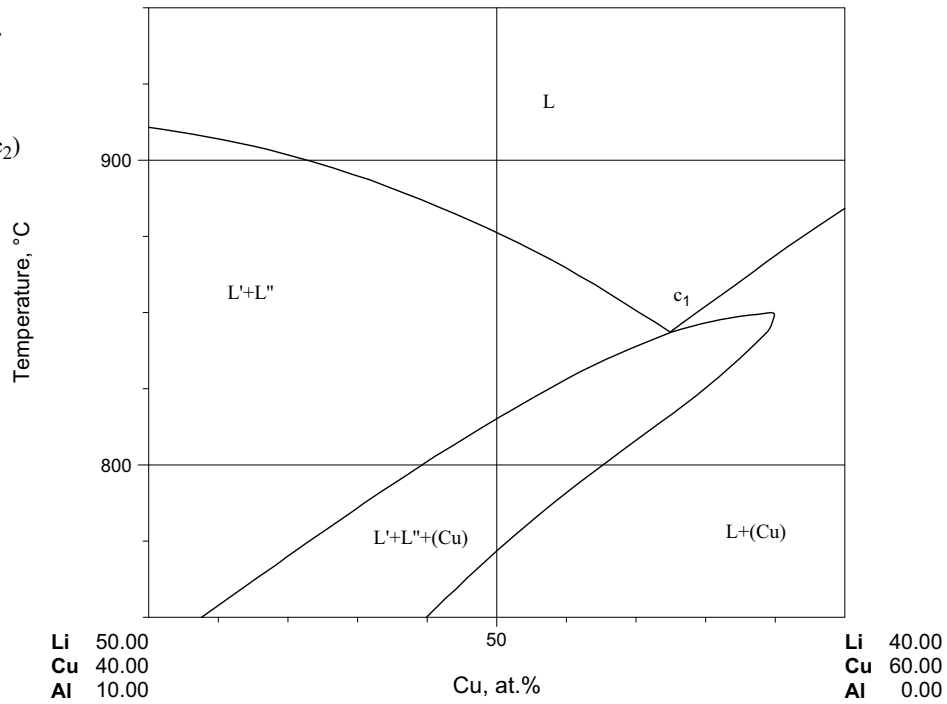


Fig. 20b: Al-Cu-Li. Vertical section through the critical points on the miscibility gap (c_1-c_2) in the vicinity of c_1 point