

Al-Cu-Zn (Aluminum-Copper-Zinc)

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Since the previous review of this system by [1992Gho], several thermodynamic descriptions have become available [1998Lia, 2002Mie, 2003Bor], with the last study reporting in addition new experimental measurements. The description of [1998Lia] is the most detailed treatment available for Al-rich alloys.

Binary Systems

The Al-Cu phase diagram [1993Sau, Massalski2] depicts a number of intermediate phases: CuAl_2 ($C16$ -type tetragonal, denoted θ), CuAl (monoclinic, η), Cu_5Al_4 (LT) (monoclinic, ζ), ε_2 (NiAs-type hexagonal), ε_1 (bcc), Cu_3Al_2 (rhombohedral, δ), Cu_9Al_4 (HT) (γ_0), Cu_9Al_4 (LT) ($D8_3$ -type cubic, γ_1), and Cu_3Al (bcc, β). In the above, HT = high-temperature and LT = low-temperature. The Al-Zn phase diagram [1993Che] contains no intermediate phases. A miscibility gap occurs in the Al-based face centered cubic (fcc) solid solution below 351 °C, where the fcc phase splits into (Al)' and (Al)''. The monotectoid reaction (Al)'' \leftrightarrow

(Al)' + (Zn) follows at 277 °C. The Cu-Zn phase diagram [1993Kow, Massalski2] is characterized by a series of peritectic reactions, which yield CuZn (β , bcc), Cu_5Zn_8 (γ , $D8_2$ -type cubic), CuZn_3 (δ , $B2$, CsCl-type cubic), and CuZn_4 (ε , cph). Zn (cph) has an axial ratio c/a much larger than ε and the two coexisting cph phases are modeled separately with different interaction parameters [1993Kow]. The β phase orders to a CsCl-type $B2$ phase (β') through a second-order transition below ~ 460 °C.

Ternary Phases

A ternary phase with rhombohedral symmetry and with the nominal composition $\text{Al}_4\text{Cu}_3\text{Zn}$ (denoted τ) is known in this system [Pearson3]. The homogeneity range of τ and its temperature dependence are not clearly defined [1998Lia]. The structurally-related, low-temperature form τ' was found to be stable between 400 °C and room temperature by [2005Hao]. [1998Lia] omitted τ' in their thermodynamic description.

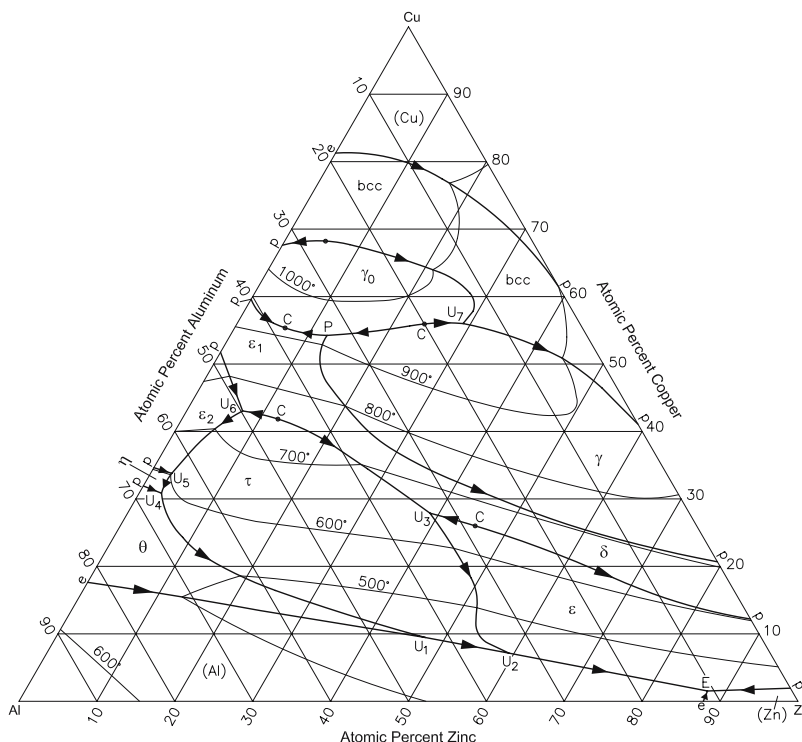


Fig. 1 Al-Cu-Zn computed liquidus projection [1998Lia]

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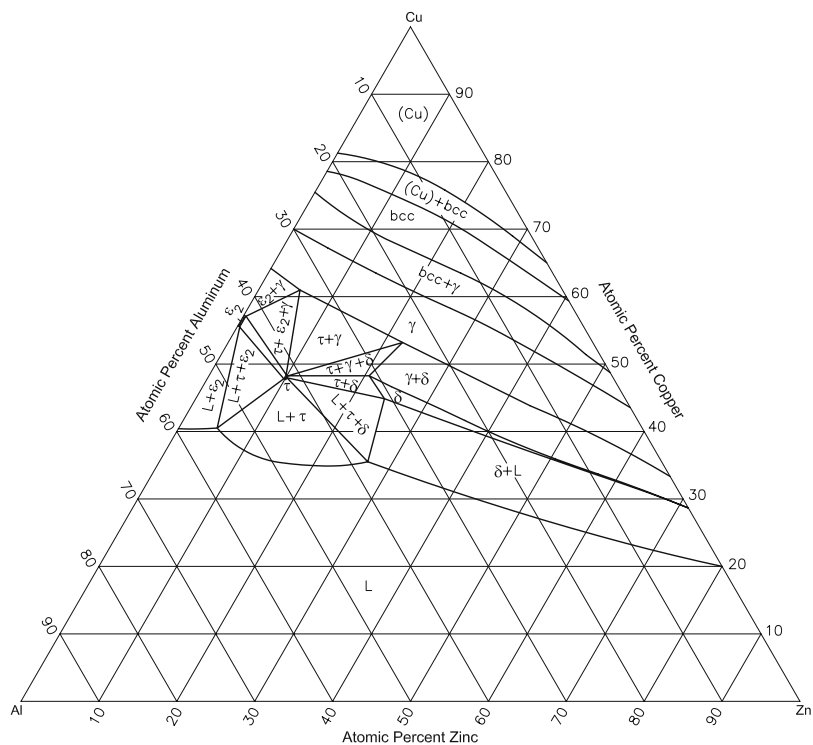


Fig. 2 Al-Cu-Zn computed isothermal section at 700 °C [1998Lia]

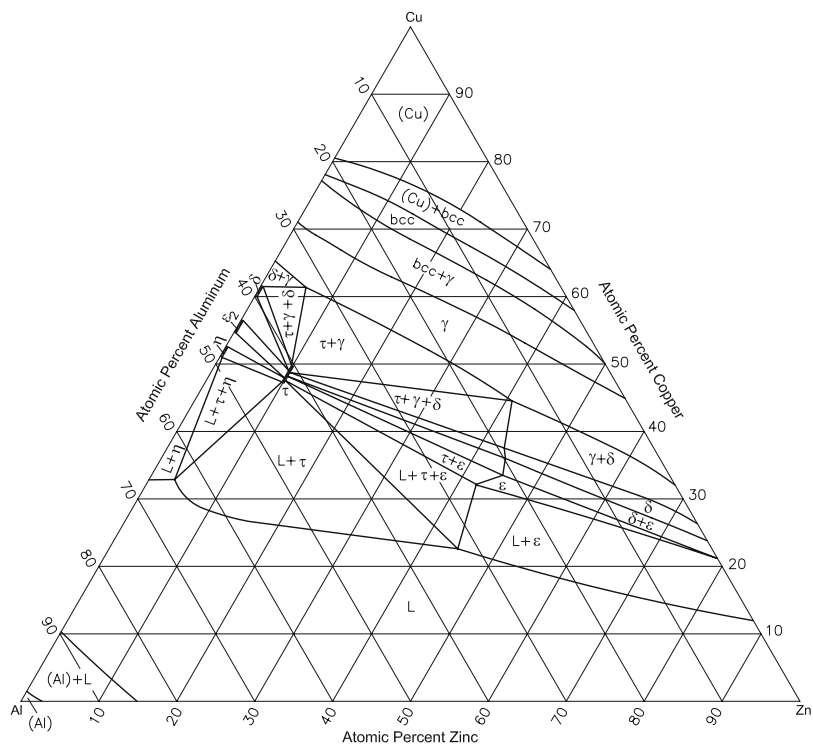


Fig. 3 Al-Cu-Zn computed isothermal section at 600 °C [1998Liaa]

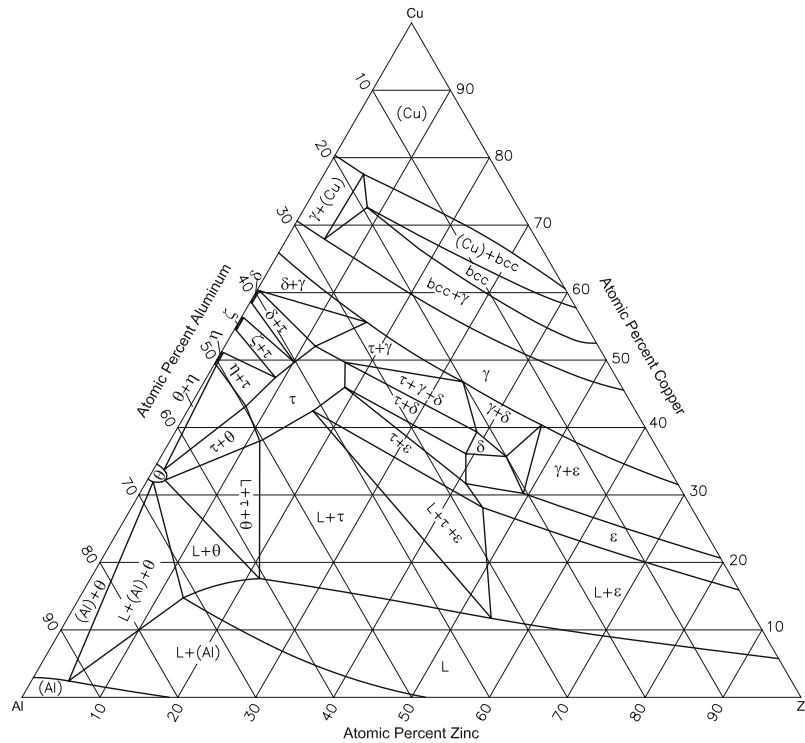


Fig. 4 Al-Cu-Zn computed isothermal section at 500 °C [1998Lia]

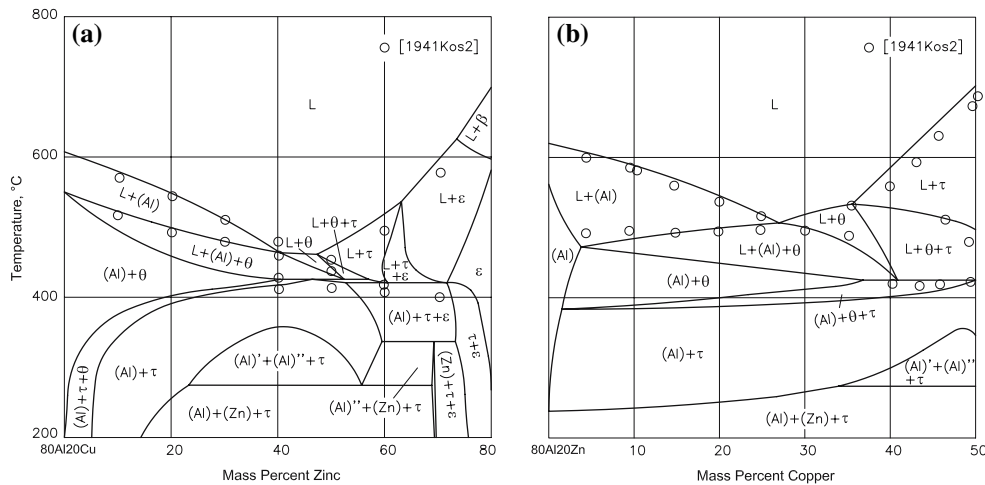


Fig. 5 Al-Cu-Zn computed vertical sections at (a) 20 mass% Cu and (b) 20 mass% Zn [1998Lia]

Computed Ternary Phase Equilibria

[1998Lia] reexamined the experimental data from the literature and presented an assessed liquidus projection and two isothermal sections at 700 and 500 °C, based mainly on the results of [1932Bau, 1941Kos1, 1941Kos2, 1960Arn]. In addition to the above assessed diagrams, the activity measurements of [1985Seb] for Al in Cu-lean liquid alloys and of [1986Sug] for Zn in Cu-rich liquid alloys were used in the optimization. In the thermodynamic modeling, the

liquid, fcc, cph (Zn), cph (ϵ) and bcc phases were treated as disordered solutions. The γ_1 -Cu₉Al₄ and γ -Cu₅Zn₈ form a continuous solid solution (denoted γ), which was simplified to a disordered bcc solution in the thermodynamic description by [1998Lia]. The τ phase was modeled as a semistoichiometric phase with the formula (Al,Cu)_{0.1}Al_{0.4}Cu_{0.4}Zn_{0.1}. The γ_0 phase was described by a three sublattice model. The binary Al-Cu compounds θ , η , ζ , δ , and ϵ were assumed to have no ternary solubility. The binary descriptions of [1993Sau] (Al-Cu), [1993Che] (Al-Zn) and

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[1993Kow] (Cu-Zn) were accepted, except for the remodeling of the γ_1 - γ continuous solid solution. The remodeled (hypothetical) parameters were such as to yield the correct Al-Cu and Cu-Zn phase diagrams, as well as the same Gibbs energies of the binary γ phases in their stable regions. The computed liquidus projection and three isothermal sections at 700, 600 and 500 °C from [1998Lia] are shown in Fig. 1-4. [1998Lia] also computed three vertical sections at 20 mass% Cu, 20 mass% Zn and 40 mass% Zn respectively. The first two of these are shown in Fig. 5.

[2002Mie] developed a thermodynamic description of this system valid for Cu-rich alloys. The reviewed experimental liquidus projection from [1992Gho], the experi-

mental isothermal sections of [1932Bau] and the activity measurements of Zn in Cu-rich liquid alloys from [1986Sug] were used in the optimization. The descriptions of the three binaries were taken from the literature. The description by [1998Lia] of the ternary γ phase as a disordered bcc solution was retained. Due to the greater weight given to the Cu-rich experimental data, the agreement in the Cu-rich region was found to be somewhat better than that obtained by [1998Lia]. The computed results of [2002Mie] for Cu-rich alloys include a liquidus projection, three vertical sections at 2, 4 and 6 mass% Al and five isothermal sections at 800, 700, 600, 515 and 475 °C. The isothermal section at 475 °C is shown in Fig. 6.

With starting metals of 99.47% Al, 99.94% Cu and 99.75% Zn, [2003Bor] induction-melted 11 ternary alloys containing up to 5 mass% Al and homogenized them between 720 and 950 °C. The compositions of the coexisting phases were measured with a scanning electron microscope equipped with energy dispersive spectrometer (SEM-EDS). In the thermodynamic calculations, the binary descriptions used by [1998Lia] were adopted. The ternary parameters for liquid and fcc phases were re-optimized taking the new experimental results into account. The computed isothermal sections for Cu-rich alloys at 800, 750 and 720 °C shown in Fig. 7 agree well with the new experimental data. They were also found to be in agreement with the calculated sections of [1998Lia].

Using starting metals of purity of ≥ 99.9 mass%, [2003Vil] induction melted 10 ternary alloys with Al contents up to 3.68 mass%. The final anneal was for 24 h between 650 and 350 °C. The compositions of the coexisting (fcc + bcc) phases were measured by the electron probe microanalyzer. The results were compared with the vertical sections at 1 and 2 mass% Al determined by [1932Bau]. They show that, at 1 mass% Al, the boundaries of the (fcc + bcc) two-phase region are shifted by about 1 mass% to the Zn-rich side, and at 2 mass% Al, they are shifted by about 1 mass% to the Cu-rich side.

Recently, Hao et al [2002Hao, 2004Che, 2005Hao] studied the low temperature equilibrium in Cu-lean alloys.

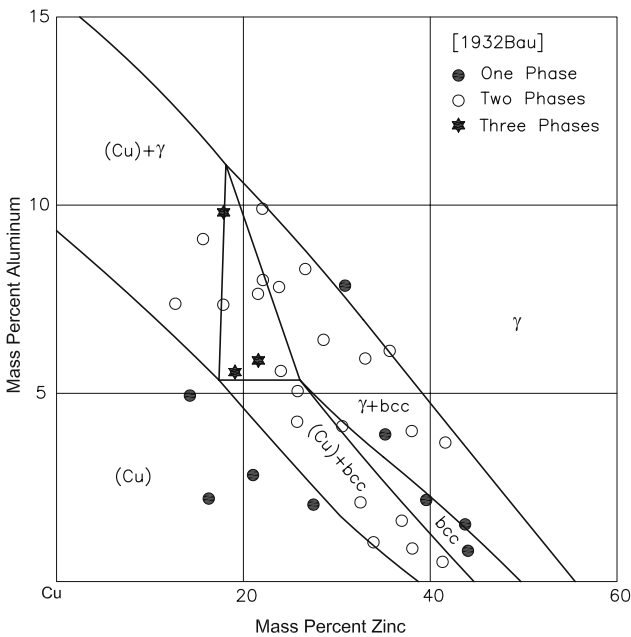


Fig. 6 Al-Cu-Zn computed isothermal section at 475 °C [2002Mie]

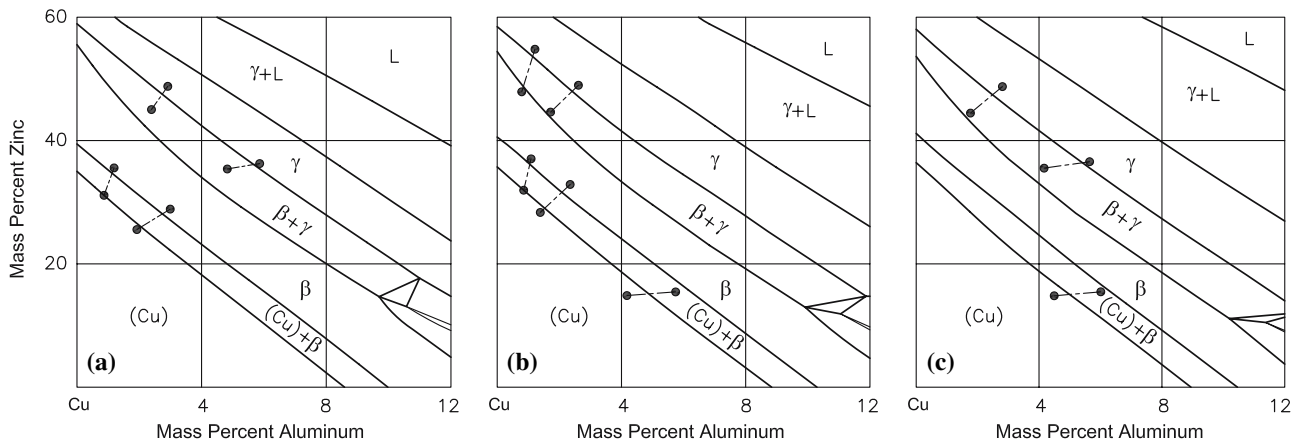


Fig. 7 Al-Cu-Zn computed isothermal sections at (a) 800, (b) 750, and (c) 720 °C. Experimental tie-lines are shown [2003Bor]

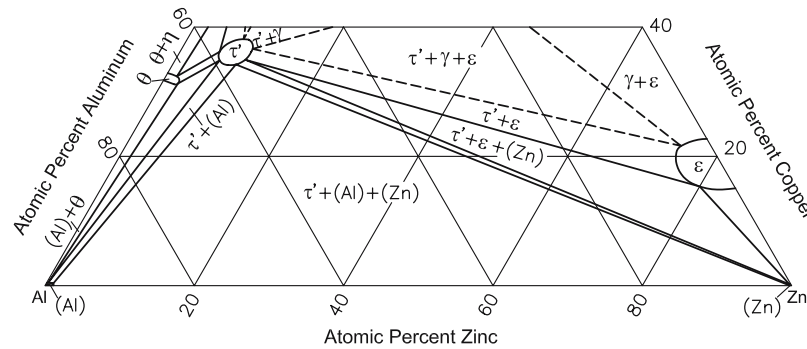


Fig. 8 Al-Cu-Zn isothermal section at 20 °C [2005Hao]

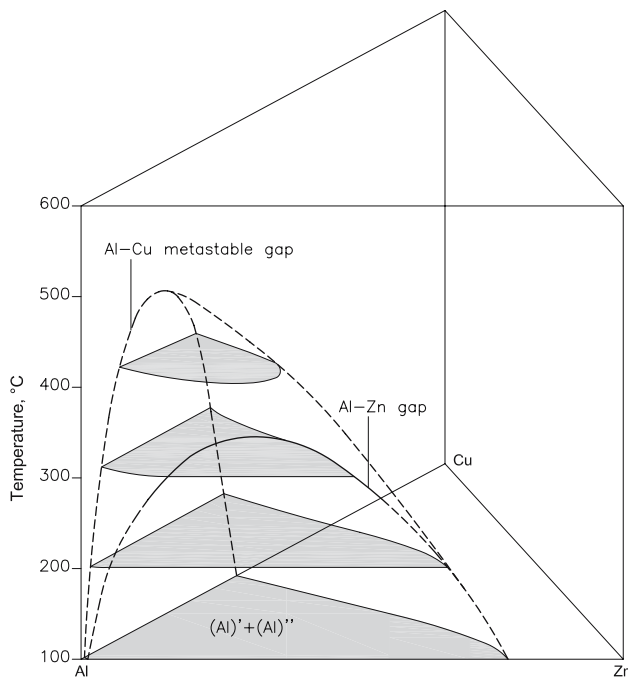


Fig. 9 Al-Cu-Zn schematic illustration of the fcc miscibility gap in the ternary region [2005Hao]

[2005Hao] prepared 14 ternary alloys, which were annealed at 400 °C and cooled at very slow cooling rates of 10-20 °C per day. The co-existing compositions were measured by the electron probe microanalyzer. The room temperature (20 °C) section constructed by [2005Hao] is shown in Fig. 8. The ternary phase τ is stable at room temperature and forms tie-lines with (Al) and (Zn). The effect of copper on the miscibility gap in the fcc phase of the Al-Zn system is illustrated schematically in Fig. 9 [2005Hao]. Copper stabilizes the Al-Zn gap to higher temperatures. The gap slants towards the Al-rich side and ends up at the metastable miscibility gap of the Al-Cu system. Also, the measured tie-lines of [2005Hao] at 320 and 360 °C show that Cu resides preferentially in the Zn-rich fcc phase.

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