Al-Cu (Aluminum-Copper)

J.L. Murray

The equilibrium solid phases of the Al-Cu system are (1) (Cu) and (Al), the terminal fcc solid solutions; (Cu) is often designated α; hence the low-temperature ordered phase based on the fcc structure is designated α_2; (2) β, the disordered bcc solid solution; β_1, the ordered bcc phase, which occurs metastably; and β_0, a high-temperature phase of unknown structure; (3) phases with structures based on γ brass, γ_0, γ_1, and δ; (4) the equiatomic phases, η_1 and η_2, and near-equiatomic phases, ζ_1 and ζ_2, with structures related to the η structures; and (5) θ, or Al_2Cu, and metastable transition phases θ' and θ' formed from supersaturated (Al) before the [θ + (Al)] equilibrium is reached. The solidus is drawn as a smooth curve joining the eutectic reaction to the melting point of Cu; the width of the two-phase [L + (Cu)] field is consistent with the thermodynamic properties of Cu.

The assessed phase diagram for the Al-Cu system is based primarily on review of the work of [Hansen], [22Sto], [24Sto], [25Taz], [26Dix], [33Sto], [34His], [36Aue], [37Dow], [53Tho], [58Vig], [71Fun], [72Lin], [76Tas], and [80San] and was obtained using thermodynamic modeling. The intermediate composition range of the diagram is inaccessible to thermodynamic modeling because of the absence of thermodynamic information on the high-temperature solid phases and the multiplicity of complex solid-state reactions. The calculated diagram agrees well with the available experimental data in all regions within experimental accuracy.

The bcc β solid solution is stable as a high-temperature phase at 70.6 to 82 at.% Cu; β melts congruently at 1049 ± 1 °C. A two-phase [(Cu) + β] field exists between the eutectic temperature and the eutectoid reaction $\beta \leftrightarrow \gamma_1$ + (Cu) at 567 ± 2 °C.

The solubility of Al in (Cu) is 19.7 at.% Al at the eutectic temperature. Solubility decreases below the peritectoid temperature. The α_2 phase exists in equilibrium with (Cu) and γ_1 below a peritectoid reaction (Cu) + $\gamma_1 \leftrightarrow \alpha_2$. The α_2 phase has an ordered fcc structure. Placement of the (Cu) solvus is uncertain. It is possible that in stable equilibrium the two-phase [α_2 + (Cu)] field may be broader than in the present diagram.

The intermetallic compounds in the Al-Cu system are very difficult to work with, because they are hard and brittle. The structures of phases at 58 to 70 at.% Cu, γ_1, δ, and γ_0, are based on the γ brass structure. The γ_1/[γ_1 + (Cu)] boundary is accurately delineated, as in the single-phase δ region. The existence of the high-temperature phase γ_0 of unknown structure was demonstrated by thermal analysis, but the $\gamma_0 + \gamma_1$ region cannot be delineated metallographically.

[71Fun] observed γ_1 and δ in equilibrium in diffusion couples annealed at 500 °C. [80San] compared quenched and slowly cooled structures. The quenched alloys revealed a long-period superlattice structure, probably γ_2. Alloys slowly cooled from 700 °C did not reveal any new structure, but contained two phases, ($\gamma_1 + \delta$). Thus, it appears that γ_2 exists as a metastable transition phase, but not as an equilibrium phase.

The homogeneity range of ζ_2 is 56.6 to 57.9 at.% Al. The equiatomic phases η_1 and η_2 are closely related structurally to the ζ_1 and ζ_2 phases.

θ crystallizes by peritectic reaction at 590 ± 1 °C. The composition range is 31.9 to 32.9 at.% Cu at the eutectic temperature. The supersaturated (Al) solid solution decomposes to form the metastable precipitates, Guinier-Preston (GP) zones, θ', and θ'. Aging treatments to prepare the desired precipitate usually are based on hardness data as a function of composition, aging temperature, and aging time.

There is evidence that the formation of GP zones below 130 °C proceeds by a spinodal mechanism. At room temperature, the initial decomposition is into the solute-rich and solute-lean areas. GP zones form continuously from the modulated microstructure.

The θ' structure has been reported to contain three (001) layers that consist of essentially pure Cu. The structure is tetragonal, not because of ordering, but because of the constraint of coherency with the matrix. The structure is thus identical to that of the GP zones, except for the thickness of the precipitate. The structure of θ' is a tetragonal distortion of the CaF_2 structure.

Because of the sluggishness of the eutectoid reaction $\beta \leftrightarrow$ (Cu) + γ_1, the β phase can be retained metastably. During quenching, metastable β alloys undergo a martensitic transformation to a β′ phase at low Al content or a γ′ phase at higher Al content. The ordering reaction $\beta \leftrightarrow \beta_1$ precedes the martensitic transformation. Thus, three martensitic phases actually appear: β′, β'_1 , and γ′. There are two metastable three-phase equilibria: the eutectoid reaction $\beta \leftrightarrow \beta_1$ + (Cu) and the peritectoid reaction $\beta + \gamma_1 \leftrightarrow \beta_1$. At intermediate cooling rates (air quenching), phase separation into $\beta + \beta_1$ occurs before the martensitic transformation.

The β ↔ (Cu) massive transformation is initiated when a β alloy is quenched into a single-phase (Cu) region. With increasing Al content, the massive transformation is interrupted or ruled out by the martensite transformation, and the maximum composition at which massive product is observed is 20.8 at.% Al.

According to the present thermodynamic calculations, the temperature interval between the eutectic and the minimum of the fcc/L T_0 curve is only about 40 °C. From this, the formation of uniform solid solutions is far more probable than the retention of the amorphous state.

Extended single-phase solid solutions have been reported, with a maximum extension of about 16 or 17 at.% Cu. The decomposition of these supersaturated solutions proceeds by the same sequence observed in solid-quenched alloys. A new phase, Al_3Cu_2, isotypic with Al_3Ni_2 was discovered by splat quenching of 45 and 50 at.% Cu alloys [74Ram].

Metastable phases and extended solubilities also can be obtained in thin films produced from the vapor phase. In films produced by cosputtering, [76Can] observed fcc solid solution between 0 and 28.5 at.% Cu, an anomalous fcc solution between 28.5 and 41.7 at.% Cu, and disordered bcc between 47.6 and 60 at.% Cu.

[77Dhe] produced the equilibrium phases γ_1, η_2, and θ by vapor evaporation, in addition to the extended solid solutions. The (Cu) solid solution was extended to about 78 at.% Cu, γ_1 was found between 65 and 70.5 at.% Cu, and η_2 at 58 at.% Cu.

22Sto: D. Stockdale, *J. Inst. Met., 28*, 273-286 (1922).
24Sto: D. Stockdale, *J. Inst. Met., 31*, 275-295 (1924).
25Taz: M. Tazaki, *Kinzoku-no Kenkyu, 2*, 490-495 (1925) in Japanese.
26Dix: E.H. Dix and H.H. Richardson, *Trans. AIME, 73*, 560-580 (1926).
33Sto: D. Stockdale, *J. Inst. Met., 52*, 111-118 (1933).
34His: C. Hisatsune, *Mem. Coll. Eng. Kyoto Univ., 8*(2), 74-91 (1934).
36Aue: H. Auer, *Z. Metallkd., 28*, 164-175 (1936) in German.
37Dow: A.G. Dowson, *J. Inst. Met., 61*, 197-204 (1937).
53Tho: D.L. Thomas and D.R.F. West, *Res. Correspondence, 6*(12), 61S-62S (1953).
58Vig: V.N. Vigdorovich, A.N. Krestovnikov, and M.V. Maltsev, *Izv. Akad. Nauk SSSR Otd. Tekh. Nauk, 3*, 110-113 (1958) in Russian.
71Fun: Y. Funamizu and K. Watanabe, *Trans. Jpn. Inst. Met., 12*(3), 147-152 (1971) in Japanese.
72Lin: G. Linden, *Prakt. Metall. (Stuttgart), 9*(1), 3-14 (1972) in German-English.
74Ram: P. Ramachandrarao and M. Laridjani, *J. Mater. Sci., 9*, 434-437 (1974).
76Can: B. Cantor and R.W. Cahn, *Acta Metall., 24*, 845-852 (1976).
76Tas: M. Tassa and J.D. Hunt, *J. Crystal Growth, 34*, 38-48 (1976).
77Dhe: F. Dherle, *Vacuum, 27*(4), 321-327 (1977).
80San: M. van Sande, J. van Landuyte, M. Avalos-Borja, G. Torres, and S. Amelinckx, *Mater. Sci. Eng., 46*, 167-173 (1980).

Published in *Int. Met. Rev., 30*(5), 1985. Complete evaluation contains 19 figures, 10 tables, and 220 references.

Special Points of the Al-Cu System

Reaction	Composition, at.% Cu			Temperature, °C	Reaction type
L ↔ Cu		100		1084.87	Melting
L ↔ (Cu) + β	83.0	84.4	82.0	1032	Eutectic
β ↔ (Cu) + γ_1	76.1	80.3	69	567	Eutectoid
L + β ↔ β_0	69.2	70.9	70.2	1037	Peritectic
β_0 ↔ β + γ_0	70.0	70.6	68.5	964	Eutectoid
γ_1 + (Cu) ↔ α_2	69	~80.3	77.25	363	Peritectoid
L + β_0 ↔ γ_0	66.1	67.6	67.4	1022	Peritectic
L ↔ β		75		1049	Congruent
γ_0 ↔ β + γ_1	~69	72.8	~69	780	Eutectoid
γ_0 + L ↔ ε_1	59.8	62.9	62.1	958	Peritectic
γ_0 + ε_1 ↔ γ_1	66.0	61.4	63.9	873	Peritectoid
γ_1 + ε_2 ↔ δ	62.8	59.2	61.9	686	Peritectoid
ε_1 + γ_1 ↔ ε_2	~61.1	62.5	~61.1	850	Peritectoid
ε_1 ↔ L + ε_2	~59.4	52.2	~59.4	848	Monotectic

					Peritectic
$L + \eta_1 \leftrightarrow \zeta$	32.2	49.8	32.8	591	Peritectic
$\varepsilon_2 \leftrightarrow \zeta_1 + \delta$	57.9	56.9	59.3	560	Eutectoid
$\zeta_1 \leftrightarrow \zeta_2 + \delta$	59.8	56.3	~59.8	530	Eutectoid
$\zeta_1 + \eta_1 \leftrightarrow \zeta_2$	55.2	52.3	55.2	570	Peritectoid
$L \leftrightarrow (Al) + \theta$	17.1	2.48	31.9	548.2	Eutectic
$\eta_1 + \theta \leftrightarrow \eta_2$	49.8	33.0	49.8	563	Peritectoid
$\varepsilon_2 + \eta_1 \leftrightarrow \zeta_1$	56.5	52.4	56.2	590	Peritectoid
$\eta_1 \leftrightarrow \eta_2 + \zeta_2$	52.3	~52.3	55.25	590	Eutectoid
$L \leftrightarrow Al$		0		660.452	Melting