Aluminium – Beryllium – Copper

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Literatute Data

Earlier investigations of phase equilibria primarily involved microstructural observations, age hardening behavior and hardness measurements [1929Mas1, 1929Mas2, 1936Ams, 1938Koc, 1938Fil, 1939Bal]. [1936Ams] reported the phase boundaries involving α, β and γ at 400, 500, 600, 700, 800 and 850°C. [1936Ams] used alloys containing up to 2 mass% Be and 5 mass% Al. [1938Fil] used alloys up to 5 mass% Be and 12.5 mass% Al, and determined vertical sections at 0.6, 1.5, 3.0 and 5.0 mass% Be.

The first comprehensive studies of phase equilibria were carried out by [1946Bad] in the Al-corner and by [1957Nic, 1958Nic] in the copper-rich region. Nickel applied metallography, differential thermal analysis (DTA), X-ray and dilatometry to investigate the Cu-corner up to 18 at.% Al and 26 at.% Be. The alloys were prepared from the pure elements and annealed in a hydrogen atmosphere at 800°C to produce a homogeneous state. Badaeva [1946Bad] investigated the Al-rich corner by DTA. A considerable number of alloys were grouped into 6 series of constant Cu:Be mass ratios of 20:1, 12:1, 10:1, 7:1, 5:1 and 2:1. Within each series the Cu content varied from 0 to about 50 mass% except in the 2:1 series in which the Cu content was 0.07 to 33.67 and correspondingly the Be content 0.03 to 16.33 mass%. Part of the results of [1946Bad] are reflected in Fig. 1, Fig. 2 and Fig. 11.

[1979Dri], [1980Cha] and [1990Eff] presented reviews of the Cu-rich part.

Binary Systems

The Al-Be system is accepted from [Mas], the Al-Cu binary phase diagram is accepted from the assessment of [2003Gro], and the Be-Cu system is accepted from [2003Wat]. The phases called γ_0 and γ_1 by [Mas] are identical to the γ' phase of [1957Nic]. The (Al) solvus in Al-Cu was calculated using the COST 507 data set [1998Ans], as for this boundary the resolution in [2003Gro] is not sufficient.

Solid Phases

In the composition range investigated no ternary phase has been found. The δ phase of the Be-Cu system has a large homogeneity range towards Al [1958Nic]. In an alloy with about 18 at.% Al and 43 at.% Be, he found a cubic Laves phase containing superstructure reflections in the X-ray diffraction pattern, and proposed a model of an ordering in this phase. This model, however, should be taken with caution, as its symmetry is reduced from cubic to tetragonal, but no other evidence of this symmetry-reduction is reported. [1967Sta] verified the 200, 222 and 420 superstructure X-ray reflections in an alloy of composition $CuBe_2Al$, but this alloy also contains θ ($CuAl_2$) indicating that the phase contains less Al than according to the formula $CuBe_2Al$. It is not clear, if this phase is a ternary solid solution of the binary Cu-Be δ phase or a ternary phase.

The phases originating from the binary systems are listed in Table 1. The distinction between γ_0 and γ_1 in the Al-Cu system as made by [Mas, 1957Nic] could not verify by optical metallography.

[1987Kar] determined the solubility of Be in the θ phase by metallographic analysis as 0.8 mass% and by EDS as 2.07 mass% (3 or 7 at.% respectively). They consider the metallographic determination as the most accurate, the value corresponds to a solubility limit at the composition $CuBe_{0.1}Al_{1.9}$.

[1977Mye] investigated the effect of Al on the solubility of Cu in Be by ion implantation followed by annealing at 500°C. They found that Al has no significant effect on the solubility of Cu in Be.

The combined solubilities of Be and Cu in (Al) [1946Bad] are shown in Fig. 1, Cu increases significantly the solubility of Be in Al.

The solubilities of Al and Be in the ternary (Cu) solid solution where investigated by [1958Nic] at 800, 700, 600, 500 and 400°C by means of optical metallography and X-ray diffraction and they are shown in Fig. 2. With decreasing temperature the maximum solubility of Al remains almost constant whereas that of Be decreases.

Invariant Equilibria

The reaction scheme of the Cu-rich part, shown in Fig. 3a, is based on the results of [1957Nic]. Six ternary invariant equilibria are reported by [1957Nic] and listed in Table 2. The compositions of all phases are taken from [1957Nic], the equilibria are plotted in Figs. 4 and 5. Slight changes have been made to comply with the accepted binaries. In particular, [1957Nic] observed a thermal effect at 1014°C and attributed it to the invariant reaction L+β_0⇌β+γ_0. In view of the accepted Al-Cu binary where β_0 is not distinguished from β, the nature of this invariant reaction can not be ascertained. Also, limited information preclude speculation of any other invariant reaction that would be compatible with the Al-Cu binary. As a result, the participation of the transition reaction U_1 is not considered in the reaction scheme and the binary L+β⇌γ_0 is considered to participate directly into the transition reaction U_2.

In the Al-rich corner of the ternary system [1946Bad] found an invariant equilibrium at 558°C. These authors reported the (Al) solid solution to have a two-phase equilibrium with the δ phase besides the two-phase equilibria (Al)+(αBe) and (Al)+θ known from the binary systems. That means, there are at least two invariant four-phase equilibria in the Al corner. As the temperature 558°C is higher than that of the binary eutectic L⇌θ+(Al) the second one at 558°C must be a transition reaction L+δ⇌θ+(Al). This implies, that the composition of the liquid phase is on the Be-poor side of the tie line (Al)-θ. The first invariant equilibrium, L+(αBe)⇌δ+(Al) is very near to the Al-Be edge of the ternary system and was not explicitly detected in the investigations of [1946Bad]. A tentative reaction scheme of the Al-rich corner is given in Fig. 3b. Both invariant equilibria are included in Table 2. The compositions of liquid and (Al) are estimated from the results of [1946Bad], that of θ from [1987Kar].

Liquidus Surface

Figure 4 shows the monovariant curves separating the areas of primary crystallization of (Cu), β, γ_0, γ_1 and δ in the Cu-rich corner. Liquidus isotherms were not reported in [1957Nic]. The monovariant curve, in which liquid is in equilibrium with β+γ, disappears at a critical tie line between β and γ at 871°C.

The liquidus surface of the Al-rich corner in Fig. 6 was constructed by [1946Bad] from six *T*-C sections. It is modified by adding tentatively the curve of double saturation L+(αBe)+δ, which was not given by [1946Bad].

Solvus Surfaces

[1946Bad] gave isotherms of the (Al) solvus surface at 530, 480, 390 and 300°C. They did not draw the lines of double saturation of (Al) with respect to θ+δ or δ+(αBe). The line, where (Al) is saturated with θ+δ can easily be deduced from the kinks of the isotherms given by [1946Bad]. The line of double saturation (Al) with δ+(αBe) is very near to pure Al (x_{Al} > 99.5 at.%). The resulting diagram is shown in Fig. 1, where also the (Al) traces of the three-phase equilibria L+(Al)+θ, L+(Al)+δ and L+(Al)+(αBe) are given tentatively, i.e. the boundaries between liquidus and solvus.

Isothermal Sections

Using a large number of alloys, [1957Nic] determined isothermal sections of the Cu-rich part (x_{Cu} > 30 at.%) at 800, 600 and 500°C which are shown in Fig. 7, Fig. 8 and Fig. 9. Minor adjustments have been made along the Al-Cu and Be-Cu edges to comply with the accepted binaries. Schematic isothermal sections (without scaling) at 647, 640, 560 and 490°C were given by [1957Nic] to clarify the phase relations in the solid state.

Temperature – Composition Sections

Cu-rich region [1957Nic]: an isopleth at 3 mass% Be is given in Fig. 10.
Al-rich region [1946Bad]: an isopleth at constant Cu:Be mass-ratio of 20:1 (mole ratio 2.836:1) is given in Fig. 11. The Al-rich part of the diagram is tentatively completed by the additional information given by [1946Bad] for the (Al) solvus (Fig. 1).

Thermodynamics

Thermodynamic properties of ternary alloys have not been determined. [1998Man] observed that the β(A2) $\rightarrow$ β_1 (DO3) ordering transition is first-order. In a Cu-Be-22.72Al (at.%) alloy, the transition temperatures are 511 and 496°C on heating and cooling, respectively. The ordering enthalpy is 1160 ± 50 J·mol^{-1}. On the other hand the enthalpy change associated with the martensitic transformation (β_1 $\rightarrow$ 18R) is 200 J·mol^{-1}. The entropy change associated with these two transformations are comparable.

Notes on Materials Properties and Applications

The copper-rich Be-Cu alloys with addition of aluminium have technical relevance because of their good hardenability.
The ternary alloys in the vicinity of Cu-3.5Be-23Al (at.%) exhibit shape memory phenomenon. Guenin [1995Gue] has provided a review of these results. The shape memory effect is strongly influenced by the quench rate of the β phase which determines the formation of α, α_2 and γ_2 phases, though in minor amounts, and the vacancy concentration [1998Man, 1999Man, 1999Rom]. [1999Rom] observed that β $\rightarrow$ β_1 ordering transition is associated with a marked increase in vacancy concentration. Also, these vacancies are primarily single vacancy type [1998Man]. The migration energy for the vacancies in β Cu-3.55Be-22.72Al (at.%) alloy is 1.0 ± 0.1 eV [1999Rom].
The shape memory behavior is also strongly influenced by stress [1992Hau, 2001Bal]. [1992Hau] studied the martensitic transformation in a Cu-11.6Al-0.52Be (mass%) alloy using single crystals oriented along [001] direction. The alloy has a natural Ms of –10°C. Below Ms, reorientation of β' (18R) or γ' (2H) martensite followed by γ' $\rightarrow$ β'' (18R$_2$) and then β'' $\rightarrow$ α' transformation takes place with increasing stress. Above Ms, β $\rightarrow$ β' and β' $\rightarrow$ α' transformation takes place with increasing stress.
[1991Rio] measured the temperature dependence of single crystal elastic constants of β Cu-11.36Al-0.78Be (mass%) and Cu-0.47Be-11.65Al (mass%) alloys by pulse echo technique. [1999Man] determined the phonon dispersion curves of b Cu-3.55Be-22.72Al (at.%) alloy using inelastic neutron scattering technique, and also the specific heat by differential scanning calorimetry. Using the phonon dispersion results, the elastic constants were calculated based on fifth-neighbor force constant.
[1946Har] developed casting and heat treatment procedure of (2 to 6)Cu-(0.1 to 1)Be-Al (mass%) alloys. He noted that Be in excess of 0.75 mass% tends to cause a decrease in useful properties. These alloys have high tensile strength, high thermal stability and good oxidation resistance.
Upon adding Be into Cu-Al alloys the cavitation-erosion resistance improves significantly.

Miscellaneous

[1967Pot] determined the partitioning ratio of Cu, between solid (Be) and liquid, in two-phase Al-Be alloys as function of temperature and discussed the results in view of purification of Be by treating with liquid Al. [1982Bre] presented a review of decomposition kinetics and microstructures of α and β phases, and associated properties. In the temperature range of 400 to 550°C, the decomposition kinetics and the microstructure of β Al-Be-Cu alloys are sensitive to alloy composition [1962Phi, 1968Hor, 1969Hor]. In general, the following transformations are observed: $\beta_1\rightarrow\alpha$, $\beta_1\rightarrow\gamma_2$, $\beta_1\rightarrow(\alpha+\gamma_2)$ and $\beta_1\rightarrow(\alpha+\gamma_2+\delta)$.

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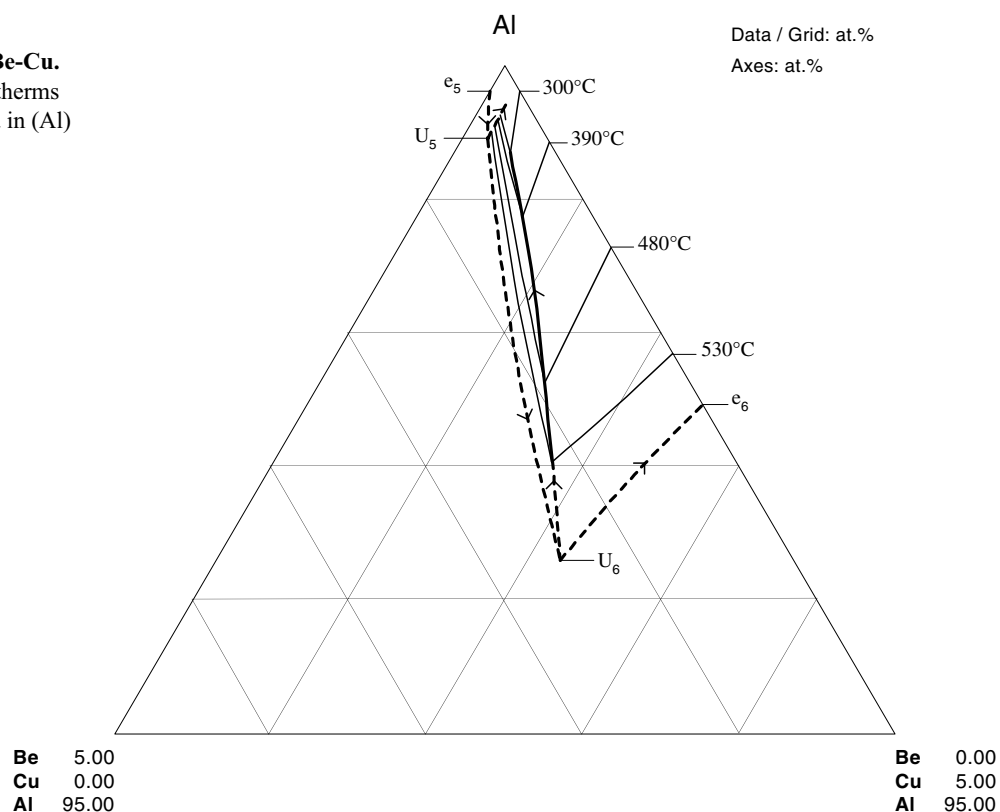**Table 1:** Crystallographic Data of Solid Phases

Phase / Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Al) < 660.452	$cF4$ $Fm\bar{3}m$ Cu	$a = 404.88$	pure Al [V-C]
(βBe) 1289-1109	$cI2$ $Im\bar{3}m$ W	$a = 255.15$	pure Be [V-C]
(αBe) < 1270	$hP2$ $P6_3/mmc$ Mg	$a = 228.58$ $c = 358.43$	pure Be [V-C]
(Cu)	$cF4$ $Fm\bar{3}m$ Cu	$a = 361.48$	pure Cu [V-C]
γ, BeCu < 930	$cP2$ $Pm\bar{3}m$ CsCl	$a = 270.2$	[V-C]
δ, $Be_{4...2}Cu$ < 1219	$cF24$ $Fm\bar{3}m$ Cu_2Mg	$a = 596.9$	[1979Ald] 18.2 - 37.6 at.% Cu
β, $BeCu_2$ AlCu₃	$CI2$ $Im\bar{3}m$ W	$a = 280$ $a = 295.64$	solid solution from $BeCu_2$ to $AlCu_3$ (h₂) [V-C] [V-C]
β₀, $AlCu_3$ 1037-964	-	-	[Mas]
α₂, $AlCu_3$ < 363			DO_{22} long period superlattice [Mas]
γ₀, ≈Al_4Cu_9(h) 1022-780	cubic	-	probably disordered form of γ₁
γ₁, Al_4Cu_9(r) < 873	$cP52$ $P\bar{4}3m$ Al_4Cu_9	$a = 870.6$	[V-C] 31-40 at.% Al
ε₁, Al_2Cu_3 958-848	-	-	[Mas]
ε₂, Al_2Cu_3 850-560	$hP6$ $P6_3/mmc$ NiAs	$a = 414.6$ $c = 506.3$	T = 630°C [V-C]
δ, Al_2Cu_3 686-RT	-	-	[Mas]
ζ₁, Al_4Cu_5 590-560	$oF88–4.7$ $Fmm2$ $Cu_{47.8}Al_{35.5}$	$a = 812.67$ $b = 1419.85$ $c = 999.28$	[Mas, 1985Mur] structure: [2002Gul]

Phase / Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ζ_2, Al_4Cu_5 < 570	$oI24-3.5$ $Imm2$ $Cu_{11.5}Al_9$	$a = 409.72$ $b = 703.13$ $c = 997.93$	55.2 to 56.3 at.% Cu [Mas, 1985Mur] structure: [2002Gul]
η_1, AlCu(h) < 624	$o*32$	$a = 401.5$ $b = 1202$ $c = 865.2$	49.8 to 52.4 at.% Cu [Mas, 1985Mur] Pearson symbol: [1931Pre]
η_2, AlCu < 563	$mC20$	$a = 1206.6$ $b = 410.5$ $c = 691.3$	[V-C]
θ, Al_2Cu < 590	$tI12$ $I4/mmc$ Al_2Cu	$a = 606.6$ $c = 487.4$ $a = 604.2 \pm 1.0$ $c = 484.8 \pm 1.0$	at $Cu_{0.98}Al_{2.08}$ [1987Kar] at $Cu_{0.86}(Al_{1.92}Be_{0.22})$

Table 2: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Al	Be	Cu
$L + \gamma_0 \rightleftharpoons \beta + \delta$	890	U_2	L	7.9	32.4	59.7
			γ_0	2.9	43.4	53.7
			β	10.0	29.9	60.1
			δ	2.1	66.0	31.9
$L + \delta \rightleftharpoons \beta + \gamma$	875	U_3	L	13.6	28.4	58.0
			δ	4.6	63.6	31.8
			β	16.9	20.1	63.0
			γ	16.9	25.4	57.7
$\beta \rightleftharpoons (Cu) + \gamma$	647	e_{max}	β	4.1	24.7	71.2
			(Cu)	6.8	7.4	85.8
			γ	0.4	47.6	52.0
$\beta + \gamma \rightleftharpoons (Cu) + \delta$	560	U_4	β	18.0	8.9	73.1
			γ	0.8	47.6	51.6
			(Cu)	15.4	2.9	81.7
			δ	0.2	69.7	30.1
$\beta \rightleftharpoons (Cu) + \gamma_1 + \delta$	490	E_1	β	20.4	7.5	72.1
			(Cu)	16.6	1.4	82.0
			γ_1	26.7	8.5	64.8
			δ	0.4	69.6	30.0
$L + (\alpha Be) \rightleftharpoons (Al) + \delta$	≈640	U_5	L	≈ 96	≈ 3	≈ 1
			(Al)	≈ 99.5	≈ 0.4	≈ 0.1
$L + \delta \rightleftharpoons (Al) + \theta$	558	U_6	L	≈ 83.6	≈ 1.4	≈ 15
			(Al)	≈ 96.3	≈ 1.5	≈ 2.2
			θ	≈ 64	≈ 3	≈ 33

Fig. 1: Al-Be-Cu.
Solubility isotherms
for Be and Cu in (Al)
[1946Bad]

Al

Data / Grid: at.%

Axes: at.%

e₅

300°C

U₅

390°C

480°C

530°C

e₆

U₆

Be	5.00	
Cu	0.00	
Al	95.00	

Be	0.00
Cu	5.00
Al	95.00

Be	0.00
Cu	80.00
Al	20.00

Data / Grid: at.%

Axes: at.%

Fig. 2: Al-Be-Cu.
Solubilities of Al and
Be in the ternary (Cu)
solid solution

10

10

600

800

700

500

400°C

90

Cu

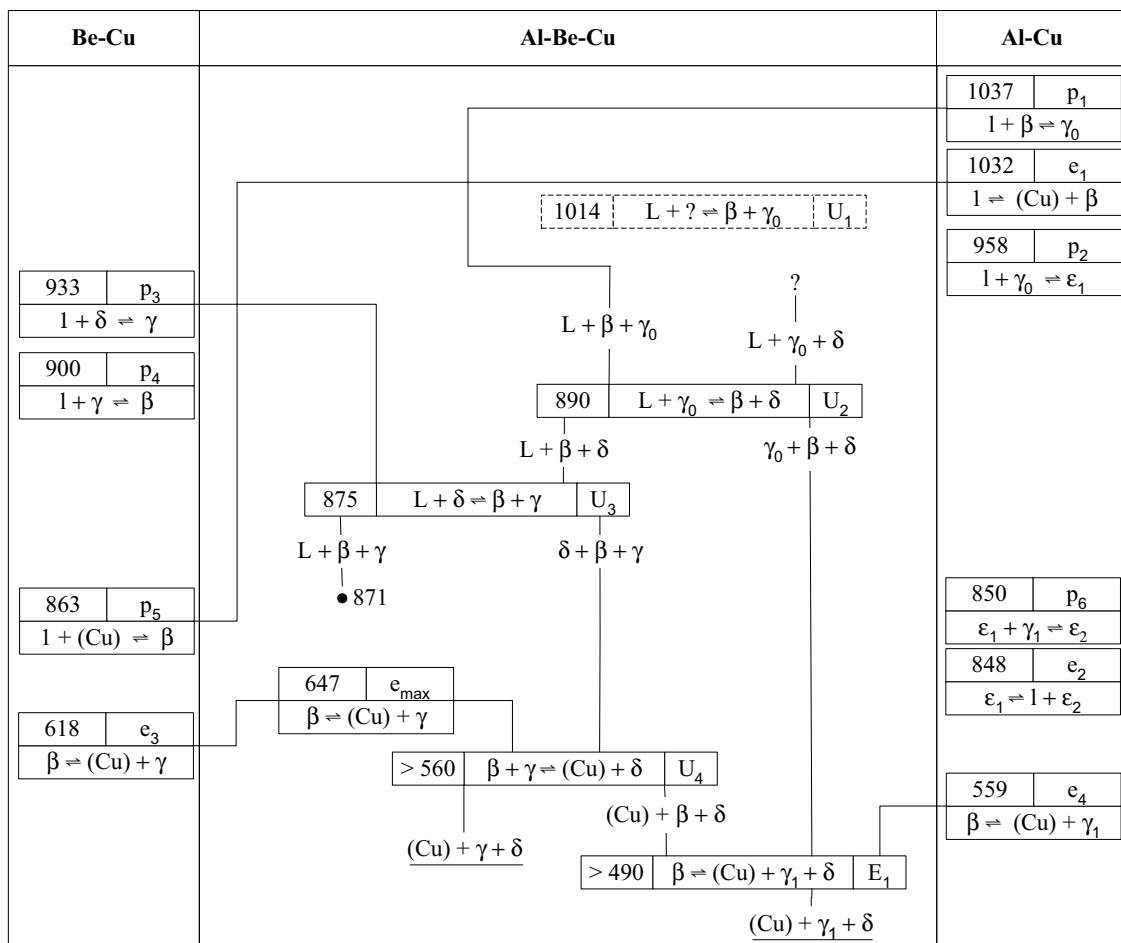|	
Be	20.00
Cu	80.00
Al	0.00

Be-Cu	Al-Be-Cu	Al-Cu
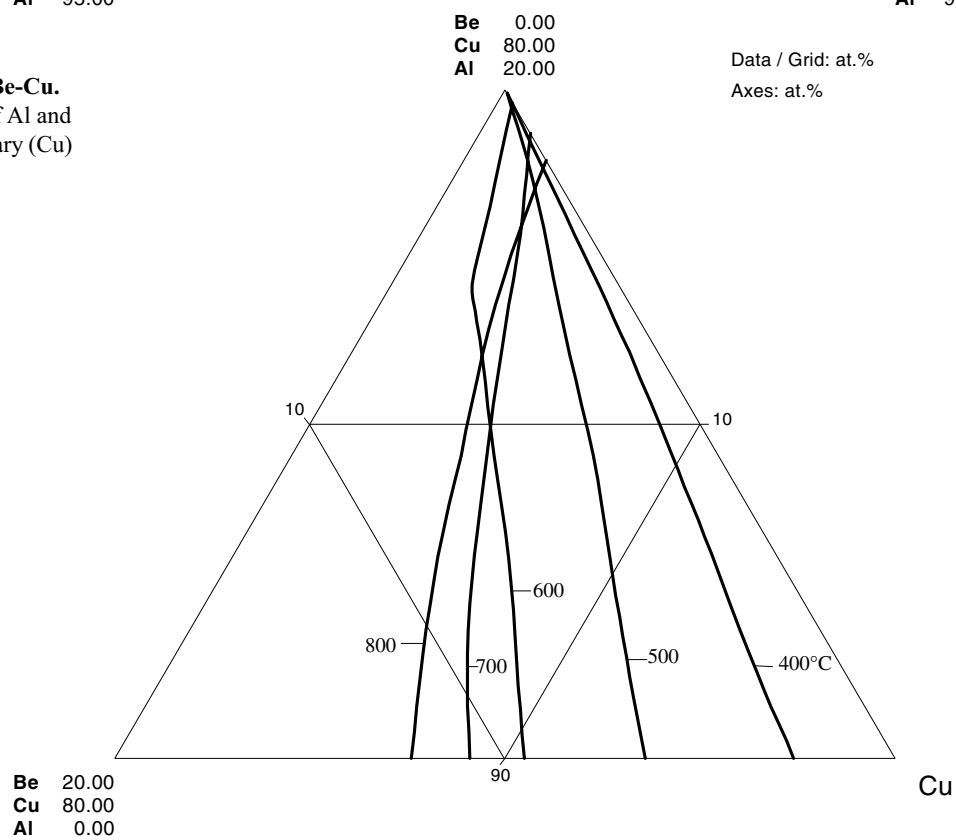
Fig. 3a: Al-Be-Cu. Reaction scheme in the Cu-rich corner

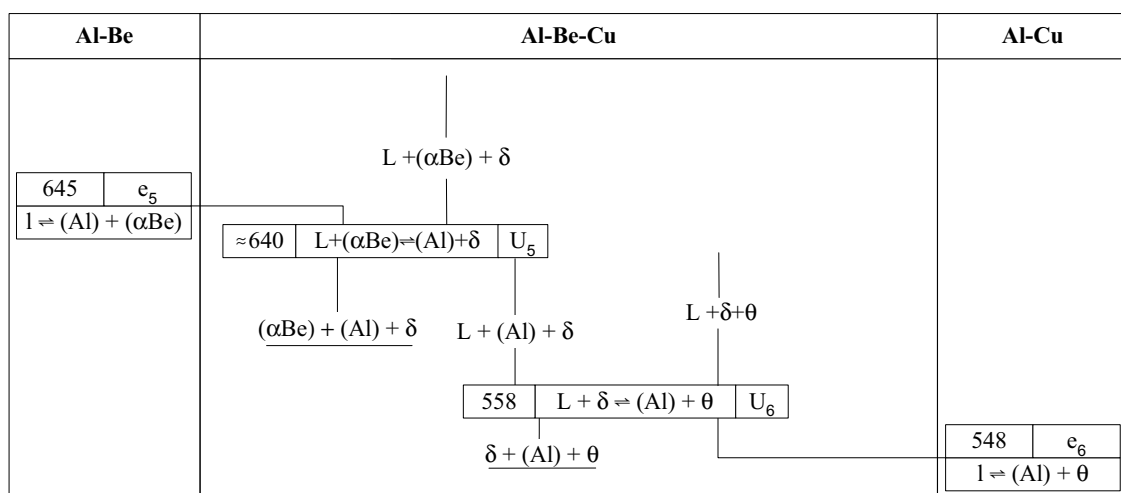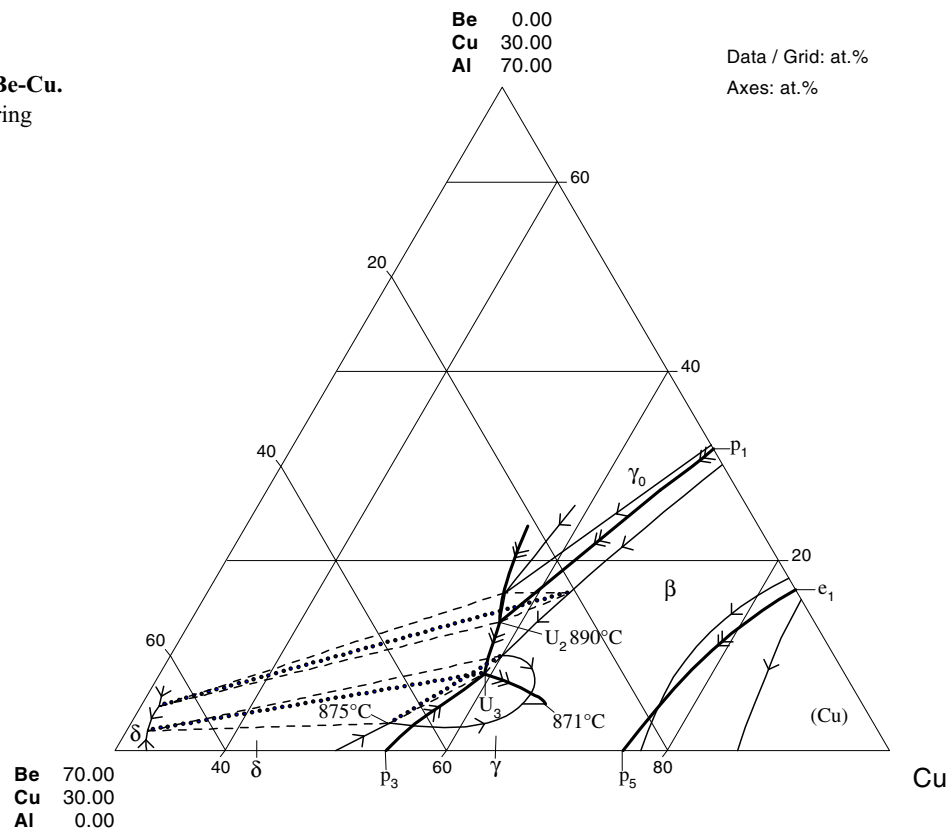| Al-Be	Al-Be-Cu	Al-Cu

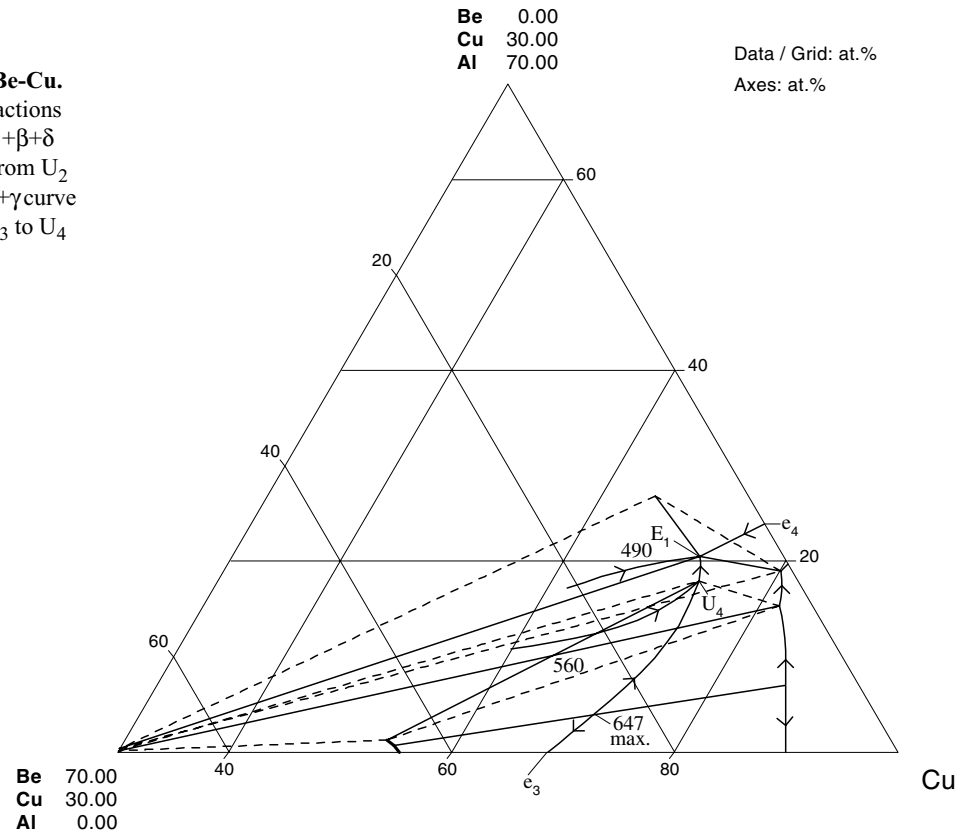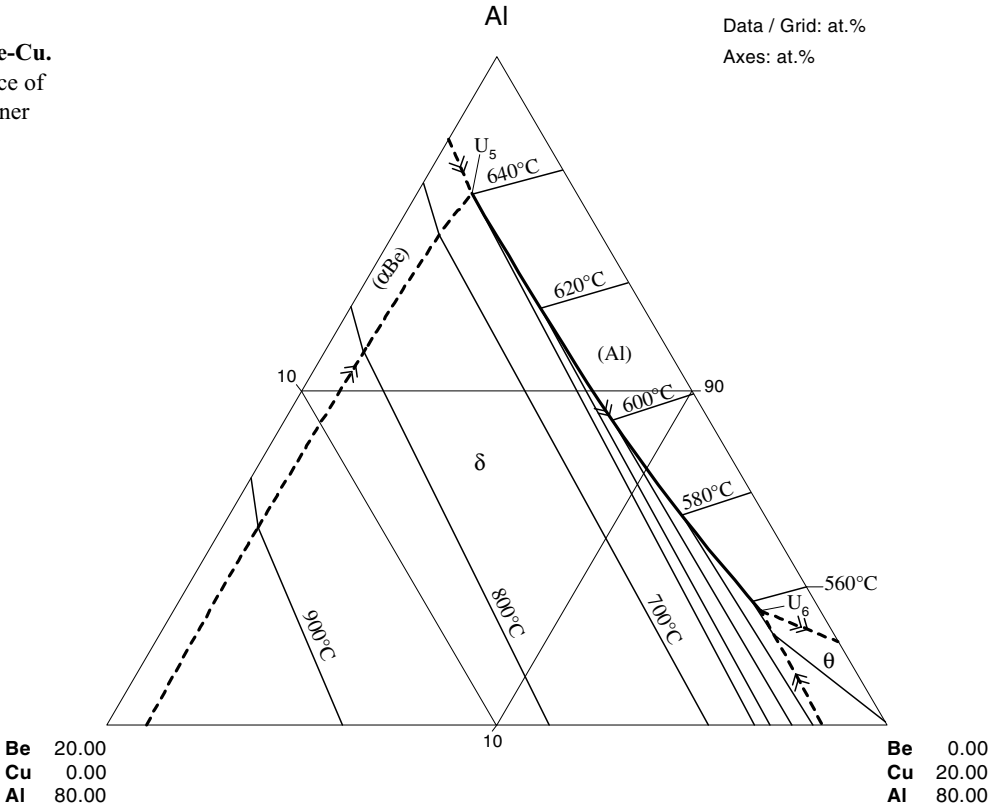**Fig. 3b: Al-Be-Cu.** Tentative reaction scheme in the Al-rich corner

Fig. 4:   Al-Be-Cu.
Reactions during
solidification

Be   0.00
Cu   30.00
Al   70.00

Data / Grid: at.%

Axes: at.%

p_1

γ_0

β

e_1

U_2 890°C

875°C U_3 871°C

(Cu)

δ

δ P_3 γ P_5

Be   70.00
Cu   30.00
Al   0.00
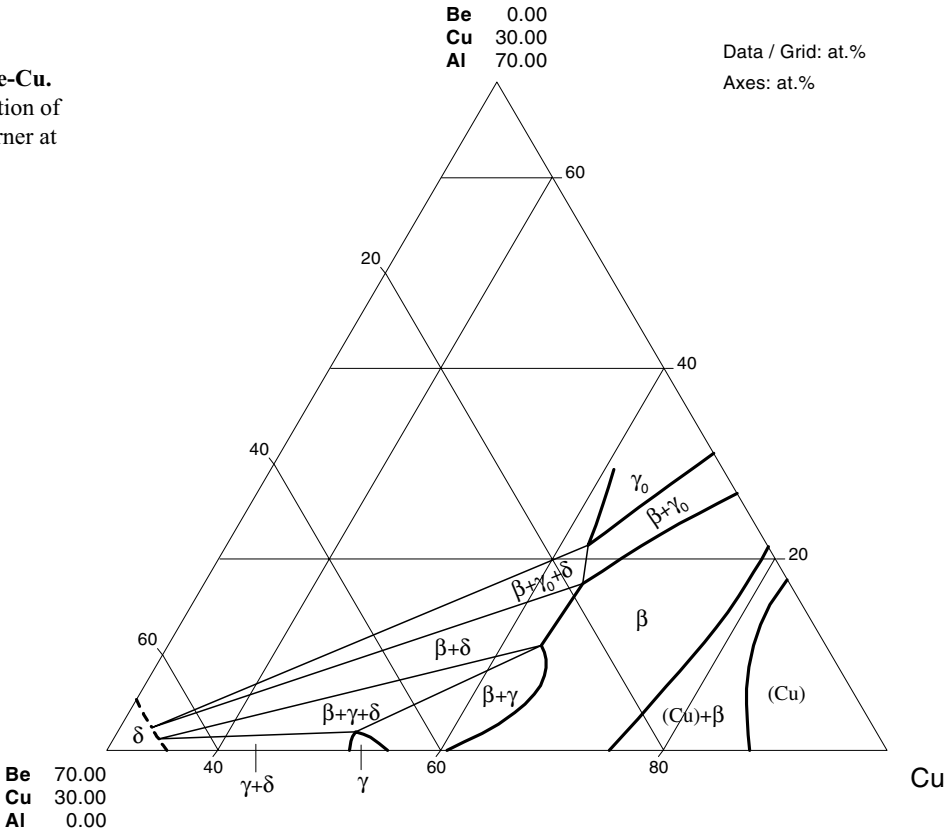
Cu

Fig. 5:   Al-Be-Cu.
Solid state reactions
comprising $\gamma_1+\beta+\delta$
curve going from U_2
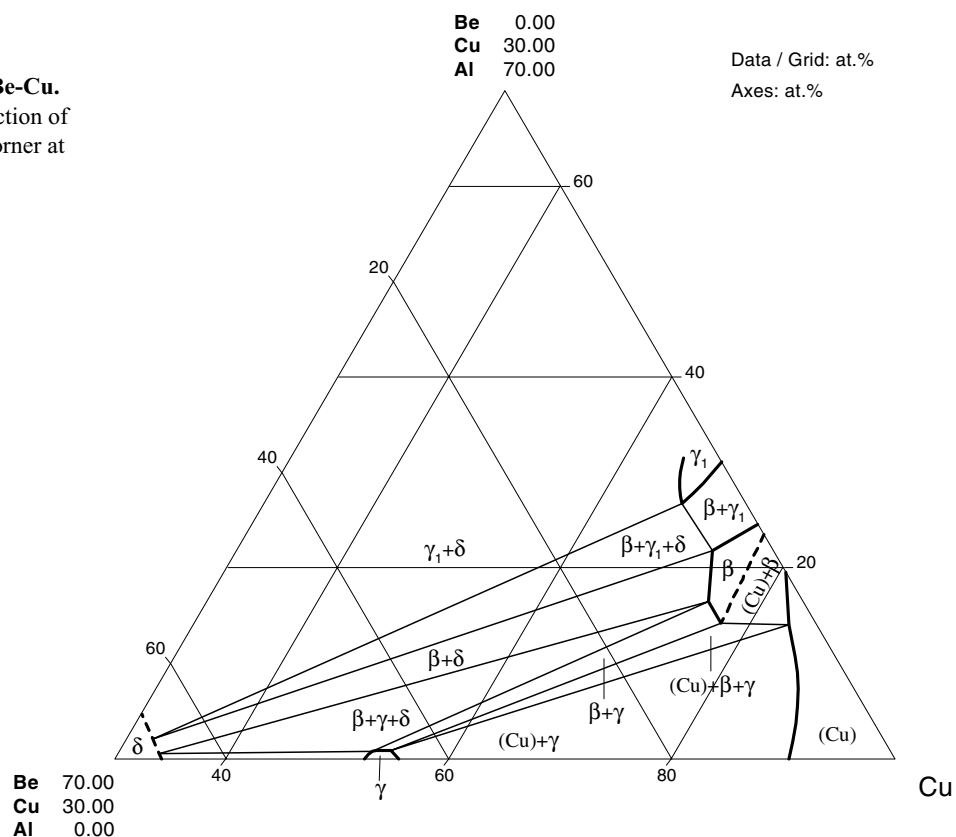to E_1 and $\delta+\beta+\gamma$ curve
going from U_3 to U_4

Be   0.00
Cu   30.00
Al   70.00

Data / Grid: at.%

Axes: at.%

e_4

490   E_1

U_4

560

647
max.

e_3

Be   70.00
Cu   30.00
Al   0.00

Cu

Fig. 6: Al-Be-Cu.
Liquidus surface of
the Al-rich corner
[1946Bad]

Al

Data / Grid: at.%

Axes: at.%

U_5
640°C

(αBe)

620°C

(Al)

10   90

δ   600°C

580°C

560°C

900°C   800°C   700°C U_6

θ

Be	20.00
Cu	0.00
Al	80.00

10

Be	0.00
Cu	20.00
Al	80.00

Be	0.00
Cu	30.00
Al	70.00

Data / Grid: at.%

Axes: at.%

Fig. 7: Al-Be-Cu.
Isothermal section of
the Cu-rich corner at
800°C

60

20

40

40

40

γ_0

$\beta+\gamma_0$

60

20

$\beta+\gamma_0+\delta$

$\beta+\delta$

β

60

$\beta+\gamma$

(Cu)

δ $\beta+\gamma+\delta$ (Cu)+β

Be	70.00
Cu	30.00
Al	0.00

40          $\gamma+\delta$ γ 60   80   Cu

Fig. 8:   Al-Be-Cu.
Isothermal section of
the Cu-rich corner at
600°C

Be   0.00
Cu   30.00
Al   70.00

Data / Grid: at.%

Axes: at.%

Be   70.00
Cu   30.00
Al   0.00

Cu

Fig. 9:   Al-Be-Cu.
Isothermal section of
the Cu-rich corner at
500°C

Be   0.00
Cu   30.00
Al   70.00

Data / Grid: at.%

Axes: at.%

Be   70.00
Cu   30.00
Al   0.00

Cu
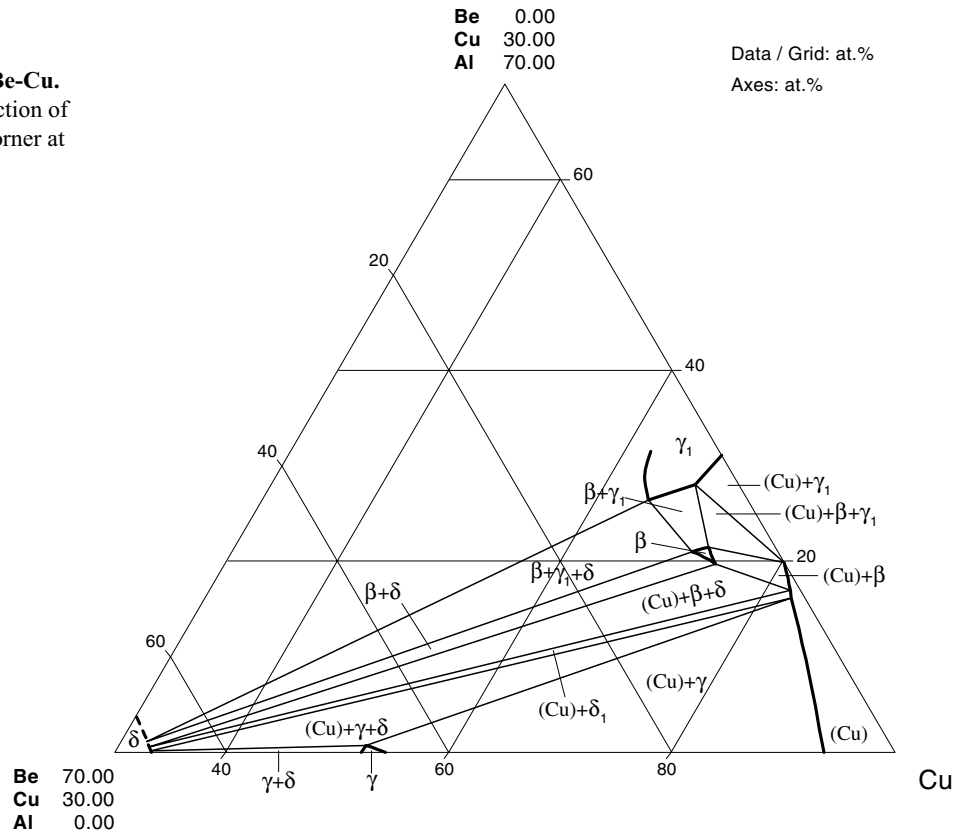
Fig. 10: Al-Be-Cu.
Isopleth in the
Cu-rich corner at
constant Be content 3
mass%
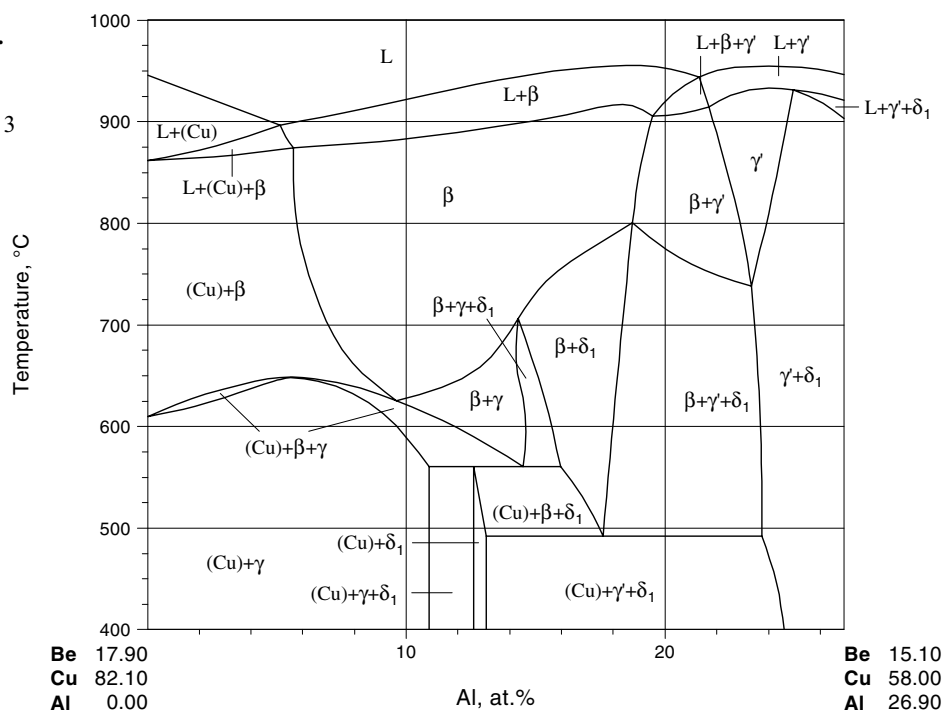
Fig. 11: Al-Be-Cu.
Isopleth along
constant mass ratio
Cu:Be = 20:1 (mole
ratio = 2.8:1)