

Aluminium – Chromium – Copper

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Literature Data

Earlier investigations [1960Zol, 1967Zar] of the phase equilibria were restricted to the Al-corner only. [1960Zol] reported the effect of up to 2% Cr on the liquidus and solidus temperatures of Al-rich alloys. [1967Zar] reported a partial isothermal section at 400°C. [1979Dri] presented a review of these results. [1972Pre] reported the solid state phase equilibria of the entire ternary system at 600 and 800°C. They prepared more than 100 ternary alloys in an arc furnace under purified Ar using the elemental metals of following purity: 99.98 mass% Al, 99.9 mass% Cr and 99.99 mass% Cu. The alloys were sealed in evacuated quartz tubes and annealed at 600°C for 400 h or at 800°C for 200 h, followed by quenching in cold water. Phase identification was carried out by means of X-ray diffraction. Later, [1981Che] reported the phase equilibria of the ternary system at room temperature. They investigated 407 ternary alloys which were prepared, using 99.9 mass% elemental metals, in an induction furnace under vacuum or under Xe atmosphere. The alloys were sealed in evacuated quartz tubes and were subjected to two different heat treatment schedules: (i) annealing at 330°C for 30 days followed by slow cooling to room temperature or (ii) annealing at 800°C for 1h followed by quenching in ice water and subsequently annealing between 340 to 350°C for 126 days followed by slow cooling to room temperature. The phase identification was performed by means of the X-ray powder diffraction method. These results were assessed by [1991Gho].

Binary Systems

The Al–Cr binary phase diagram is accepted from [Mas]; the Al–Cu binary phase diagram is accepted from the assessment of [2003Gro], and the Cr–Cu binary phase diagram is accepted from [2003Ans].

Solid Phases

[1958Kho] reported the solid solubility of Cr and Cu in (Al). The solubility isotherms are plotted in Fig. 1. Recent investigations [1972Pre] and [1981Che] suggest that, in the ternary regime, the solid solubilities of Cr in (Cu) and Cu in (Cr) are much higher than those in the binary alloys (for example see Fig. 3 and Fig. 4). These data differ with those reported by [1939Ale].

Based on the wet chemical analysis of extracted particles, [1960Zol] reported that CrAl_7 dissolves at least 1.04 at.% Cu. [1972Pre] reported four ternary phases, which are designated here as τ_1 , τ_2 , τ_3 and τ_4 , as existing at 600°C. They can be represented as $\text{Cr}_{23}\text{Cu}_{20}\text{Al}_{57}$, $\text{Cr}_{20}\text{Cu}_{10}\text{Al}_{70}$, $\text{Cr}_{15}\text{Cu}_{13}\text{Al}_{72}$ and $\text{Cr}_{15}\text{Cu}_{18}\text{Al}_{67}$, respectively. τ_3 and τ_4 are not stable at 800°C or above. Except for the τ_2 phase, other ternary phases have nominal solid solubility. The authors [1972Pre] reported the crystal structure of the τ_2 phase only. [1981Che] reported the existence of five ternary phases at room temperature, which are designated as τ_5 , τ_6 , τ_7 , τ_8 and τ_9 . The τ_5 phase has a small region of homogeneity and can be represented as $\text{Cr}_{4.5}\text{Cu}_{31}\text{Al}_{64.5}$. Its crystal structure was reported to be orthorhombic. The other ternary phases have solid solubility ranges, but their crystal structures were not reported by [1981Che]. In the absence of the crystal structure data of all the ternary phases, it is difficult to conclude whether all of them are different phases or whether some of them are the same.

The details of the crystal structures, lattice parameters, etc. of the binary and ternary phases are listed in Table 1.

Liquidus Surface

Experimental data on the melting equilibria of the ternary system is very meager. Figure 2 shows the liquidus surface of the Al corner [1943Mon] which exhibits the presence of a U type and a E type invariant reactions. Limited data of [1933Roe] and [1941Kna] suggest the ternary eutectic reaction as $\text{L} \rightleftharpoons (\text{Al}) + \text{CuAl}_2 + \text{Cr}_7\text{Al}_{45}$. Also, the vertical section reported by [1982Lit] and the observation of the

(Al)+CuAl₂+Cr₇Al₄₅ three-phase field at the 400°C isothermal section [1967Zar] confirm the above eutectic reaction. The ternary eutectic occurs at about 28.5 mass% Cu, 1.5 mass% Cr, with a melting point of about 545°C [1982Lit]. However, [1943Mon] reported that the transition reaction $L + Cr_7Al_{45} \rightleftharpoons CrAl_5 + (Al)$ followed by the presence of Cu hinders the formation of the Cr₇Al₄₅ phase, and accordingly he proposed the transition reaction $L + Cr_7Al_{45} \rightleftharpoons CrAl_5 + (Al)$ followed by the ternary eutectic, $L \rightleftharpoons (Al) + CuAl_2 + CrAl_5$ for which there is no experimental evidence so far.

Isothermal Sections

The isothermal section of the Al–Cr–Cu system at 600°C [1972Pre] is shown in Fig. 3. The doubtful portion of this diagram is shown as dotted. Except for the absence of the τ_3 and τ_4 phases, the phase boundaries at 800°C essentially remain the same as those at 600°C [1972Pre]. Figure 4 shows the isothermal section at room temperature [1981Che]. After very slow cooling of the binary and ternary alloys, [1981Che] did not observe the α_2 phase (of the Al–Cu binary system) at room temperature. According to [1981Che], γ and β phases of the Al–Cr system form a solid solution (β') well within the ternary regime, whereas they are immiscible in ternary alloys close to the binary edge. Such a situation is quite unlikely and further investigation in this composition range is needed. Also, the above feature was not observed in the 600°C isothermal section by [1972Pre]. In both Figs. 3 and 4, the results along the Cu₂Al–Cr₂Al section are consistent with those reported by [1964Ram] and [1965Ram]. Minor adjustments have been made in Figs. 3 and 4 in order to comply with the accepted binary phase diagrams. The doubtful portions of the phase diagrams are shown by dashed lines.

[1967Zar] reported an isothermal section of the Al corner at 400°C. In the composition range of Al–12.5Cr–33.3Cu (at.%), they observed an (Al)+Cr₇Al₄₅+CuAl₂ three-phase field and the corresponding two-phase fields.

Temperature – Composition Sections

Figure 5 shows the vertical section from Al to 2.5 mass% Cr [1982Lit]. Addition of Cr to Al–Cu alloys increases the $\beta \rightleftharpoons (Cu) + \gamma_1$ transformation temperature [1969Hor].

Thermodynamics

Experimental thermodynamic data and CALPHAD modeling of phase equilibria are known only for the relevant binary systems.

Notes on Materials Properties and Applications

[2000Grz] investigated the effect of 1.65 at.% Cr on the properties of Al–9.9Cu (at.%) alloy. They found that Cr addition reduces β phase coarsening at high temperature and refines γ_2 lamellae in the eutectoid microstructure. The quenched microstructure consists of fine acicular $\beta' + \beta'_1$ martensite. Refinement of microstructure leads to significant increase in strength without any significant change in ductility, both in annealed and quenched conditions.

[1983Sid] determined the resistivity and the temperature coefficient of resistivity of vapor deposited thin-film, Cu-rich ternary alloys.

Miscellaneous

Recently, the ternary system has received renewed interest because of the ability to synthesize quasicrystals in Al-rich compositions. In particular, compositions around Cr₁₅Cu₂₀Al₆₅ [1988Tsa, 1991Eba, 1992Sel, 1995Kha, 1997Kha, 1999Qi, 2001Pon], Cr₂₀Cu₁₀Al₇₀ [1992Oka], Cr₁₅Cu_xAl_{85-x} ($0 \leq x \leq 20$) [1993Sel] have been investigated extensively. The quasicrystals are mainly two types: icosahedral and decagonal. A lower e/a ratio favors the former while a higher e/a favors the latter. The stability [1999Qi] and bulk modulus [2001Pon] of the quasicrystals is also related to the e/a ratio.

[1988Tsa] rapidly solidified the alloy $\text{Cr}_{15}\text{Cu}_{20}\text{Al}_{65}$ and showed that a quasi-crystalline icosahedral phase forms. For compositions $\text{Cr}_{15}\text{Cu}_x\text{Al}_{85-x}$ a quasi-crystalline phase forms on rapid solidification of alloys with $x = 0$ and 5. For $x = 10$ and 15, a mixture of CuAl_2 and a quasi-crystalline phase is formed. At $x = 20$ only the quasi-crystalline phase forms. On heating at $40 \text{ K}\cdot\text{min}^{-1}$ up to 600°C the $\text{Cr}_{15}\text{Cu}_{20}\text{Al}_{65}$ quasi-crystalline phase showed no exothermic effects. The high thermal stability, as confirmed by unpublished work, indicates the formation of a thermodynamically stable quasi-crystalline phase in conventionally solidified material. [1992Oka] observed that the decagonal quasicrystal in $\text{Cr}_{20}\text{Cu}_{10}\text{Al}_{70}$ is stable up to 1000°C . It is worth noting that the τ_4 phase [1972Pre] is close in composition to the alloy $\text{Cr}_{15}\text{Cu}_{20}\text{Al}_{65}$. A detailed description of these quasicrystals can be found in the comprehensive review by [1996Yam].

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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	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 404.96$	[Mas2], pure Al at 24°C
(Cr) < 1863	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 288.4$	[V-C], pure Cr at 27°C
(Cu) < 1085	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 361.48$	[V-C], pure Cu at 25°C
CrAl_7 ($\text{Cr}_2\text{Al}_{13}$)	<i>mC104</i> <i>C2/m</i> V_7Al_{45}	$a = 2519.6$ $b = 757.4$ $c = 1094.9$ $\beta = 128.7$	at room temperature 13.5 at.% Cr [2003Cor]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group Prototype	Lattice Parameters [pm]	Comments/References
Cr ₂ Al ₁₁ (CrAl ₅)	Orthorhombic	$a = 1240$ $b = 3460$ $c = 2020$	quenched from 920°C 16.9 to 19.2 at.% Cr; [2003Cor]
	<i>oC584</i> <i>Cmcm</i>	$a = 1252.1$ $b = 3470.5$ $c = 2022.3$ $a = 1260$ $b = 3460$ $c = 2000$	single crystal “εCrAl ₄ ” [2003Cor] “εCrAl ₄ ” [2003Cor]
μ, CrAl ₄ < 1031	<i>hP574</i> <i>P6₃/mmc</i> μMnAl ₄	$a = 1998$ $c = 2467$ $a = 2010$ $c = 2480$	at room temperature, 20.9 ± 0.3 at.% Cr [2003Cor] 20.6 to 21.2 at.% Cr [2003Cor]; 22.3 ± 0.1 at.% Cr at Cr-rich border at 1000°C [2003Cor]
βCr ₄ Al ₉	<i>cI52</i> <i>I43m</i> Cu ₄ Al ₉	$a = 912.3$	~31 to 45 at.% Cr quenched from liquid [1941Kna, Mas2]; 29 at.% Cr at Al-rich border at 920°C [2003Cor]
αCr ₄ Al ₉ < 700 (?)	<i>hR52</i> <i>R3m</i> Cr ₄ Al ₉	$a = 1291$ $c = 1567.7$	32.8 to 35 at.% Cr [Mas2, 2003Cor]
γ, Cr ₄ Al ₉ ≤ 1060	---	---	---
βCr ₅ Al ₈ ≥ 1100 (?)	<i>cI52</i> <i>I43m</i> Cu ₅ Zn ₈	$a = 910.4$ to 904.7	30 to 42 at.% Cr, quenched from liquid [1989Ell]
αCr ₅ Al ₈ ≤ 1100 (?)	<i>hR26</i>	$a = 1271.9$	[1977Vis, Mas2]
	<i>R3m</i>	$c = 793.6$	
	Cr ₅ Al ₈	$a = 1272.8$ $c = 794.2$	[1977Bra]
		$a = 1281.3$ $c = 795.1$	[1989Ell]
η, Cr ₂ Al < 910	<i>tI6</i>	$a = 300.45$	~65.5 to ~71.4 at.% Cr
	<i>I4/mmm</i>	$c = 864.77$	[1937Bra, 1963Koe, 1998Mur]
	MoSi ₂	$a = 300.5$ to 302.8	[1989Ell]
		$c = 864.9$ to 875.5	
β ₁	<i>cF16</i> <i>Fm3m</i> BiF ₃	$a = 585$	Metastable, supercell of β [1994Mur]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group Prototype	Lattice Parameters [pm]	Comments/References
α_2 , $\text{Cu}_{1-x}\text{Al}_x$ < 363	- long period superlattice $\approx \text{TiAl}_3$)	$a = 366.6$ $c = 367.5$ $a = 366.8$ $c = 367.7$ $a = 366.8$ $c = 368.0$	[1985Mur], at 77.9 at.% Cu [1985Mur], at 77.2 at.% Cu [1985Mur], at 76.4 at.% Cu solid solubility ranges from 76.5 to 78.0 at.% Cu
β , $\text{Cu}_{1-x}\text{Al}_x$ 1037-964	$cI2$ $Im\bar{3}m$ W	-	[1985Mur], solid solubility ranges from 67.6 to 70.2 at.% Cu
γ_0 , Cu_2Al 1037-800	$cI52$ $I\bar{4}3m$ Cu_5Zn_8	-	[1985Mur], solid solubility ranges from 59.8 to 69.0 at.% Cu
γ_1 , Cu_9Al_4 ≤ 890	$cP52$ $P\bar{4}3m$ Cu_9Al_4	$a = 871.32$	[V-C], at 69.23 at.% Cu solid solubility ranges from 62.5 to 69.0 at.% Cu
δ , $\text{Cu}_{1-x}\text{Al}_x$ < 686	hR^* $R\bar{3}m$	$a = 1226$ $c = 1511$	[1985Mur, V-C], at 61.6 at.% Cu solid solubility ranges from 59.3 to 61.9 at.% Cu
ϵ_1 , $\text{Cu}_{1-x}\text{Al}_x$ 958-848	cubic(?)	-	[1985Mur], solid solubility ranges from 59.4 to 62.1 at.% Cu
ϵ_2 , $\text{Cu}_{2-x}\text{Al}_x$ 850-560	$hP6$ $P6_3/mmc$ Ni_2In	$a = 414.6$ $c = 506.3$	[V-C], at 57.5 at.% Cu solid solubility ranges from 55.0 to 61.1 at.% Cu
ζ_1 , $\sim\text{Cu}_{47.8}\text{Al}_{35.5}(\text{h})$ 590-530	$oF88 - 4.7$ $Fmm2$ $\text{Cu}_{47.8}\text{Al}_{35.5}$	$a = 812$ $b = 1419.85$ $c = 999.28$	55.2 to 59.8 at.% Cu [Mas2, 1994Mur] structure: [2002Gul]
ζ_2 , $\text{Cu}_{11.5}\text{Al}_9(\text{r})$ < 570	$oI24 - 3.5$ $Imm2$ $\text{Cu}_{11.5}\text{Al}_9$	$a = 409.72$ $b = 703.13$ $c = 997.93$	55.2 to 56.3 at.% Cu [Mas2, 1985Mur] structure: [2002Gul]
η_1 , $\text{CuAl}(\text{h})$ 624-560	$o*32$	$a = 408.7$ $b = 1200$ $c = 863.5$	49.8 to 52.4 at.% Cu [V-C2, Mas2, 1985Mur] Pearson symbol: [1931Pre]
η_2 , $\text{CuAl}(\text{r})$ < 560	$mC20$ $C2/m$ $\text{CuAl}(\text{r})$	$a = 1206.6$ $b = 410.5$ $c = 691.3$ $\beta = 55.04^\circ$	[1985Mur], unknown composition, solid solubility ranges from 49.8 to 52.3 at.% Cu
θ , CuAl_2 < 591	$tI12$ $I4/mcm$ Al_2Cu	$a = 606.3$ $b = 487.2$	solid solubility ranges from 31.9 to 33.0 at.% Cu [V-C]
$*\tau_1$, $\text{Cr}_{23}\text{Cu}_{20}\text{Al}_{57}$ < 800	?	-	[1972Pre], nominal solid solubility

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group Prototype	Lattice Parameters [pm]	Comments/References
* τ_2 , Cr ₂₀ Cu ₁₀ Al ₇₀ < 800	?	-	[1972Pre], Al varies from 70 to 75 at.% and Cu varies from 5 to 10 at.%
* τ_3 , Cr ₁₅ Cu ₁₃ Al ₇₂ < 800	?	-	[1972Pre], nominal solid solubility
* τ_4 , Cr ₁₅ Cu ₁₈ Al ₆₇	<i>hP*</i>	$a = 1282.0$ $c = 1271.0$	[1972Pre], nominal solid solubility
* τ_5 , Cr _{4.5} Cu ₃₁ Al _{64.5}	<i>oP*</i>	$a = 409.04$ $b = 349.82$ $c = 290.28$	[1981Che], nominal solid solubility
* τ_6 , Cr ₁₇ Cu ₈ Al ₇₅	?	-	[1981Che], Cr varies from 16.2 to 18.0 at.% and Cu varies from 5.2 to 8.6 at.%
* τ_7 , Cr ₁₆ Cu ₄ Al ₈₀	?	-	[1981Che], Cr varies from 15.5 to 16.6 at.% and Cu varies from 2.6 to 7.4 at.%
* τ_8 , Cr ₂₀ Cu ₄ Al ₇₆	?	-	[1981Che], Cr varies from 19.0 to 20.5 at.% and Cu varies from 0.6 to 6.5 at.%
* τ_9 , Cr ₁₈ Cu ₄ Al ₇₈	?	-	[1981Che], Cr varies from 17.5 to 18.0 at.% and Cu varies from 2.0 to 5.3 at.%

Fig. 1: Al-Cr-Cu.
Solvus surface of the
(Al) phase

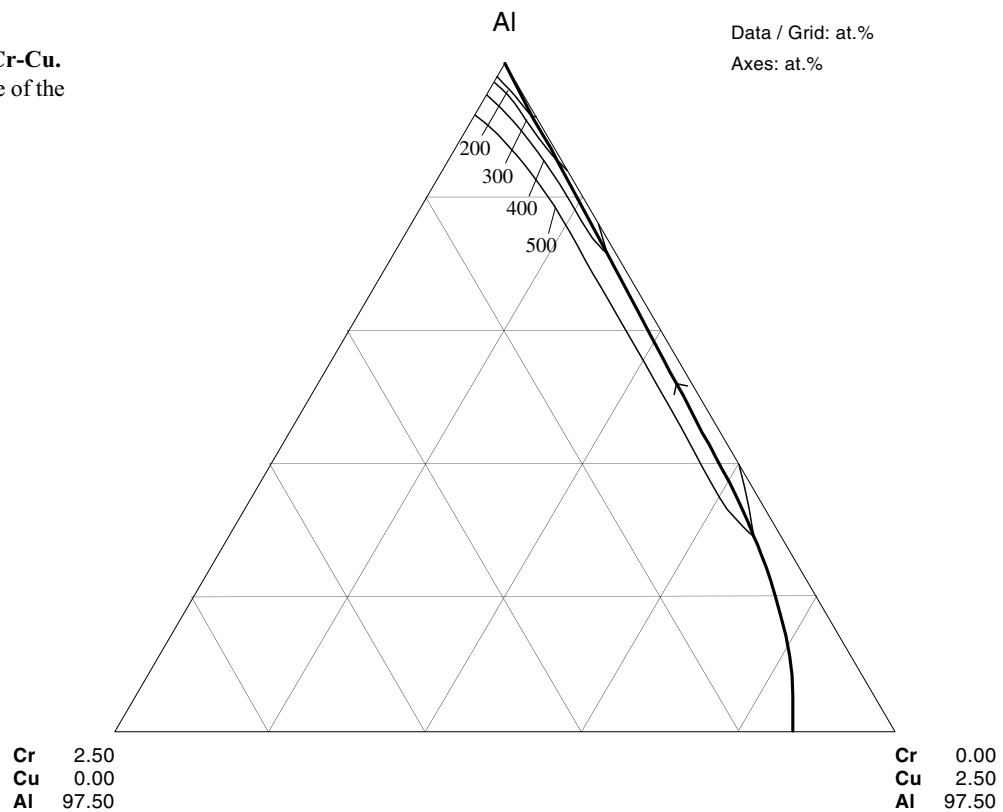


Fig. 2: Al-Cr-Cu.
Liquidus surface of
the Al-corner

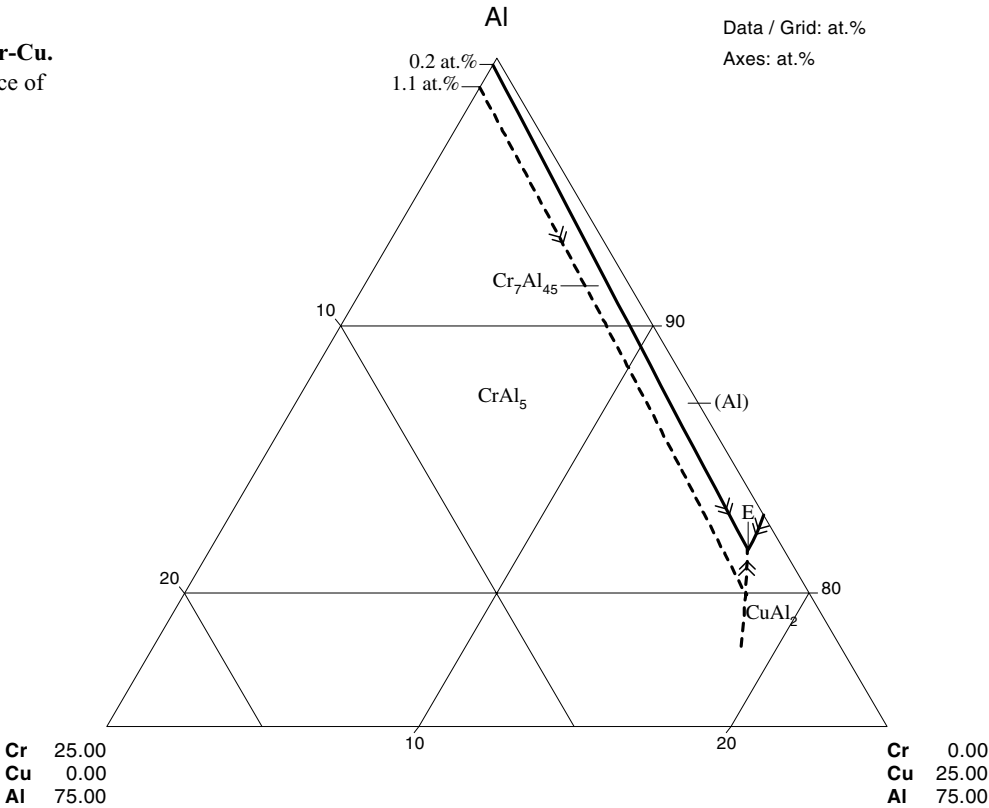


Fig. 3: Al-Cr-Cu.
Isothermal section at
600°C

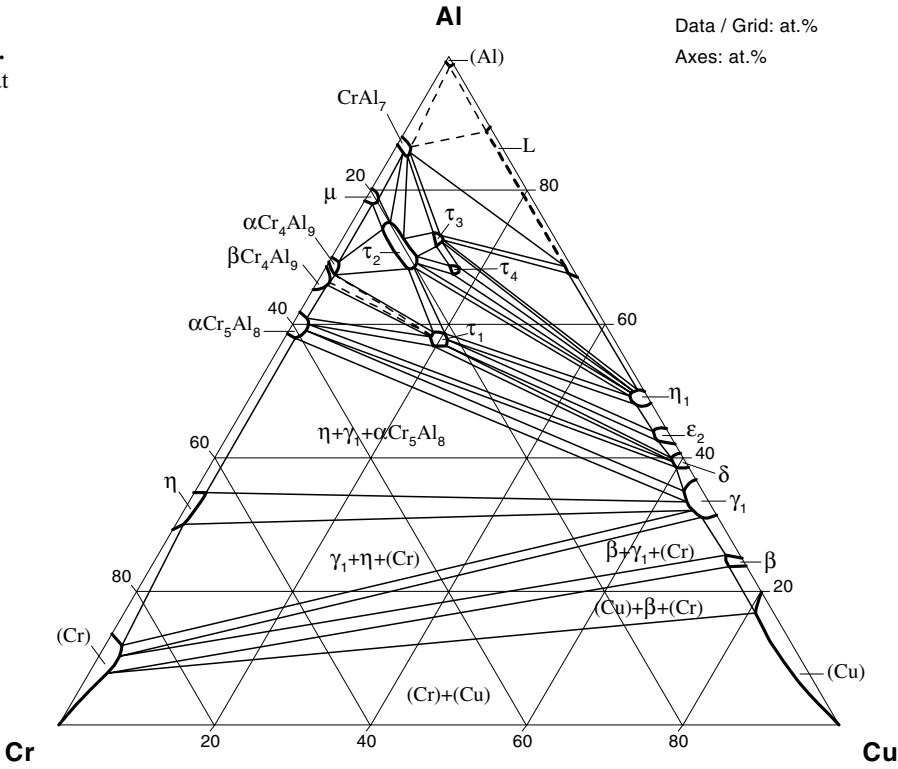


Fig. 4: Al-Cr-Cu.
Isothermal section at
room temperature

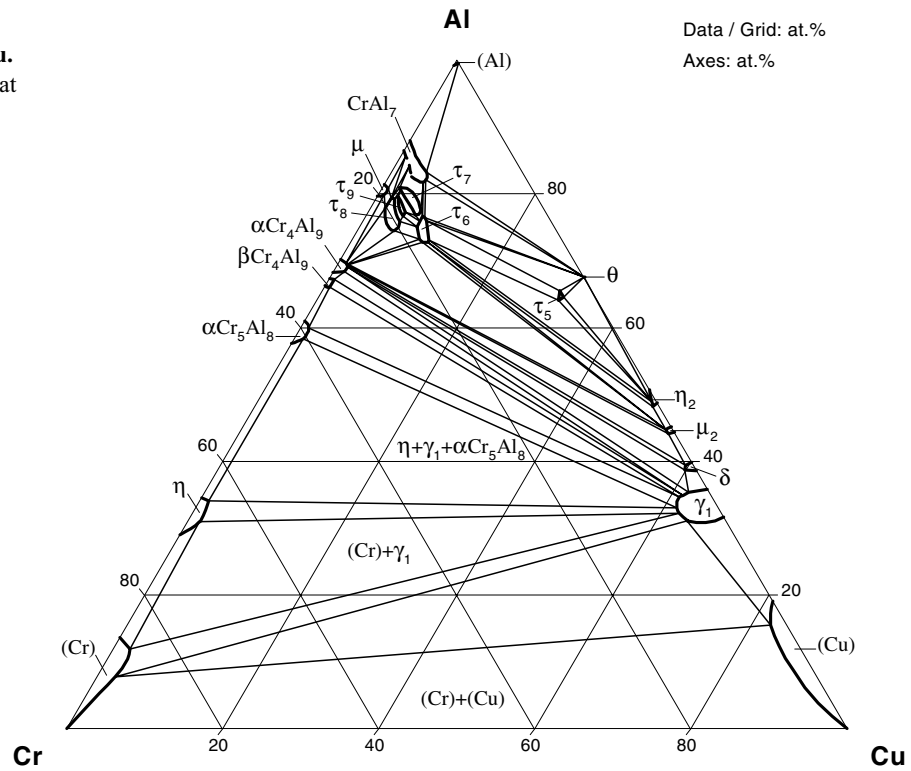


Fig. 5: Al-Cr-Cu.
Vertical section at
2.5 mass% Cr

