Aluminium – Chromium – Silicon

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Literature Data

Two ternary phases have been seen in a superficial study of the liquidus surface of the Al-corner [1943Mon]. The shape of the liquidus surface was found to be quite different in a more extensive study [1951Pra1] in which primary crystals from slowly cooled alloys were extracted from sectioned samples and studied by chemical and X-ray analysis. In addition, annealing experiments of chill-cast alloys at 550°C for 21 days and some at 559 to 580°C were performed and the microstructures of these and the slowly cooled samples were studied [1951Pra1]. In a follow-up paper [1951Pra2] results are discussed in view of alloying theory. The basic shape of the liquidus surface and the resulting equilibria [1951Pra1] agree qualitatively with a very detailed study of the Al-corner in the range 0 to 5 mass% Cr and 0 to 14 mass% Si by DTA, metallography on air-cooled and slowly-cooled (DTA) samples and X-ray analysis [1965Ess].
The crystal structures of the two assumed ternary phases, τ and β, were determined by [1953Rob1] and [1953Rob2] who used the samples of [1951Pra1]. Single crystals of τ with almost stoichiometric $Cr_4Al_{13}Si_4$ composition were used for a detailed X-ray structure analysis (reported space group T_d^2 - *F3m*) and a powder photograph was used for determination of the cubic unit cell dimension [1953Rob1]. A probable range of homogeneity of τ was also noted [1951Pra1]. The second "ternary" phase, β, turned out to be a solid solution of Al in $CrSi_2$ as determined by X-ray analysis of single crystals and powders [1953Rob2]. This was confirmed in a detailed X-ray investigation of the solid state equilibria of pressed samples, annealed at 1300°C [1961Bru]. Homogeneous $CrSi_{2-x}Al_x$ (β) samples up to 25 at.% Al were obtained [1961Bru], while a β-crystal, precipitated from an Al-rich liquid, contained only 14.3 at.% Al in replacement of Si [1953Rob2] and [1951Pra1]. The lattice parameters given for β at $x = 0.43$ ($a = 449.6$, $c = 637.7$ pm) [1953Rob2] essentially agree with the data of [1961Bru] (Table 1). The possibility of (spinodal) decomposition of the β phase at room temperature is mentioned by [1961Bru] since measured lattice parameters form two groups, separated by about 2 to 5 pm. [1961Bru] also detected extensive solid solubility of Al in the Cr_5Si_3 and the Cr_3Si phase.
A solubility of Si in Cr_2Al (ξ) was detected by X-ray investigation in cast samples, annealed at 700°C for 60 to 80 h [1964Ram]. A sample of composition $Cr_{67}Al_{30}Si_3$ was still homogeneous (ξ), but $Cr_{67}Al_{27}Si_6$ contained ξ and Cr_3Si (ε). The alloy $Cr_{67}Al_{17}Si_{16}$ consisted of mostly ε and some Cr_5Si_3 (δ) and Cr_5Al_8 (ζ_2). The solubility of Al in Cr_5Si_3 (δ) was also mentioned by [1964Ram], but not quantitatively given as was done at 1300°C by [1961Bru]. The influence of Si on the primary crystallization of $CrAl_7$ was investigated by thermal analysis and metallography [1960Zol] and the data of [1951Pra1] were essentially confirmed. Chemical analysis of extracted primary $CrAl_7$ crystals gave a negligible solubility of Si in $CrAl_7$ which was confirmed by microhardness and X-ray measurements [1960Zol]. A diffusion couple study Al-Cr/Al-Si at 550°C for 7 days was briefly described and a reaction product in the contact zone, probably CrSi, was found in proximity to non-reacted $CrAl_7$ [1935Bos].
The critical evaluation made by [1991Sch] covers literature published until the year 1989. The present evaluation updates this work and considers all data available.

Binary Systems

The binary systems Cr-Si, Al-Si and Al-Cr are accepted from [2003Leb], [2003Luk], [2003Cor], respectively. The crystal structures of the Al-Cr phases in the region from 58 to 70 at.% Al have been reinvestigated by [1989Ell], who did not confirm the existence of Cr_3Al as claimed from TEM analyses [1981Bro]. The Al-Cr phase diagram is essentially based on [1998Mur], and Cr-Si on [2000Du].

Solid Phases

The solid phases observed in this system are given in Table 1. The solubility limit of Si in ξ is estimated [1964Ram]. The lattice parameters of ε, δ and β are from [1961Bru]. They are averaged at the solubility limits from data of the homogeneous region with special emphasis on the *c*/*a* ratio in the case of β.

Invariant Equilibria

A partial reaction scheme for Al-rich liquids involving the solidification of phases in the Al-Si-$CrSi_2$(β)-Cr_2Al_{11}(η) subsystem was taken from [1965Ess] and adapted to the accepted binaries (Fig. 1). It also agrees with the data of [1951Pra1]. The peritectic formation of τ at 710°C (P) was only measured by [1965Ess] while [1961Bru] speculated about a possible congruent melting point at about 600°C which cannot be accepted.

Liquidus Surface

The liquidus surface of the Al-corner corresponding to Fig. 1 is given in Fig. 2 [1965Ess]. The solid (Al)-phase participating in the three phase equilibria is marked by a line with one arrow. The liquidus surface of τ becomes very narrow at higher Si content. It intersects the liquidus surface of Si between the points U_3 and E, which cannot be seen from Fig. 2, but easily from the reaction scheme in Fig. 1.

Isothermal Sections

The isothermal section at 1300°C in Fig. 3 is based upon [1961Bru]; however, the equilibria with the liquid phase are estimated from the binaries. An isothermal section at 500°C was constructed in Fig. 4 based upon the scattered data of [1951Pra1, 1965Ess] and [1964Ram] and the assumption of similar solubilities of β, γ, δ and ε at 1300°C. The ternary compound τ plays a dominant role in the Al-Si-β-$CrAl_4$ subsystem, despite its rather low incongruent melting temperature. It probably exhibits a range of homogeneity [1951Pra1].

Temperature – Composition Sections

Vertical sections at 5 mass% Cr and 4 mass% Si in the Al-corner are also reported by [1965Ess]. A typical error in the slope of intersecting liquidus lines in that (Al+4%Si)-Cr section was pointed out by [1988Zak]. The effect of Cr additions (0.25, 0.5 and 0.8 mass%) on the microstructure of cast, near-eutectic Al-Si alloys was examined by [1930Ota].

Thermodynamics

The enthalpy of the liquid phase at 1677°C was shown in a ternary plot of iso-enthalpy lines, calculated by an extrapolation scheme from the binary systems [2001Sud].

Miscellaneous

The structure and thermal stability of rapidly solidified alloys $Cr_{14}Al_{86-x}Si_x$ with *x* up to 24 was studied by XRD and DTA. Below 24 at.% Si the amorphization was not complete at quenching rates of $1.5 \cdot 10^6$ $K \cdot s^{-1}$. Crystallization temperatures are around 320°C [1986Dun].
The crystal structure of the phase τ, $Cr_4Al_{13}Si_4$ was studied in relation to “stuffed pyrochlore” [1983Nym].

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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	*cF*4 $Fm\bar{3}m$ Cu	a = 404.96	at 25°C [Mas] 0 to 0.37 at.% Cr in equilibria; to 3 at.% Cr after spinning; to 5 at.% Cr by gun technique [1998Mur]
(Al) (I)	*hP*2 $P6_3/mmc$ Mg	a = 269.3 c = 439.8	at 25°C, 20.5 GPa [Mas2]
(Cr) < 1907	*cI*2 $Im\bar{3}m$ W	a = 288.47 a = 288.47 ± 5 a = 288.09 ± 2	at 25°C [Mas2] 0 - 13 at.% Si [2001Oka] at 4.5 ± 0.2 at.% Si [1993Sut] at 1200°C at 6.7 ± 0.2 at.% Si [1993Sut] at 1400°C
(Cr) (I)	*tI*2 *I*4/*mmm* α'Cr	a = 288.2 c = 288.7	at 25°C, high pressure phase [Mas2]
(Si) < 1414	*cF*8 $Fd\bar{3}m$ C (diamond)	a = 543.06	at 25°C [Mas2] ≈ 100 at.% Si [2001Oka]
(Si) (III)	*hP*4 $P6_3/mmc$ αLa	a = 380 c = 628	at 25°C, 16 GPa → 1 bar [Mas2]
(Si) (II)	*cI*16 $Ia\bar{3}$ γSi	a = 663.6	at 25°C, 16 GPa [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Si) (I)	*tI*4 $I4_1/amd$ βSn	*a* = 468.6 *c* = 258.5	at 25°C, 9.5 GPa [Mas2]
θ, Cr_2Al_{13} ($CrAl_7$) <790	*mC*104 *C*2/*m* V_7Al_{45}	*a* = 2519.6 *b* = 757.4 *c* = 1094.9 β = 128.7	at room temperature 13.5 at.% Cr [1960Coo, 1975Ohn, 1995Aud]
η, Cr_2Al_{11} ($CrAl_5$) 940-790	Orthorhombic *oC*584 *Cmcm*	*a* = 1240 *b* = 3460 *c* = 2020 *a* = 1252.1 *b* = 3470.5 *c* = 2022.3 *a* = 1260 *b* = 3460 *c* = 2000	quenched from 920°C 16.9 to 19.2 at.% Cr; [1995Aud, 2000Mah] single crystal "εCrAl$_4$" [1997Li, 1998Li] "εCrAl$_4$" [1992Wen]
$CrAl_4$ < 1030	*hP*574 $P6_3/mmc$ μMnAl$_4$	*a* = 1998 *c* = 2467 *a* = 2010 *c* = 2480	at room temperature, 20.9 ± 0.3 at.% Cr [1995Aud, 2000Mah] [1990Ram] 20.6 to 21.2 at.% Cr [1995Aud]; 22.3 ± 0.1 at.% Cr at Cr-rich border at 1000°C [2000Mah]
Cr_4Al_9 (h2) 1170-1060			[2003Cor]
Cr_4Al_9 (h1) ≲ 1060	*cI*52 $I\bar{4}3m$ Cu_4Al_9	*a* = 912.3	~31 to 45 at.% Cr quenched from liquid [1941Kna, Mas2]; 29 at.% Cr at Al-rich border at 920°C [1995Aud]
Cr_4Al_9 (r) < 700 (?)	*hR*52 $R\bar{3}m$ Cr_4Al_9	*a* = 1291 *c* = 1567.7	32.8 to 35 at.% Cr [1968Lin, Mas2]
ζ_1, Cr_5Al_8 (h) ≳ 1100 (?)	*I*52 $I\bar{4}3m$ Cu_5Zn_8	*a* = 910.4 to 904.7	30 to 42 at.% Cr, quenched from liquid [1989Ell]
ζ_2, Cr_5Al_8 (r) ≲ 1100 (?)	*hR*78-1.50 *R*3*m* Cr_5Al_8	*a* = 1271.9 *c* = 793.6 *a* = 1272.8 *c* = 794.2 *a* = 1281.3 *c* = 795.1	[1977Vis, Mas2] [1977Bra] [1989Ell]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ξ, $Cr_2Al_{1-x}Si_x$	*tI*6		$0 \le x \le 0.12$ at 700°C [1964Ram]
	*I*4/*mmm*	$a = 300.45$	at $x = 0$, binary Al-Cr
Cr_2Al	$MoSi_2$	$c = 864.77$	~65.5 to ~71.4 at.% Cr
< 910		$a = 300.5$ to 302.8	[1937Bra, 1963Koe, 1998Mur]
		$c = 864.9$ to 875.5	[1989Ell]
		$a = 300$	at $x = 0$ [1964Ram]
		$c = 864$	
$Cr_2Al_{0.91}Si_{0.09}$		$a = 300$	$x = 0.09$ [1964Ram]
		$c = 861$	
X(Al-Cr)	Cr_5Al_3 or		~75 to ~80 at.% Cr [1981Bro, 1981Ten];
≤ 400	Cr_3Al super lattice		possibly metastable [1998Mur]
"ε'$CrAl_4$"	*Pmcm*		in as-cast alloy 15 at.% Cr, lattice parameters are the same as for "ε'$CrAl_4$" metastable [1994Sel]
i$CrAl_4$	icosahedral		in spinning alloy of 8 to 13 at.% Cr; by decomposition of amorphous 20 at.% Cr, metastable [1998Mur]
d$CrAl_4$	decagonal		19 at.%, 4 at.% Si [1994Sel]
ω(Al-Cr)	-	-	in quenched Al-Cr alloy of 60-100 at.% Cr, like metastable ωTi [2000Sha1, 2000Sha2]
ε, $Cr_3Si_{1-x}Al_x$	*cP*8		$0 \le x \le 0.5$ [1961Bru]
	$Pm\bar{3}n$	$a = 455.60 \pm 0.04$	at $x = 0$, binary Cr-Si [V-C2]
(Cr_3Si)	Cr_3Si		20.8 - 25.3 at.% Si [2001Oka]
< 1780		$a = 456.27 \pm 0.04$	at 22.5 ± 0.4 at.% Si, at 1200°C, [1993Sut]
		$a = 456.46 \pm 0.02$	at 21.5 ± 0.4 at.% Si, at 1400°C, [1993Sut]
		$a = 456.67 \pm 0.02$	at 20.8 ± 0.4 at.% Si, at 1600°C, [1993Sut]
		$a = 456.65 \pm 0.03$	as solidified [1993Sut]
		$a = 454.7$	at $x = 0$ [1961Bru]
$Cr_3Si_{0.5}Al_{0.5}$		$a = 456.3$	at $x = 0.5$ [1961Bru]
Cr_5Si_3 (h)			37.5 - 37.7 at.% Si [2001Oka]
1666-1488			
δ, $Cr_5(Si_{1-x}Al_x)_3$ (r)	*tI*32		$x = 0$ to 0.2 [1961Bru]
	*I*4*mcm*	$a = 917.0$	at $x = 0$, binary Cr-Si [V-C2]
Cr_5Si_3(r)	W_5Si_3	$c = 463.6$	37.5 at.% Si [2001Oka]
< 1488		$a = 914$	at $x = 0$ [1961Bru]
		$c = 463$	
$Cr_5Si_{2.4}Al_{0.6}$		$a = 915.7$	at $x = 0.2$ [1961Bru]
		$c = 464.2$	
γ, CrSi	*cF*8	$a = 462.2 \pm 0.1$	[V-C2]
< 1424	$P2_13$		50 at.% Si [2001Oka]
	FeSi		

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
β, $Cr(Si_{1-x}Al_x)_2$	*hP*9 $P6_422$		x = 0 to 0.75 [1961Bru], microhardness 8530 MPa [1965Ess]
$CrSi_2$ < 1438 ± 2	$CrSi_2$		at x = 0, binary Cr-Si 66.3 - 68 at.% Si [2000Du]
		a = 442.83 ± 0.01 c = 636.80 ± 0.09	[2001Oka] [2001Tan]
		a = 442.0 c = 635.4	at x = 0 [1961Bru]
$CrSi_{1.25}Al_{0.75}$		a = 453.2 c = 639	at x = 0.375 [1961Bru]
* τ, $Cr_4Al_{13}Si_4$ < 710	*cF*84 $F\bar{4}3m$ $Cr_4Al_{13}Si_4$	a = 1091.7 ± 0.1	[1953Rob1], probably with a range of homogeneity [1951Pra1], microhardness 5710 MPa [1965Ess]

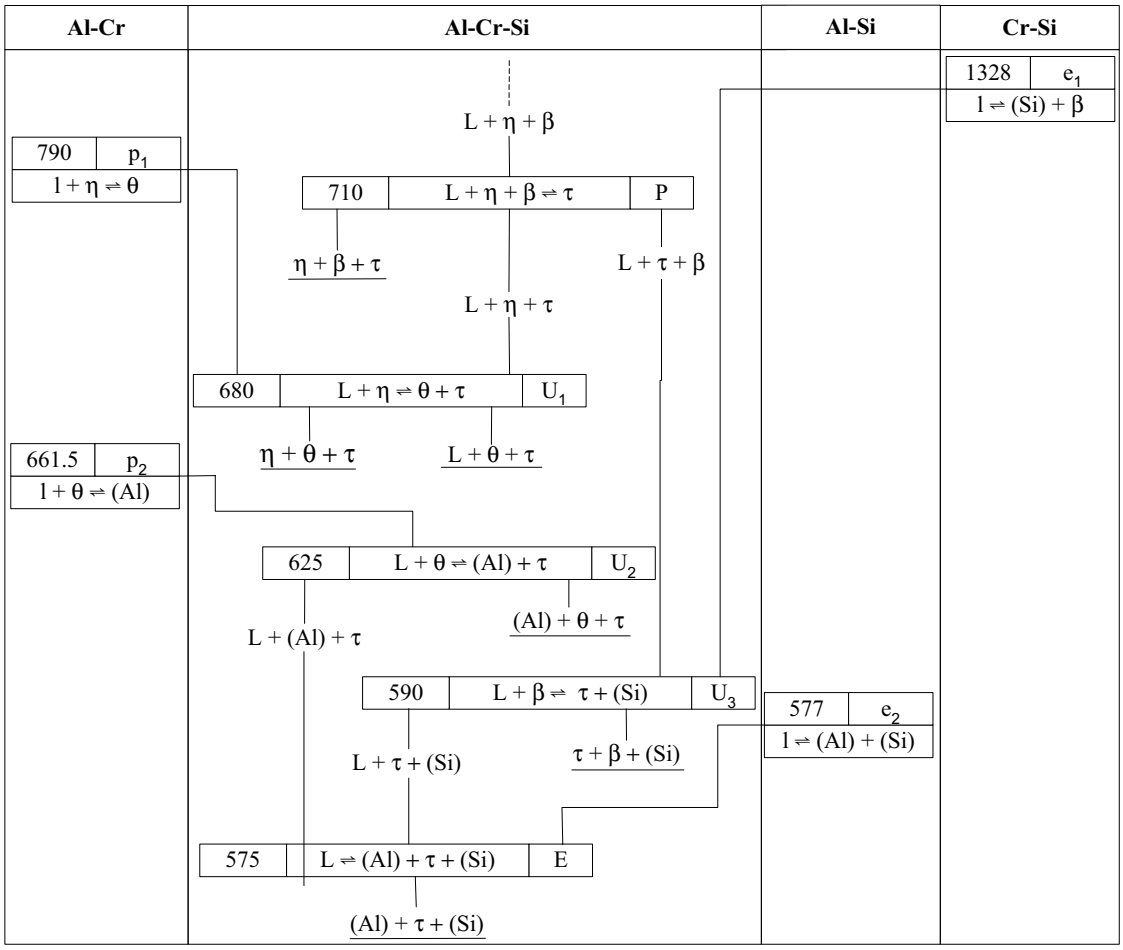

Fig. 1: Al-Cr-Si. Partial reaction scheme

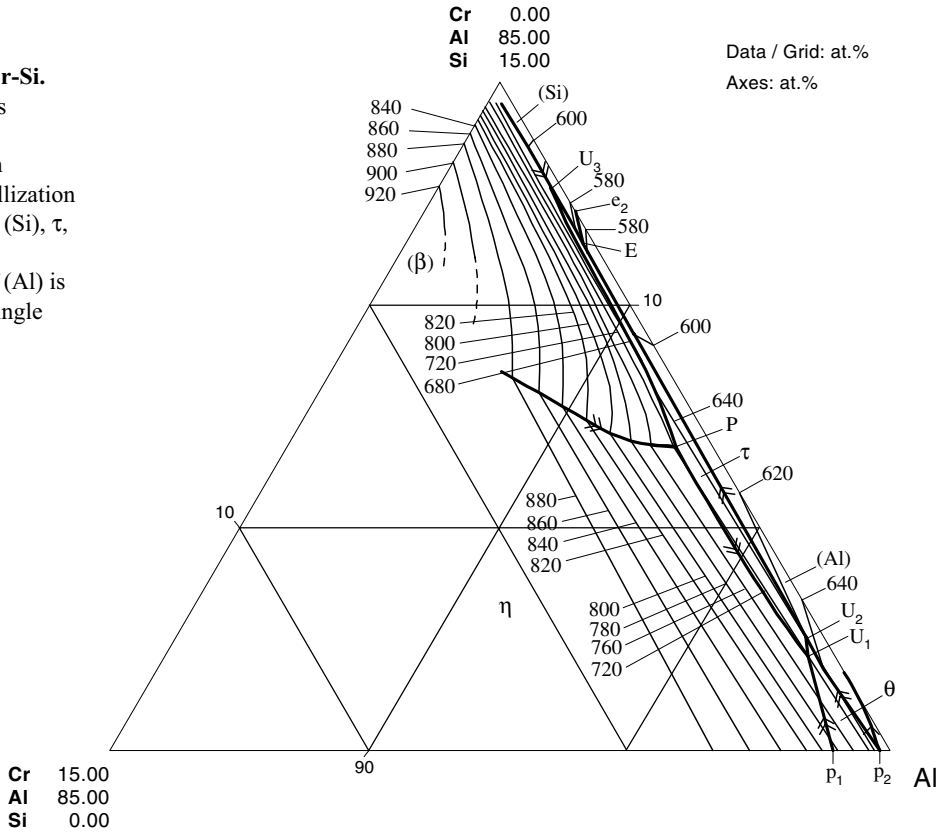

Fig. 2: Al-Cr-Si. Partial liquidus surface of the Al-corner with primary crystallization fields of (Al), (Si), τ, β, η and θ. The solidus of (Al) is marked by a single arrow

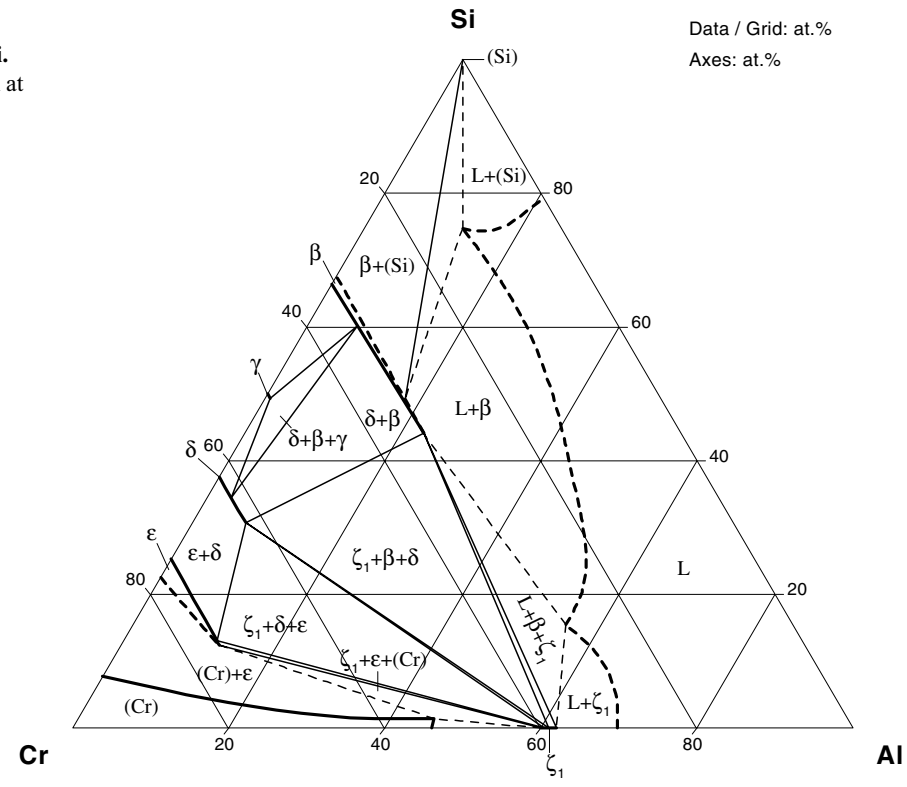

Fig. 3: Al-Cr-Si. Isothermal section at 1300°C

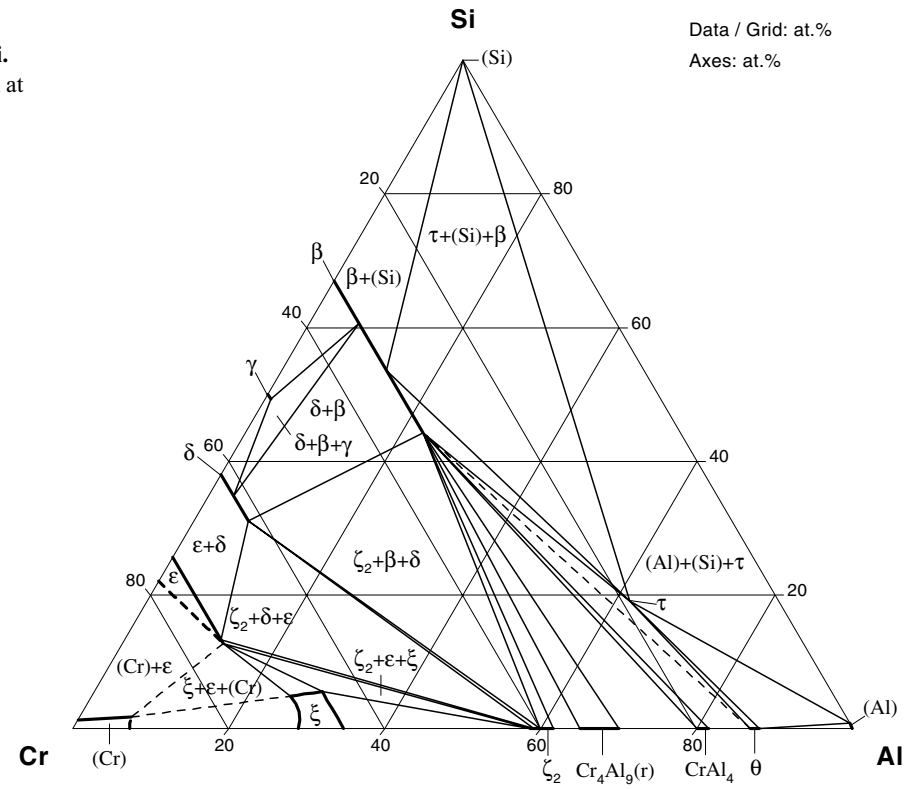

Fig. 4: Al-Cr-Si. Isothermal section at 500°C