Aluminium – Chromium – Zirconium

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Literature Data

In this system experimental information on phase equilibria comprises isothermal sections at several temperatures: 800°C [1970Mar], 620 and 450°C [1972Kad], 400°C [1967Zar] and series of isopleths in the Zr-rich region at fixed composition ratios of Al:Cr = 4:1, 1:1, 1:4 and at fixed content of 3 mass% Cr [1968Gru]. [1970Mar] studied phase equilibria at 800°C on 114 alloys, prepared by melting pure elements (above 99.9% purity) under argon in an arc furnace. The specimens were annealed at 800°C for 1000 h followed by quenching in cold water and examined by X-ray and metallographic analysis. The phase compositions of solid alloys in the Al corner at 400°C were established by [1967Zar] where arc melted ingots were annealed for 1000 h at 400°C and quenched in toluene. Using optical microscopy and electrical resistivity measurements, [1972Kad] investigated the solubility of Cr and Zr in Al at 450 and 620°C. Alloys were homogenized for 48 h at 500°C and after hot-working heated for 280 h at 620°C with an additional annealing for 100 h at 620°C after cold-working to ensure that equilibrium was reached. The Zr corner of the system was investigated by [1968Gru]. However, the results are in contradiction to [1970Mar] and are not shown here. The thermodynamic calculations made by [1977Cha] are not accepted in this evaluation as they do not take into account the well confirmed existence of the continuous solid solution between $ZrCr_2$ and $ZrAl_2$ at high temperatures. A short review of the system is given by [1990Kum].
[1989Sok1], [1989Sok2] and [1992Dob] observed an increase of solubility of Cr and Zr in Al in metastable state which is achieved by cooling the alloys rapidly at rates of 10^6 to $10^7 K \cdot s^{-1}$. The authors also investigated the corrosion behavior and the kinetics of decay of these solid solutions. [1991Des] examined the $ZrAl_3$ based $L1_2$ phase in the mechanically alloyed samples. [1993Tai] studied microstructure and some mechanical properties of samples obtained by powder extrusion. The present evaluation updates the review made by [1991Guz].

Binary Systems

The ternary description presented here is consistent with the edge boundary systems Al-Cr as published by [2003Cor] and Cr-Zr by [2002Per]. For the Al-Zr edge the description by [2003Sch] is accepted.

Solid Phases

No stable ternary phases have been found. The phase with $L1_2$ structure, found by [1991Des] in mechanically alloyed two-phase sample with an over-all composition of Al-12.5Cr-25Zr (at.%) is most probably metastable, although the authors do not exclude that it is stable at low temperatures.
In the as cast state a continuous series of solid solutions exists between $ZrCr_2$ and $ZrAl_2$. At 800°C solid solutions based on $ZrCr_2(\lambda_2)$ and $ZrAl_2$ (λ_1) are formed with limited concentrations of Al and Cr, up to 7.5 and 54 at.%, respectively [1970Mar]. The known solid phases are listed in Table 1.

Liquidus Surface

No experimental investigations seem to exist. Figure 1 shows a partial liquidus projections extrapolated thermodynamically from binary data using a Muggianu formalism [1986Sau]. Three transition reactions (U-type) are shown with liquid phase composition very close to the Al-Cr side.

Isothermal Sections

Figure 2 displays the isothermal section at 800°C after [1970Mar] with minor corrections to meet the boundary system, in particular to account for the homogeneity range of the binary intermetallic compound $ZrCr_2$. Furthermore, [1970Mar] plotted an δ, $CrAl_3$, phase which, by more recent assessment [1986Sau],

has been proved to exist only at temperatures higher than 1060°C, as the high-temperature modification of the compound Al_9Cr_4.

Figure 3 shows the Al corner at 620°C [1972Kad]. Cr and Zr solubility in (Al) decrease with decreasing temperature from 0.187 at.% Cr and 0.049 at.% Zr at 620°C to 0.057 at.% Cr and 0.016 at.% Zr at 450°C. The agreement between the experimental phase boundaries by [1972Kad] and the calculated ones by [1986Sau] in the Al-rich corner of the 620°C and 450°C isothermal sections is very good and the calculations proved to be insensitive to any ternary interaction parameter in the fcc-(Al) phase [1986Sau].

Temperature – Composition Sections

Two polythermal sections, (1) at constant mass ratio Zr:Cr = 5:7 and (2) at $ZrAl_3$ - $CrAl_7$ have been constructed by [1989Sok1]. They are in general agreement with the solid state equilibria presented in Figs. 2 and 3. However, both sections do not reflect the present knowledge on the edge binary systems, in particular with respect to the temperature at which the $CrAl_7$ phase forms; also temperature scale is not shown by [1989Sok1] for the Zr:Cr = 5:7 section. Therefore, these sections are not presented in this evaluation.

Notes on Materials Properties and Applications

[1989Sok1, 1989Sok2] studied the corrosion behavior of supersaturated Al based solid solutions. [1991Des] investigated mechanical properties of the probably metastable $L1_2$ phase which turned out to be slightly more ductile than the equilibrium $ZrAl_3$ phase. [1993Tai] reports the microstructure, mechanical properties and thermal stability of the Al-1.6Cr-1.6Zr (at.%) alloy prepared by hot-extrusion of rapidly solidified powder.

Magnetic susceptibilities have been recorded by [1984Sup] for the $MgZr_2$ type solution $ZrCr_{2-x}Al_x$ revealing Pauli-paramagnetism for all compositions x.

Miscellaneous

Figure 4 shows the metastable solubility of Cr and Zr in (Al) after solidification at different cooling rates, compared with equilibrium data by [1972Kad] at 620°C (curve 1). Curves 2 and 3 by [1977Ela] relate to material cooled at 10 K·s^{-1} and 100 K·s^{-1} rates, respectively. Additions of Zr to an Al-Cr alloy increased the maximum solid solubility of Cr from 5 to 8 mass% in alloys produced by the atomization splat quenching method [1987Kim]. Rapidly solidified alloys (10^6-10^7 K·s^{-1}) showed a maximum solid solubility of 6.5 at.% Cr and 0.55 at.% Zr, respectively [1989Sok1]. Figure 5 presents the limits of metastable solubility at cooling rates of 10^3 to 10^6 K·s^{-1} [1992Dob].

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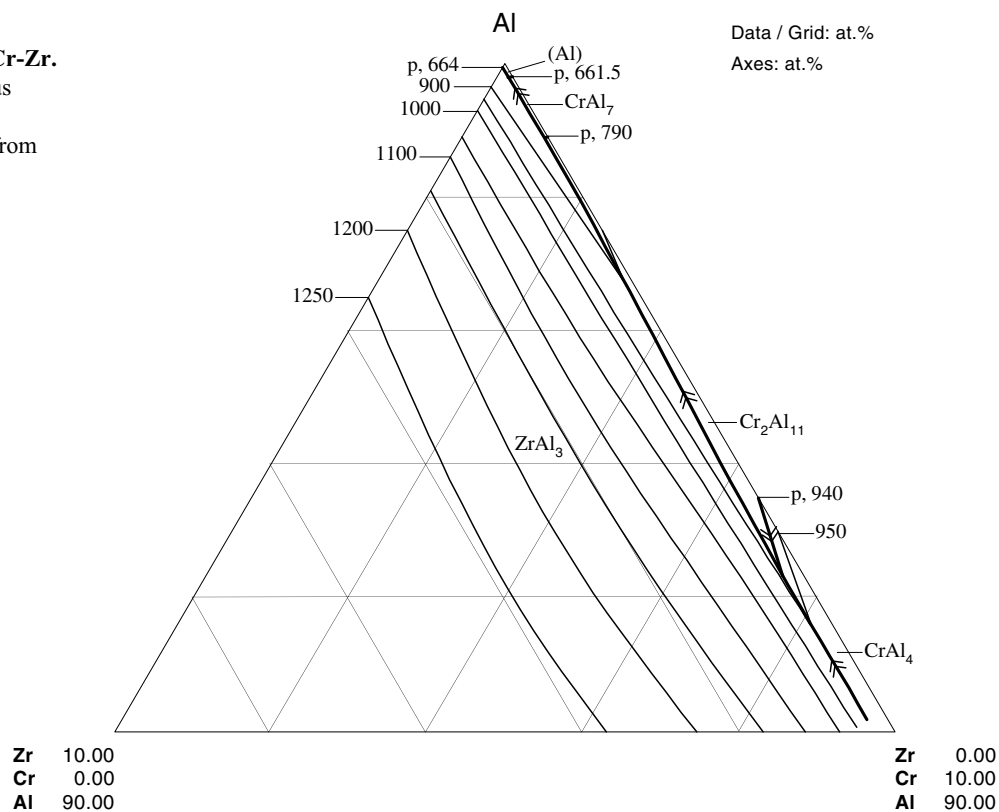**Table 1:** Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Al) < 660.452	$cF4$ $Fm\bar{3}m$ Cu	$a = 404.96$	at 25°C [Mas2] 0.37 at.% Cr at 661.5°C 0.07 at.% Zr at 660.8°C
(Cr) < 1863	$cI2$ $Im\bar{3}m$ W	$a = 288.48$	at 25°C [Mas2] 46 at.% Al at 1350°C 0.6 at.% Zr at 1592°C
(βZr)(h) 1855-863	$cI2$ $Im\bar{3}m$ W	$a = 356.90$	at 25°C [V-C2] 8 at.% Cr at 1332°C 26 at.% Al at 1350°C
(αZr)(r) < 863	$hP2$ $P6_3/mmc$ Mg	$a = 323.2$ $c = 514.7$	at 915°C [V-C2] 8.3 at.% Al at 910°C 0.5 at.% Cr at 836°C
Cr_2Al_{13} ($CrAl_7$) < 790	$mC104$ $C2/m$ V_7Al_{45}	$a = 2519.6$ $b = 757.4$ $c = 1094.9$ $\beta = 128.7$	at room temperature 13.5 at.% Cr [1960Coo, 1975Ohn, 1995And]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Cr_2Al_{11} ($CrAl_5$) 940-790	Orthorhombic	a = 1240 b = 3460 c = 2020	quenched from 920°C 16.9 to 19.2 at.% Cr; [1995Aud, 2000Mah]
	$oC584$ $Cmcm$	a = 1252.1 b = 3470.5 c = 2022.3	single crystal "εCrAl$_4$" [1997Li, 1998Li]
		a = 1260 b = 3460 c = 2000	"εCrAl$_4$" [1992Wen]
$CrAl_4$ < 1030	$hP574$ $P6_3/mmc$ μ$MnAl_4$	a = 1998 c = 2467	at room temperature, 20.9 ± 0.3 at.% Cr [1995Aud, 2000Mah]; [1990Ram] 20.6 to 21.2 at.% Cr [1995Aud];
		a = 2010 c = 2480	22.3 ± 0.1 at.% Cr at Cr-rich border at 1000°C [2000Mah]
$ε_1$, Cr_4Al_9 (h2) 1170-1060			[2003Cor]
$ε_2$, Cr_4Al_9 (h1) <~ 1060	$cI52$ $I\bar{4}3m$ 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]
$ε_3$, Cr_4Al_9 (r) < 700 (?)	$hR52$ $R\bar{3}m$ Cr_4Al_9	a = 1291 c = 1567.7	32.8 to 35 at.% Cr [1968Lin, Mas2]
$ζ_1$, Cr_5Al_8 (h) ≥ 1100 (?)	$I52$ $I\bar{4}3m$ 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 (?)	$hR78$-1.50 $R3m$ Cr_5Al_8	a = 1271.9 c = 793.6	[1977Vis, Mas2]
		a = 1272.8 c = 794.2	[1977Bra]
		a = 1281.3 c = 795.1	[1989Ell]
Cr_2Al < 910	$tI6$ $I4/mmm$ $MoSi_2$	a = 300.45 c = 864.77 a = 300.5 to 302.8 c = 864.9 to 875.5	~65.5 to ~71.4 at.% Cr [1937Bra, 1963Koe, 1998Mur] [1989Ell]
X(Al-Cr) ≤ 400	Cr_5Al_3 or Cr_3Al super lattice		~75 to ~80 at.% Cr [1981Bro, 1981Ten]; 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]
$iCrAl_4$	icosahedral		in spinning alloy of 8 to 13 at.% Cr; by decomposition of amorphous 20 at.% Cr, metastable [1998Mur]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
dCrAl$_4$	decagonal		19 at.%, 4 at.% Si [1994Sel]
ω(Al-Cr)			in quenched Al-Cr alloys of 60-100 at.% Cr, like metastable ωTi [2000Sha1, 2000Sha2]
ZrAl$_3$ (m)	$cP4$ $Pm\bar{3}m$ Cu$_3$Au	$a = 408$	[1987Vec] at 16.5 at.% Zr
ZrAl$_3$ < 1580	$tI16$ $I4/mmm$ ZrAl$_3$	$a = 399.93 \pm 0.05$ $c = 1728.3 \pm 0.02$	[1992Mur, 2003Sch]
λ_1, Zr(Cr$_x$Al$_{1-x}$)$_2$	$hP12$ $P6_3/mmc$ MgZn$_2$	$a = 519$ $c = 848$	$0 \le x \le 0.8$ [1970Mar] at 33 at.% Cr; 80 h at 700°C [1964Ram]
ZrAl$_2$ <1660		$a = 528.24$ $c = 874.82$	[V-C]
Zr$_2$Al$_3$ <1590	$oF40$ $Fdd2$ Zr$_2$Al$_3$	$a = 960.1 \pm 0.2$ $b = 1390.6 \pm 0.2$ $c = 557.4 \pm 0.2$	[2003Sch]
ZrAl < 1275±25	$oC8$ $Cmcm$ CrB	$a = 335.9 \pm 0.1$ $b = 1088.7 \pm 0.3$ $c = 427.4 \pm 0.1$	[2003Sch]
Zr$_5$Al$_4$(h) 1550-~1000	$hP18$ $P6_3/mcm$ Ti$_5$Ga$_4$	$a = 844.8$ $c = 580.5$	[2003Sch]
Zr$_4$Al$_3$ <~1030	$hP7$ $P6/mmm$ Zr$_4$Al$_3$	$a = 543.3 \pm 0.2$ $c = 539.0 \pm 0.2$	[12003Sch]
Zr$_3$Al$_2$ <1480	$tP20$ $P4_2/mnm$ Zr$_4$Al$_3$	$a = 763.0(1)$ $c = 699.8(1)$	[2003Sch]
Zr$_5$Al$_3$(h) <1400	$tI32$ $I4/mcm$ W$_5$Si$_3$	$a = 1104.4$ $c = 539.1$	[2003Sch]
Zr$_5$Al$_3$(r?)	$hP16$ $P6_3/mcm$ Mn$_5$Si$_3$	$a = 817.4$ $c = 569.8$	[2003Sch]
Zr$_2$Al <1350	$hP6$ $P6_3/mmc$ Ni$_2$In	$a = 489.39 \pm 0.05$ $c = 592.83 \pm 0.05$	[2003Sch]
Zr$_3$Al <1019	$cP4$ $Pm\bar{3}m$ Cu$_3$Au	$a = 437.2 \pm 0.3$	[2003Sch]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Zr(Al,Cr)$_3$ metastable	cP4 $Pm\bar{3}m$ AuCu$_3$	a = 438.0 a = 465.2	in Al-Zr binary (metastable) [V-C2] [1991Des], two-phase sample, no composition of phase is given
γZrCr$_2$ 1677-1625	hP12 $P6_3/mmc$ MgZn$_2$	a = 510.2 c = 828.9 a = 511.1 c = 834.1	C14 structure [1995Sou] at 20°C [1997Kur] at 300°C [1997Kur]
βZrCr$_2$ 1625-1546	hP24 $P6_3/mmc$ MgNi$_2$	a = 510.0 c = 1661	C36 structure [1986Ari]
λ$_2$, Zr(Cr$_{1-x}$Al$_x$)$_2$ αZrCr$_2$ < 1560	cF24 $Fd\bar{3}m$ MgCu$_2$	a = 721.8 a = 719.4 a = 720.4	0 ≤ x ≤ 0.1, 64 to 69 at.% Cr [1970Mar], [1973Pet] at 64 at.% Cr [1973Pet] at 69 at.% Cr C15 structure [1995Sau]

Fig. 1:   Al-Cr-Zr.
Partial liquidus
projection
extrapolated from
binary data

Fig. 2: Al-Cr-Zr.
Isothermal section at
800°C

Data / Grid: at.%

Axes: at.%

Al

L

L+ZrAl₃+Cr₂Al₁₁

Cr₂Al₁₁

CrAl₄

ZrAl₃

ε₂

ZrAl₂

ζ₂

Zr₂Al₃

ZrAl

Zr₄Al₃

Zr₃Al₂

ζ₂+λ₁+Cr₂Al

Zr₂Al

Cr₂Al

Zr₃Al

(Cr)

(αZr)+λ₁+Zr₃Al

λ₁

(αZr)

(αZr)+λ₂+λ₁

λ₂

Zr

Cr
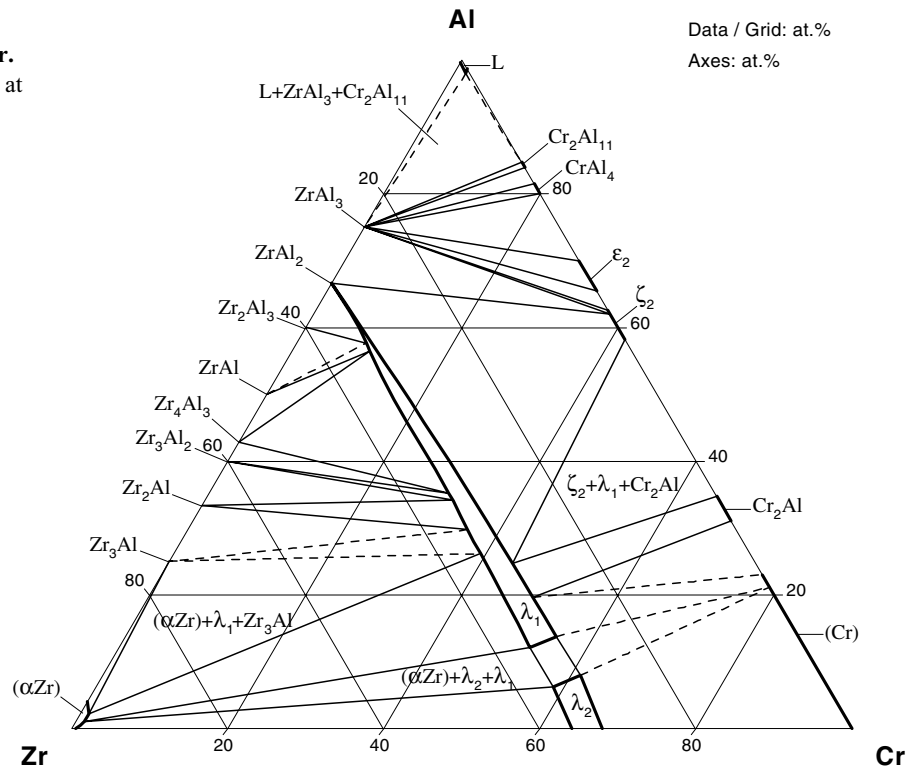
Fig. 3: Al-Cr-Zr.
Isothermal section of
the Al-corner at
620°C

Data / Grid: at.%

Axes: at.%

Al

(Al)

(Al)+ZrAl₃

(Al)+CrAl₇

(Al)+ZrAl₃+CrAl₇

Zr	1.00
Cr	0.00
Al	99.00

Zr	0.00
Cr	1.00
Al	99.00
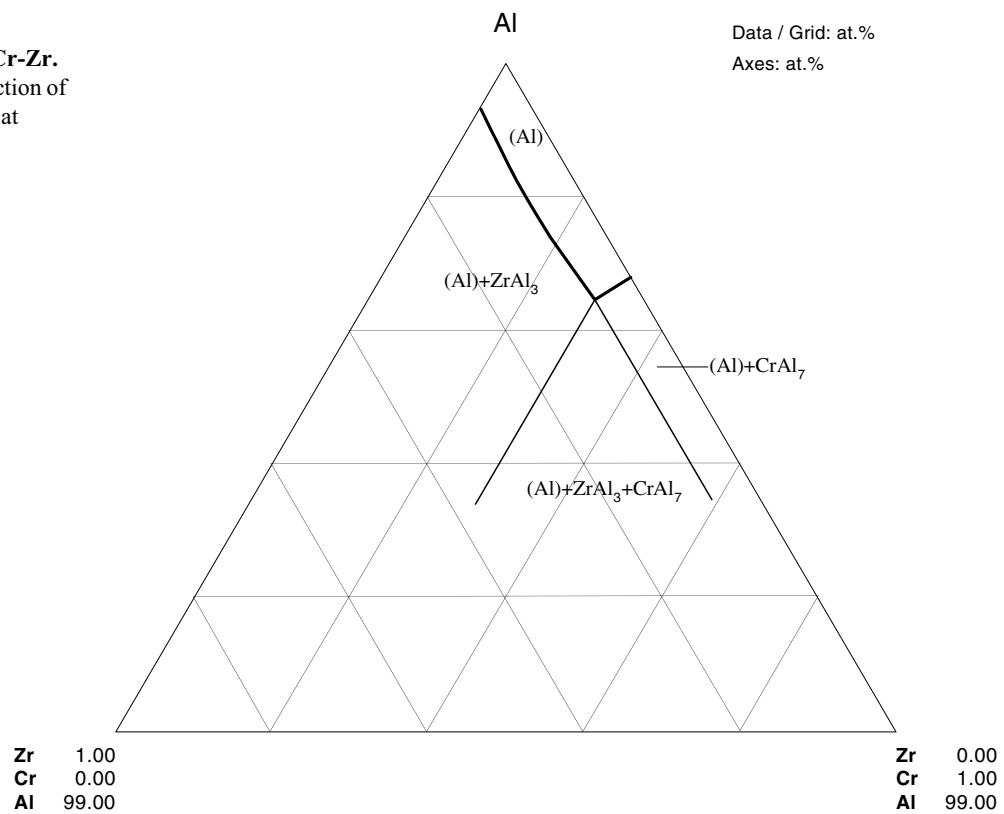
Fig. 4:   Al-Cr-Zr.
Anomalous
solubility curves of
Cr and Zr in (Al)

Al

Data / Grid: at.%

Axes: at.%

1: equilibrium solubility at 640°C 1972Kad;
2: metastable solubility at 20°C
   (cooling rate 10 K/s);
3: metastable solubility at 20°C
   (cooling rate 100 K/s)

1

2

3

Zr	2.00
Cr	0.00
Al	98.00

Zr	0.00
Cr	2.00
Al	98.00
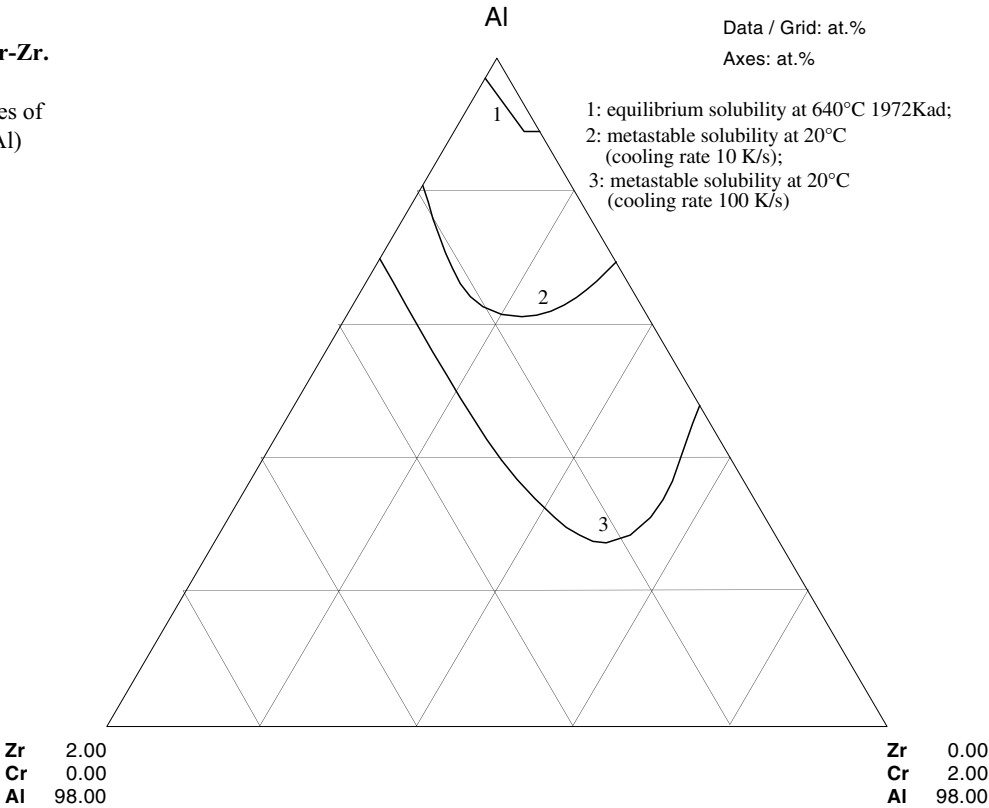
Fig. 5:   Al-Cr-Zr.
Limits of Cr and Zr
solubility in (Al) for
metastable alloys

Al

Data / Grid: mass%

Axes: mass%

1: at cooling rate 1000 K/s;
2: at cooling 10^6 K/s;
3: at cooling rate 10^8 K/s.

1

2

3

10   90

10

Zr	14.00
Cr	0.00
Al	86.00

Zr	0.00
Cr	14.00
Al	86.00