Aluminium – Chromium – Niobium

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Literature Data

Forty-six ternary alloys located in the Nb-$NbCr_2$-$NbAl_3$ portion of the ternary system have been investigated by means of metallography and X-ray diffraction analysis by [1964Sve]. The alloys were prepared by arc melting under purified Ar using 99.99 mass% Al, 99.95 mass% Cr and 99.4 mass% Nb (0.4 mass% Ta, 0.06 mass% Ti, 0.06 mass% Si and 0.07 mass% Fe). Annealing was carried out under purified Ar for 17 to 30 h at 1500°C and for 105 h at 1200°C. The samples were cooled after annealing at 100°C per minute.

[1968Hun] used 22 alloy compositions to determine the constitution of the Nb-Cr-$NbAl_3$ portion of the ternary system at 1000°C. Alloys were arc melted under Ar using 99.999 Al and Cr and 99.9 mass% Nb. Samples were annealed for 168 h at 1000°C in evacuated quartz capsules and subsequently air-cooled. Only X-ray diffraction analysis was used to establish a tentative section at 1000°C. Within the MSIT Evaluation Program [1991Gam] made a critical review of the data published until the year 1986.

Because of the serious discrepancies between the results of [1964Sve] and [1968Hun], [2001Mah] performed a new study of the Al-Cr-Nb ternary system, combining X-ray diffraction and electron probe microanalysis together with direct reaction calorimetry. Powders (99.5 Al, 99.5 Cr and 99.8 mass% Nb) of the components of the alloy were mixed together at room temperature in the right proportions, inside a glove box under purified Ar. The mixture was compressed in order to make small pellets of about 30-150 mg, which were loaded in an argon tight sample dispenser. Then, the dispenser was connected to the calorimeter and the samples were dropped, one after the other, from room temperature into the crucible of the calorimeter. The calorimeter temperature was high enough to ensure a quick diffusion of the elements into each other, but lower than the melting point or peritectic temperature of the compound. Some binary and ternary compounds were synthesized in this way whilst determining their enthalpies of formation.

[1986Bla, 1985Tho] examined the 66.67 at.% Cr section. Six alloy compositions were arc melted under gettered Ar using only 99 mass% Al with 99.2 mass% Cr and 99.5 mass% Nb. Samples were annealed for a minimum of 170 h at temperatures in the range 800-1200°C and presumably air-cooled.

[1977Ale] determined the limit of solubility of Cr in Nb_3Al along the constant Al section by X-ray diffraction analysis. Samples were homogenized for 5 h at 1650°C and the annealed for 250 h at 700°C. The solubility of Cr in Nb_3Al was found to be 4.5 at.% Cr. The lattice parameter of Nb_3Al is reduced by only 0.47 pm per at.% Cr.

[1975Sha] reported the same data as [1977Ale]. These results are almost the same as received by [2001Mah].

In a cursory examination of the Al-Cr-Nb system, [1964Ram] studied the phases present in three alloys after annealing for 80 h at 700°C. They detected $NbCr_2$(h) as one of the phases in all three alloys.

Computer calculated isothermal sections were reported by [1973Kau] for temperatures 2000, 1800, 1700, 1600, 1500, 1400, 1200 and 1000°C. A calculated liquidus projection was also given. [1978Cha] reported a calculated 1500°C section.

[1975Tho] arc melted 9 alloy compositions in the vicinity of the predicted ternary eutectic of [1973Kau]. Alloys were arc melted under Ar using 99.95 Al, 99.99 Cr and 99.8 mass% Nb.

Some problems related to the mechanical properties of intermetallics in the Al-Cr-Nb system have been examined by [1990Kum, 1996Mac].

Binary Systems

The accepted Al-Cr phase diagram is taken from [2003Cor]. The Al-Nb binary system is taken from [2003Vel]. The Cr-Nb phase diagram is taken from [2003Iva].

Solid Phases

Solid phases observed in this system are given in Table 1.

Liquidus Surface

[1973Kau] predicted a pseudobinary saddle point on the Cr_5Al_8 - $NbAl_3$ section at 1375°C and 30 Cr, 7 at.% Nb. A ternary eutectic at 1317°C was calculated to occur at 34 Cr, 12 at.% Nb. [1975Tho] checked the results of this calculation and showed that the predicted ternary eutectic contained $NbAl_3$ primary crystals with eutectic after slow cooling from the melt. It appears that the alloy with 34 Cr and 12 at.% Nb lies on a monovariant eutectic curve that descends towards the pseudobinary eutectic between Cr_5Al_8 and $NbAl_3$. It should be noted that the liquidus projection calculated by [1973Kau] disagrees with the calculated 1500°C isothermal section. The isothermal section does not show any evidence of the transition reaction at 1500°C indicated on the liquidus projection.

Isothermal Sections

There are substantial differences between the 1200°C section of [1964Sve] and the 1000°C section of [2001Mah] at one side, and the 1000°C section of [1968Hun] with respect to another. According to [1968Hun], the Nb_3Al phase extends into the ternary along the line of constant Nb content as opposed to that given by [1964Sve] and [2001Mah]. It should be noted, that the location of the Nb_3Al phase field given by [1968Hun] is similar to that proposed by [1989Sub], who investigated two alloys by XRD and EPMA: Al-15Nb-25Cr and Al-25Nb-12.5Cr (at.%) annealed at 1300°C. Based on his own data and that of [1968Hun] it was suggested that Cr substitutes preferentially for Al with constant Nb content. At the same time, [1989Sub] showed that Fe, Mo and W substituted for Nb with constant Al content on dissolving in Nb_3Al. This result may be regarded as argument in favor of the [1964Sve] and [2001Mah] data. The homogeneity region of Nb_2Al was shown by [1968Hun] as having considerably more solubility for Cr than indicated by [1964Sve, 2001Mah]. The $NbCr_2$(h) phase is stable at 1000°C. But the homogeneity range presented by [1968Hun] included higher Nb contents than shown by [1964Sve] and [2001Mah] whose results are very similar.

X-Ray diffraction analysis performed by [1986Bla] showed that alloys containing 0-20 at.% Al were single phase with a $NbCr_2$(h) structure. This result disagrees with the 1000°C data of [1964Sve, 2001Mah]. Since [1964Sve] shows a wide $NbCr_2$(h) region along the section $NbCr_2$-$NbAl_3$ at 1200°C, it is difficult to accept that the $NbCr_2$(h) region will have an extension along a constant Cr content as shown by [1986Bla].

[1973Kau] compared their calculated isothermal sections with the 1000°C section of [1968Hun] and with a 1500 and 1200°C sections that are probably data from [1964Sve]. The calculated 1500°C isothermal section does not indicate Cr_5Al_8-$NbAl_3$ to be a stable join although the experimental data of [1964Sve] suggested it to be so.

The isothermal sections at 1500 and 1200°C are presented in Fig. 1 and Fig. 2 taken from [1964Sve]. The isothermal section at 1200°C is presented in accordance with the accepted Al-Nb binary system. The isothermal section at 1000°C is presented in Fig. 3 taken from [2001Mah]. It has been slightly modified in accordance with assessed Al-Cr and Al-Nb systems and reflects the existence of a two-phase region between $NbCr_2$(h) and $NbCr_2$(r). The three new three-phase regions are marked by dashed lines. The compositions of the phases in equilibrium at 1000°C are presented in Table 2 in accordance with [2001Mah] considering the width of homogeneity regions of Cr_4Al_9 and Cr_5Al_8 compounds.

Slight discrepancies between location of phase boundaries in the accepted Al-Cr phase diagram and data presented by [2001Mah] exist because of Nb solubility. It should be noted that compositions of the $(Nb,Cr)Al_3$ phase in equilibria 3, 4 and 5 do not allow correct connections of the tie-triangles with the single-phase field of $(Nb,Cr)Al_3$, therefore these compositions have been changed slightly in the diagram presented in Fig. 3.

Thermodynamics

The enthalpies of formation of $(Nb,Cr)_3Al$, $Nb_2(Cr,Al)$, $(Nb,Cr)Al_3$, $Nb(Cr,Al)_2$ as a function of composition have been measured by [2001Mah] and are presented in Table 3.

Notes on Materials Properties and Applications

The solubility of Cr in Nb_3Al lowered the critical temperature of the transition to the superconductive state. The concentration dependence of T_c is $T_c = 18.6 - 0.74 \cdot$ (at.% Cr) K [1977Ale].
The $Nb(Cr,Al)_2$ phase has high hardness and high brittleness. The substitution of Cr for Al in $Nb(Cr,Al)_2$ lowered the microhardness of the C14 high temperature Laves phase from 9.32 GPa to 8.47 GPa. [1990Kum] found that the brittle to ductile transition temperature of Nb_3Al occurred around 1200 K. [1996Mac] investigated various Al containing ternary Laves phases having the hexagonal *C*14 structure. It was shown that NbCrAl phase had very low thermal shock resistance. After arc melting + levitation remelting the specimen was cracked severely and could not be used for mechanical testing.

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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
(βAl)	*hP*2 $P6_3/mmc$ Mg	a = 269.3 c = 439.8	at 25°C, 20.5 GPa [Mas2]
(αAl) < 660.452	*cF*4 $Fm\bar{3}m$ Cu	a = 404.96	at 25°C [Mas2]
(Cr) < 1863	*cI*2 $Im\bar{3}m$ W	a = 288.48	Pure Cr at 25°C, [Mas2] ≤ 5.59 ± 0.31 at.% Nb at 1668°C, [1992Tho]
		a = 290.01 ± 0.17	97.54 ± 0.32 at.% Cr, cooled from 1400°C, [1992Tho]
		a = 289.70 ± 0.51	98.51 ± 0.07 at.% Cr, cooled from 1300°C, [1992Tho]
		a = 289.43 ± 0.30	98.80 ± 0.24 at.% Cr, cooled from 1200°C, [1992Tho]
		a = 289.20 ± 0.18	98.72 ± 0.11 at.% Cr, cooled from 1100°C, [1992Tho]
		a = 288.80 ± 0.12	98.98 ± 0.21 at.% Cr, cooled from 950°C, [1992Tho]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Nb) < 2469	*cI*2 $Im\bar{3}m$ W	*a* = 330.04 *a* = 325.95 ± 0.89 *a* = 326.27 ± 0.35 *a* = 327.21 ± 0.51 *a* = 328.08 ± 0.75 *a* = 328.89 ± 0.31	Pure Nb at 25°C, [Mas2] <24.42 ± 0.88 at.% Cr at 1703 14.37 ± 0.51 at.% Cr, cooled from 1400°C, [1992Tho] 12.53 ± 075 at.% Cr, cooled from 1300°C, [1992Tho] 9.10 ± 0.26 at.% Cr, cooled from 1200°C, [1992Tho] 9.02 ± 0.56 at.% Cr, cooled from 1100°C, [1992Tho] 9.44 ± 0.31 at.% Cr, cooled from 950°C, [1992Tho]
βNbCr$_2$(h) 1730 - 1585	*hP*12 $P6_3mmc$ MgZn$_2$	*a* = 493.1 *c* = 812.3	at 25°C, 66.7 at.% Cr, [1986Bla]
αNbCr$_2$(l) < 1625	*cF*24 $Fd\bar{3}m$ MgCu$_2$	*a* = 702.25 ± 0.26 to 699.50 ± 0.12 *a* = 701.81 ± 0.22 to 700.02 ± 0.12 *a* = 701.56 ± 0.24 to 700.96 ± 0.39 *a* = 701.02 ± 0.16 to 699.67 ± 0.22 *a* = 700.53 ± 0.33 to 699.49 ± 0.22	63.59 ± 0.27 - 68.04 ± 0.53 at.% Cr, cooled from 1400°C, [1992Tho] 63.99 ± 0.43 - 67.95 ± 0.40 at.% Cr, cooled from 1300°C, [1992Tho] 64.51 ± 0.32 - 67.79 ± 0.45 at.% Cr, cooled from 1200°C, [1992Tho] 65.73 ± 0.41 - 67.49 ± 0.27 at.% Cr, cooled from 1100°C, [1992Tho] 63.57 ± 0.46 - 68.27 ± 0.32 at.% Cr, cooled from 950°C, [1992Tho]
Nb$_3$Al < 2060	*cP*8 $Pm\bar{3}n$ Cr$_3$Si	*a* = 518.6	[V-C2] 18.6 to 25 at.% Al [Mas2]
Nb$_2$Al < 1940	*tP*30 $P4_2/mnm$ σCrFe	*a* = 994.3 *c* = 518.6	[V-C2] 30 to 42 at.% Al [Mas2]
NbAl$_3$ < 1680	*tI*8 *I*4/*mmm* Al$_3$Ti	*a* = 384.1 ± 1 *c* = 860.9 ± 2	[V-C2]
Nb$_3$Al$_2$ < ~1450	*tP*20 $P4_2/mnm$ Al$_2$Zr$_3$	*a* = 707 ± 8 *c*/*a* ~ 0.05	[1993Bar] 42.4 at.% Nb
CrAl$_7$ (Cr$_2$Al$_{13}$) < 790	*mC*104 *C*2/*m* V$_7$Al$_{45}$	*a* = 2519.6 *b* = 757.4 *c* = 1094.9 β = 128.7	at room temperature 13.5 at.% Cr [1995Aud, 1998Mur]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Cr_2Al_{11} ($CrAl_5$) < 940	Orthorhombic	*a* = 1240 *b* = 3460 *c* = 2020	quenched from 920°C 16.9 to 19.2 at.% Cr; [1995Aud, 2000Mah]
	*oC*584 *Cmcm*	*a* = 1252.1 *b* = 3470.5 *c* = 2022.3	single crystal "$\epsilon CrAl_4$" [1997Li, 1998Li]
		a = 1260 *b* = 3460 *c* = 2000	"$\epsilon CrAl_4$" [1992Wen]
$\mu CrAl_4$ < 1030	*hP*574 $P6_3/mmc$ $\mu MnAl_4$	*a* = 1998 *c* = 2467	at room temperature, 20.9 ± 0.3 at.% Cr [1995Aud, 2000Mah]
		a = 2010 *c* = 2480	20.6 to21.2 at.% Cr [1995Aud]; 22.3 ± 0.1 at.% Cr at Cr-rich border at 1000°C [2000Mah]
βCr_4Al_9 < 1060	*cI*52 $I\bar{4}3m$ Cu_4Al_9	*a* = 912.3	~31 to 45 at.% Cr quenched from liquid [Mas2]; 29 at.% Cr at Al-rich border at 920°C [1995Aud]
αCr_4Al_9 < 700	*hR*52 *R3m* Cr_4Al_9	*a* = 1291 *c* = 1567.7	32.8 to35 at.% Cr [Mas2]
βCr_5Al_8 ~ 1350 - 1110	*cI*52 $I\bar{4}3m$ Cu_5Zn_8	*a* = 910.4 to 904.7	30 to42 at.% Cr, quenched from liquid [1989Ell]
αCr_5Al_8 < ~1150	*hR*26 *R3m* Cr_5Al_8	*a* = 1279.9 *c* = 793.6 *a* = 1272.8 *c* = 794.2 *a* = 1281.3 *c* = 795.1	[Mas2] [1977Bra] [1989Ell]
Cr_2Al < 910	*tI*6 *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 [1963Koe, 1998Mur] [1989Ell]
X ≤ 400	Cr_5Al_3 or Cr_3Al superlattice		~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 "$\epsilon CrAl_4$" metastable [1994Sel]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$iCrAl_4$	icosahedral		in spinning alloy of 8 to 13 at.% Cr; by decomposition of amorphous 20 at.% Cr, metastable [1998Mur]
$dCrAl_4$	decagonal		19 at.%, 4 at.% Si [1994Sel]
T			in quenched alloy of 60-100 at.% Cr, like metastable ωTi [2000Sha1, 2000Sha2]

Table 2: Compositions of the Phases in Equilibrium, at 1000°C, in the Al-Cr-Nb System, [2001Mah]

Domain number in Figure 3	Phases involved in the equilibrium	Composition of phases by EPMA (at.%)		
		Al	Cr	Nb
1	$Nb_2(Cr,Al)$	25.5	8	66.5
	$(Nb,Cr)_3Al$	19	4.4	76.6
	(Nb)	7	5.2	87.8
2	$Nb_2(Cr,Al)$	24.4	10.7	64.9
	(Nb)	9.7	11.5	78.8
	$\beta NbCr_2(h)$	14	49.7	36.3
3	$(Nb,Cr)Al_3$	73.8 (73.97)*	0.2 (0.48)*	26 (25.55)*
	$Nb_2(Cr,Al)$	37.6	2.7	59.7
	$\beta NbCr_2(h)$	44.4	21.3	34.3
4	$(Nb,Cr)Al_3$	73.9 (73.6)*	0.9 (1.4)*	25.2 (25.0)*
	$\beta NbCr_2(h)$	38.4	27.4	34.2
	(Cr)	30	69.4	0.6
5	$(Nb,Cr)Al_3$	72.8 (73.6)*	1.3 (2.2)*	25.9 (24.2)*
	Cr_5Al_8	57.4	42.4	0.2
	(Cr)	39.3	60.6	0.1
6	$(Nb,Cr)Al_3$	74.3	10.8	14.9
	$CrAl_4$	77.8	22.1	0.1
	Cr_4Al_9	69.9	29.9	0.2
7	$(Nb,Cr)Al_3$	75.5	3.7	20.8
	$CrAl_4$	79.5	20.4	0.1
	Liquid	86.2	13.6	0.2
8	Cr_4Al_9	~66	~33.9	~0.1
	Cr_5Al_8	~64	~35.9	~0.1
	$(Nb,Cr)Al_3$	~73.4	~7.09	19.51
9	(Nb)	~6	~12	~82
	$\beta NbCr_2(h)$	~10	~54	~36
	$\alpha NbCr_2(l)$	~7.4	~55.8	~36.8
10	(Cr)	~12	~87.5	~0.5
	$\beta NbCr_2(h)$	~10.5	~57	~32.5
	$\alpha NbCr_2(l)$	~8	~59	~33

* values is brackets show compositions presented in the diagram Fig. 3.

Table 3: Enthalpies of Formation of Some Binary and Ternary Compounds in the Al-Cr-Nb System, Referred to Al (liq), Cr (bcc) and Nb (bcc) at *T*

Alloy Composition	Calorimeter Temperature [°C]	Enthalpy of Formation, $\Delta_f H$ [kJ· mole^{-1} of atoms]	References
$Al_{0.61}Cr_{0.39}$ (Al_8Cr_5)	1203	- 23.5 ± 0.5	[2001Mah]
$Al_{0.61}Cr_{0.39}$ (Al_8Cr_5)	1010	-23.7 ± 0.4	[2001Mah]
$Al_{0.69}Cr_{0.31}$ (Al_9Cr_4)	940	-24.8 ± 0.5	[2001Mah]
$Al_{0.805}Cr_{0.195}$ (Al_4Cr)	921	-24.8 ± 0.8	[2001Mah]
$Al_{0.84}Cr_{0.16}$ ($Al_{11}Cr_2$)	843	-20.05 ± 0.4	[2001Mah]
$Al_{0.87}Cr_{0.13}$ (Al_7Cr)	710	-22.6 ± ?	[2001Mah]
$Nb_{0.80}$ $Al_{0.20}$	1426	- 19.7 ± 2.3	[2001Mah]
$Nb_{0.79}Cr_{0.02}Al_{0.19}$	1428	- 17.2 ± 1.0	[2001Mah]
$Nb_{0.77}Cr_{0.04}Al_{0.19}$	1423	- 12.3 ± 1.8	[2001Mah]
$Nb_{0.67}$ $Al_{0.33}$	1426	- 29.8 ± 1.0	[2001Mah]
$Nb_{0.67}Cr_{0.05}Al_{0.28}$	1387	- 27.7 ± 1.0	[2001Mah]
$Nb_{0.63}Cr_{0.04}Al_{0.33}$	1450	- 30.2 ± 1.2	[2001Mah]
$Nb_{0.26}$ $Al_{0.74}$	1001	- 54.6 ± 0.9	[2001Mah]
$Nb_{0.24}Cr_{0.02}Al_{0.74}$	1000	- 52.55 ± 1.2	[2001Mah]
$Nb_{0.22}Cr_{0.04}Al_{0.74}$	1001	- 50.6 ± 1.8	[2001Mah]
$Nb_{0.20}Cr_{0.06}Al_{0.74}$	1001	- 49.0 ± 0.8	[2001Mah]
$Nb_{0.18}Cr_{0.08}Al_{0.74}$	1000	- 46.9 ± 0.95	[2001Mah]
$Nb_{0.16}Cr_{0.10}Al_{0.74}$	1001	- 45.2 ± 0.8	[2001Mah]
$Nb_{0.333}Cr_{0.567}Al_{0.10}$	1485	- 11.6 ± 1.4	[2001Mah]
$Nb_{0.333}Cr_{0.467}Al_{0.20}$	1485	- 20.3 ± 0.4	[2001Mah]
$Nb_{0.333}Cr_{0.367}Al_{0.30}$	1485	- 26.5 ± 0.8	[2001Mah]
$Nb_{0.333}Cr_{0.267}Al_{0.40}$	1485	- 34.9 ± 1.4	[2001Mah]

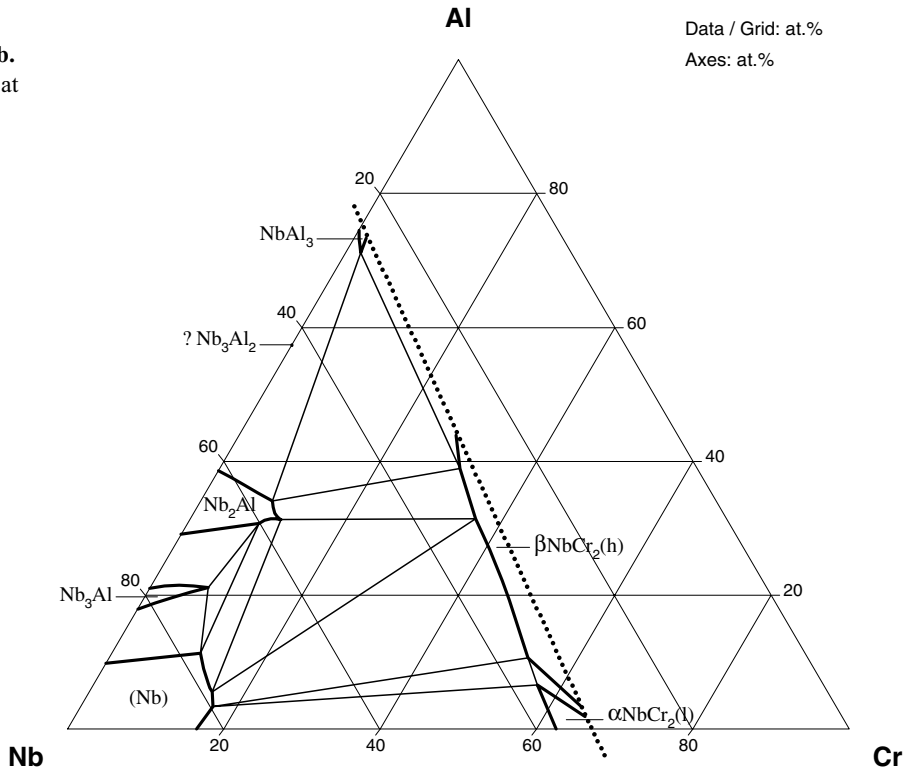

Fig. 1: Al-Cr-Nb. Isothermal section at 1500°C [1964Sve]

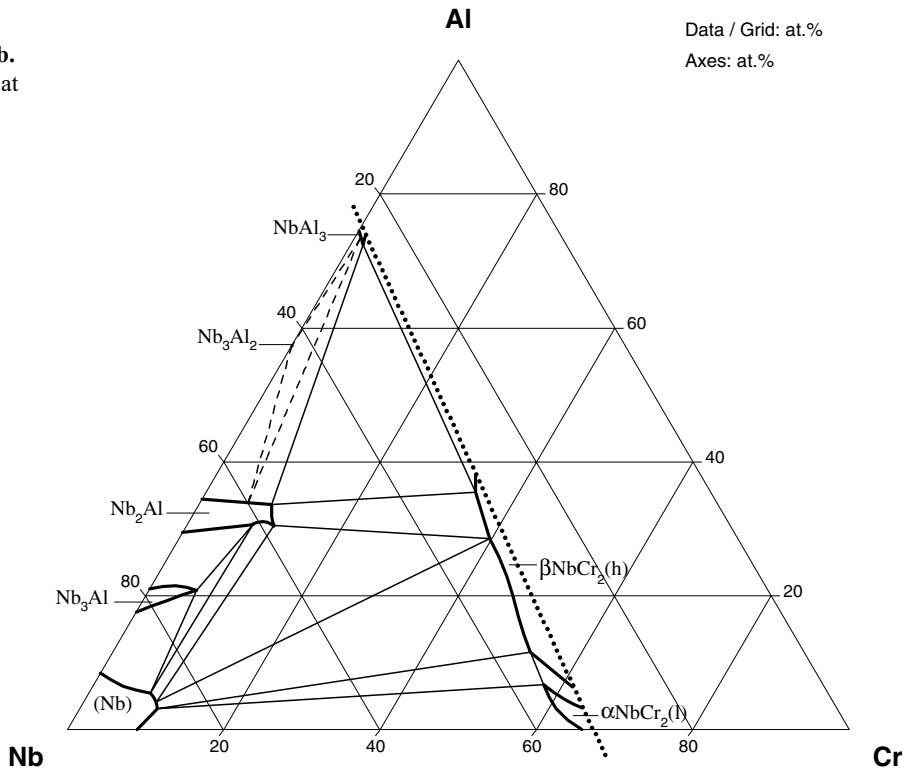

Fig. 2: Al-Cr-Nb. Isothermal section at 1200°C [1964Sve]

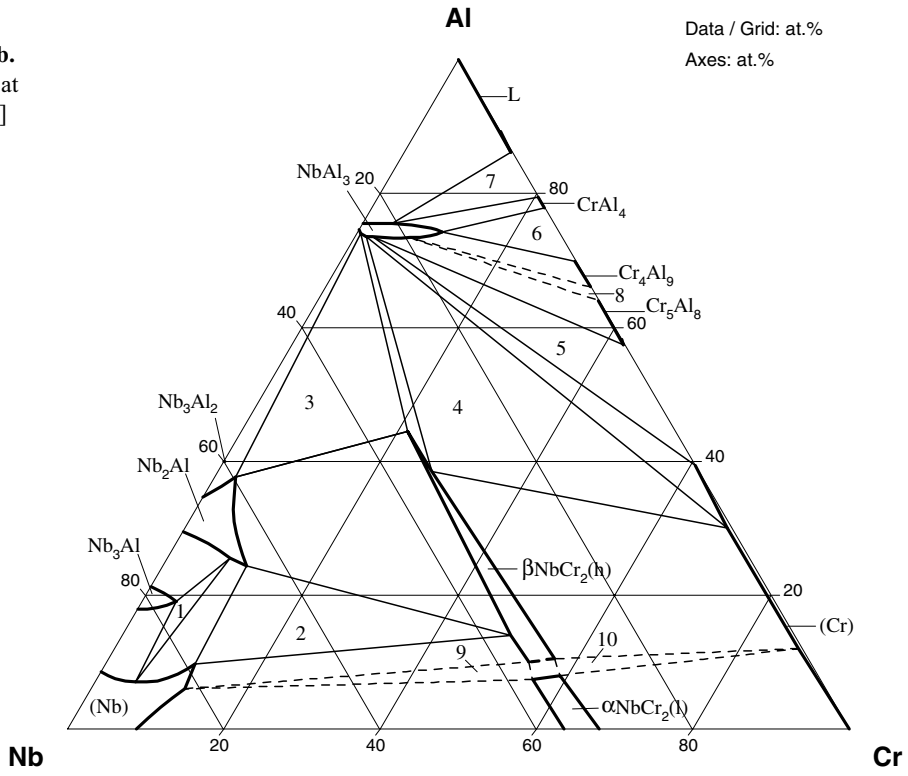

Fig. 3: Al-Cr-Nb. Isothermal section at 1000°C [2001Mah]