Aluminium – Cobalt – Iron

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Literature Data

Phase relationships in the Al-Co-Fe system are relatively well known in the composition range up to approximately 35 mass% Al. Both the Al-Fe system and the Al-Co systems contain ordered bcc structures of the CsCl-type (*cP*2) and form extensive solid solution ranges between them. At intermediate temperatures, the (αFe) phase (*cI*2) in the Co-Fe system characterizes the ternary system. The major contribution to the understanding of the liquidus and solidus relationships in the ternary system up to 35 mass% Al is due to [1933Koe], who examined alloys by thermal, metallographic and magnetic methods. Equilibria in the Al rich region have been established by [1948Ray, 1982Ray] using X-ray investigations of alloys that had undergone long annealing treatments. Thermal analysis was used to determine phase boundaries in vertical sections at high Al-contents. [1941Edw] used X-ray measurements to define single and 2-phase fields in Co-rich regions of the phase diagram. Alloys were prepared from pure material by induction melting, homogenizing at 1300°C, annealing at 800°C for 1 day and quenching. Phase separation of ordering alloys in the Fe rich range has been determined by electron microscopy and magnetization measurements, [1949Iva] and [1987Miy]. More recently, a series of articles presenting the results of TEM studies and calculated phase equilibria based on the Bragg-Williams-Gorsky approximation to model phase separation have been published [1994Koz1, 1994Koz2]. Despite the similar alloy preparation and experimental techniques employed, some disagreement was found with the previous work of [1987Miy] in relation to the location of the phase boundaries of the two-phase regions associated with the phase separation. A critical review of the then available data made by [1991Kub] provides the bases of the present evaluation. 1999Koz] used the information from [1994Koz1] together with new studies in the remaining regions of the section to produce a complete isothermal section for 650°C. Some solubility for the third element was reported in $FeAl_2$, Fe_2Al_5, $FeAl_3$, Co_2Al_9, Co_2Al_5 and Co_4Al_{13}. Furthermore, DTA investigations revealed how the A2+B2 phase field varied with temperature.

Binary Systems

The Al-Co and Al-Fe systems are taken from the MSIT Binary Evaluation Program [2003Gru, 2003Pis]. The Co-Fe diagram is taken from [2002Ohn].

Solid Phases

The Fe-rich region of the ternary system exhibits two different types of phase separation at temperatures below 700°C. The disordered A2 phase (α) separates into a two phase region comprising the A2 and the ordered B2 (α') phase of the Al-Fe and Co-Fe systems. Also, a region of $\alpha'_1+\alpha'_2$ exists adjacent to the α+α' two phase field. All known phases of the Al-Co-Fe system and those in equilibrium with (Al) are listed in Table 1. No ternary phases have been found.

Invariant Equilibria

A ternary eutectic exists at 653.9°C as determined by [1948Ray] using thermal analysis. The composition was estimated to be 1.55Fe-0.35Co-98.1Al (mass%) by interpolation of cooling curve data. A partial reaction scheme for the Al corner is shown in Fig. 1.

Liquidus Surface

Figure 2 shows liquidus contours at Al contents greater than 40 at.% based on the results of [1933Koe] and [1982Ray]. The 1400°C liquidus contour has been amended so that it converges with the Al-Co binary L ⇌ (αCo) + CoAl eutectic point, in contrast to the original publication where two contours converge at the ends

of the two solidus lines in the Al-Co binary. Also shown are projections of the liquidus and solidus lines (the latter denoted a_1a_2 and b_1b_2). The monovariant reaction line extends from the peritectic point p_1 in the Co-Fe system to the eutectic point e_1 in the Al-Co system and passes through a minimum; the composition is approximately 70Co-7.5Al (mass%), but the temperature is uncertain. The ordered AlCo phase forms a continuous solid solution with (δFe) at appropriate temperatures. The maximum melting point of CoAl (1645°C) persists in the ternary system as Fe replaces Co. The remainder of the liquidus surface of the ternary system is unknown except for the surfaces in the extreme Al rich corner that were established by [1948Ray] and depicted in Fig. 3.

Isothermal Sections

Figure 4 shows part of the isothermal section at 800°C as presented by [1941Edw], and Fig. 5 shows the location of the phase boundary separating the A2 (α) and B2 (α') phase fields at 700°C, taken from [1987Miy]. Figure 6 shows the complete isothermal section determined at 650°C taken from [1994Koz2, 1999Koz]. The iron rich part of the diagram showing equilibria between α and α′ phases is in excellent agreement with the diagram calculated at the same temperature [1999Koz, 2001Miy] by computer simulation of the phase decomposition process using the Bragg-Williams-Gorsky approximation. Some minor changes have been made to the points where the phase boundaries meet the binary edges to make the section consistent with the accepted binary phase diagrams. Figures 7 and 8 are partial Al-rich sections determined at 640 and 600°C by [1948Ray]. The lines depict two sides of the (Al)+Co_2Al_9+$FeAl_3$ three-phase region. There is some disparity between the locations of these phase boundaries (together with those in the vertical sections presented by [1948Ray]) and those given in Fig. 6 [1999Koz]. For this reason, the exact locations of the phase boundaries at high-Al contents remain unclear. Complete solubility exists between CoAl and FeAl [1966Rid, 1973Sid]. A detailed discussion is given by [1982Ray].

Temperature – Composition Sections

Figures 9 and 10 show vertical sections at 98.75 and 97.5 mass% Al, respectively, taken from [1948Ray]. A third section (at 98.5 mass% Al) was also presented in the article, but the liquidus and eutectic temperatures for 0 mass% Co were approximately 10°C lower than given in the accepted Al-Fe binary phase diagram, and were not consistent with the other two vertical sections either. For this reason, this section has been omitted from this review.

Notes on Materials Properties and Applications

[1996Cha] studied the crystal structure and the magnetic moment of $(Fe_xCo_{(1-x)})_{0.9}Al_{0.1}$ alloys where the mean number of 3*d*+4*s* electrons per transition atom was 9-*x* for $0 < x < 1$. It was found that the presence of the Al atom causes inflation of the unit cell and a corresponding decrease in the magnetic moment of the transition metals atoms. This resulted in a decrease in the Curie temperatures and an increase in the resistivity. [2000Szy] conducted Mössbauer and magnetic studies of $Fe_{3-x}Co_xAl$. It was found that Co modifies the lattice parameter and Debye temperature by causing lattice shrinkage through Al-Co pair interactions. The magnetic moment of Co was measured as ~ 0.05 μ_B at $x = 0.0$ and 1.15 μ_B at $x = 2.0$. The magnetic moment of Fe was given as ~1.9 μ_B for $x < 1$ and 2.7 μ_B for $x = 2$. The saturation magnetization at room temperature and 1.2 T measured by VSM is
$\sigma(x) = 5.47 \times (2\text{-}1.2(1)x\text{+}0.46(4)x^2)\ \mu_B$.

Miscellaneous

The extent of the α+α' phase field with respect to temperature was studied by DTA [1994Koz1]. Temperature contours are shown in Fig. 11. Small Al additions increase the ordering temperature of CoFe [1955Gri]. Co additions lead to a slight increase of the ordering temperature of Fe_3Al ($D0_3$) [1969Bul]. This is a characteristic of elements (Co, Cr, Mn, Ni), which substitute to the Al site in Fe_3Al [1999Mek].

References

[1933Koe] Köster, W., "The System Iron-Cobalt-Aluminium" (in German), *Arch. Eisenhuettenwes*., **7**, 263-264 (1933) (Equi. Diagram, Experimental, 2)

[1941Edw] Edwards, O.S., "An X-Ray Investigation of the Aluminium-Cobalt-Iron System", *J. Inst. Met.*, **67**, 66-77 (1941) (Crys. Structure, Equi. Diagram, Experimental, 16)

[1948Ray] Raynor, G.V, Waldron, M.B., "The Constitution of the Aluminium Rich Aluminium-Cobalt-Iron Alloys, with Reference of the Role of Transitional Elements in Alloy Formation", *Proc. Roy. Soc. A*, **194**, 362-374 (1948) (Equi. Diagram, Experimental, 12)

[1949Iva] Ivanov, I.O.S., Skryabina, M.A., "Phase Constitution of Alloys Between Iron and the Compound CoAl" (in Russian), *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 242-253 (1949) (Crys. Structure, Equi. Diagram, Experimental, 12)

[1955Gri] Griest, A.J., Libsch J.F., Conard, G.P., "Effect of Ternary Additions of Si and Al on the Ordering Reaction in Fe-Co", *Acta Metall*., **3**, 509-510 (1955) (Experimental, 7)

[1966Rid] Ridley, N., "Defect Structures in Binary and Ternary Alloys Based on CoAl", *J. Inst. Met.*, **94**, 255-258 (1966) (Crys. Structure, Equi. Diagram, Experimental, 9)

[1969Bul] Bulycheva, Z.N., Kondrat'ev, V.K., Pogosov V.Z, Svezhova, S.I., "The Effect of Chromium and Cobalt on the Structure and Properties of Ordered Fe-Al Alloys" (in Russian), *Sb. Tr. Nauchno-Issled. Inst. Chern. Met*., **71**, 55-62 (1969) (Equi. Diagram, 7)

[1973Sid] Sidorenko, F.A., Kotov, A.P., Zelenin L.P., Gel'd, P.V., "Physical Properties of FeAl-CoAl Solid Solutions" (in Russian), *Fiz. Metall. Metalloved*., **35**, 218-219 (1973) (Crys. Structure, Experimental, 5)

[1982Ray] Raynor, G.V., Rivilin, V.G., "Critical Evaluation of Constitution of Aluminium-Cobalt-Iron System", *Int. Met. Rev*., **27**(3), 169-183 (1982) (Equi. Diagram, Review, 24)

[1987Miy] Miyazaki, T., Isobe, K., Kozakai T., Doi, M., "The Phase Separations of Fe-Al-Co Ordering Alloys", *Acta Metall*., **35**(2), 317-326 (1987) (Equi. Diagram, Experimental, 30)

[1991Kub] Kubaschewski, O., "Aluminium - Cerium - Iron", MSIT Ternary Evaluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), MSI, Materials Science International Services GmbH, Stuttgart; Document ID: 10.15955.1.20, (1991) (Crys. Structure, Equi. Diagram, Assessment, 15)

[1994Bur] Burkhardt, U., Grin, J., Ellner, M., Peters, K., "Structure Refinement of the Iron-Aluminium Phase with the Approximate Composition Fe_2Al_5", *Acta Crystallogr., Sect. B: Struct. Crystallogr. Crys. Chem.*, **B50**, 313-316 (1994) (Crys. Structure, Experimental, 9)

[1994Koz1] Kozakai, T., Miyazaki, T., "Experimental and Theoretical Studies on Phase Separations in the Fe-Al-Co Ordering Alloy System", *J. Mater. Sci.*, **29**(3), 652-659 (1994) (Equi. Diagram, Experimental, Calculation, 25)

[1994Koz2] Kozakai, T., Miyazaki, T., "Experimental And Theoretical Investigations on Phase Diagrams of Fe Base Ternary Ordering Alloys", *ISIJ Int.*, **34**(5), 373-383 (1994) (Equi. Diagram, Magn. Prop., 18)

[1996Bur] Burkhardt, U., Grin, J., Ellner, M., Grin, Yu., "Powder Diffraction Data for the Intermetallic Compounds Co_2Al_5, Monoclinic m-Co_4Al_{13} and Orthorhombic o-Co_4Al_{13}", *Powder Diffr*., **11**(2), 123-128, (1996) (Crys. Structure, Experimental, 23)

[1996Cha] Chadjivasiliou, S.C., Efthimiadis, K.G., Tsoukalas, I.A., Hesse, J., "Crystal Structure, Magnetization and Resistivity of 3d-Transition Metal Alloys with 10% Al Admixtures", *Mater. Res. Bull*., **31**(12), 1471-1477 (1996) (Crys. Structure, Magn. Prop., Experimental, 10)

[1996Gru] Grushko, B., Wittenberg, R., Bickmann, K., Freiburg, C., "The Constitution of Aluminium-Cobalt Alloys between Al_5Co_2 and Al_9Co_2", *J. Alloys Compd.*, **233**, 279-287 (1996) (Crys. Structure, Equi. Diagram, Experimental, 18)

[1999Koz] Kozakai, T., Okamoto, R., Miyazaki, T., "Phase Equilibria in the Fe-Al-Co Ternary System at 923 K", *Z. Metallkd*., **90**(4), 261-266 (1999) (Equi. Diagram, Experimental, #, 12)

[1999Mek] Mekhrabov, A.O., Akdeniz, M.V., "Effect of Ternary Alloying Elements Addition on Atomic Ordering Characteristics of Fe-Al Intermetallics", *Acta Mater.*, **47**(7), 2067-2075 (1999) (Calculation, Theory, Thermodyn., 63)

[2000Szy] Szymanski, K., Biernacka, M., Dobrzynski, L., Perzynska, K., Recko, K., Satula, D., Waliszewski, J., Zaleski, P., "Mössbauer and Magnetic Studies of $Fe_{3-x}Co_xAl$", *J. Magn. Magn. Mater.*, **210**, 150-162 (2000) (Moessbauer, Magn. Prop., 36)

[2001Miy] Miyazaki, T., "Computational Investigation on the Microstructure Formation in Multi-Component Alloy Systems Based on the Phase Field Method", *Calphad*, **25**(2), 231-239 (2001) (Calculation, Equi. Diagram, 15)

[2002Ohn] Ohnuma, I., Enoki, H., Ikeda, O., Kainuma, R., Ohtani, H., Sundman, B., Ishida, K., "Phase Equilibria in the Fe-Co Binary System", *Acta Mater.*, **50**, 379-393 (2002) (Equi. Diagram, Thermodyn., Experimental, Assessment, 50)

[2003Gru] Grushko, B, Cacciamani, G., "Al-Co (Aluminium - Cobalt)", MSIT Binary Evaluation Program, in *MSIT Workplace,* Effenberg, G. (Ed.), MSI, Materials Science International Services, GmbH, Stuttgart; to be published, (2003) (Equi. Diagram, Assessment, Crys. Structure, 72)

[2003Pis] Pisch, A., "Al-Fe (Aluminum-Iron)" MSIT Binary Evaluation Program, in *MSIT Workplace,* Effenberg, G. (Ed.), MSI, Materials Science International Services, GmbH, Stuttgart; to be published, (2003) (Equi. Diagram, Crys. Structure, Assessment, 58)

Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ,$Fe_{1-x-y}Co_xAl_y$	*cF*4 $Fm\bar{3}m$		
(Al) < 660.452	Cu	a = 404.96	pure Al at 25°C [Mas2]
(γCo) 1495-422		a = 354.47	pure γCo at 25°C [Mas2]
(γFe)(h1) 1394-912		a = 364.67	pure γFe at 915°C [Mas2]
(εCo) < 422	*hP*2 $P6_3/mmc$ Mg	a = 250.71 c = 406.86	at 25°C [Mas2]
α,$Fe_{1-x-y}Co_xAl_y$	*cI*2 $Im\bar{3}m$		$0 \le x \le 0.77$ at $y = 0$ $0 \le y \le 0.55$ at $x = 0$
(δFe)(h2) 1538-1394	W	a = 293.15	at 1480°C [Mas2]
(αFe)(r) < 912		a = 286.65	at 25°C [Mas2]
α',$(Fe_xAl_{1-x})(Fe_yCo_{1-y})$	*cP*2 $Pm\bar{3}m$ CsCl		$0 \le y \le 1$ at $x = 0$ [1966Rid]
CoAl < 1640		a = 286.2	50 at.% Al (from 20 to 54 at.% Al at 1400°C) [2003Gru]
FeAl < 1310		a = 290.9	50 at.% Al (from 36 at 50 at.% Al at 500°C) [2003Pis]
FeCo < 730		a = 285.71	50 at.% Co [V-C2] (from 25 to 70 at.% Co at 500°C) [2002Ohn]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Co_2Al_5 < 1188	*hP*28 *P6₃/mmc* Co_2Al_5	*a* = 767.2 *c* = 760.5	[1996Gru] [1996Bur]
O-Co_4Al_{13} < 1080	*oP*102 *Pmn2₁* O-Co_4Al_{13}	*a* = 815.8 *b* = 1234.7 *c* = 1445.2	[1996Gru] [1996Bur]
Co_2Al_9 < 970	*mP*22 *P2₁/a* Co_2Al_9	*a* = 855.65 *b* = 629.0 *c* = 621.3 β = 94.76°	[2003Gru]
Fe_3Al < 547	*cF*16 $Fm\bar{3}m$ BiF_3	*a* = 579.23	[V-C2]. Ordered $D0_3$ phase
$FeAl_2$ < 1156	*aP*18 *P1* $FeAl_2$	*a* = 487.8 *b* = 646.1 *c* = 880.0 α = 91.75° β = 73.27° γ = 96.89°	at 66.9 at.% Al [V-C2]
Fe_2Al_5 < 1169	*oC*24 *Cmcm*	*a* = 765.59 *b* = 641.54 *c* = 421.84	at 71.5 at.% Al [1994Bur]
$FeAl_3$ < 1160	*mC*102 *C2/m* $FeAl_3$	*a* = 1549.2 *b* = 807.8 *c* = 1247.1 β = 107.69°	at 76.0 at.% Al [2003Pis] Sometimes called Fe_4Al_{13} in the literature

Table 2: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Al	Co	Fe
L ⇌ (αCo) + CoAl	?	e (min)	L	~14.9	~63.5	~21.5
L ⇌ (Al) + $FeAl_3$ + Co_2Al_9	653.9	E_1	L	99.08	0.16	0.76
			(Al)	~100	~0	~0
			$FeAl_3$	?	?	?
			Co_2Al_9	81.8	18.2	~0

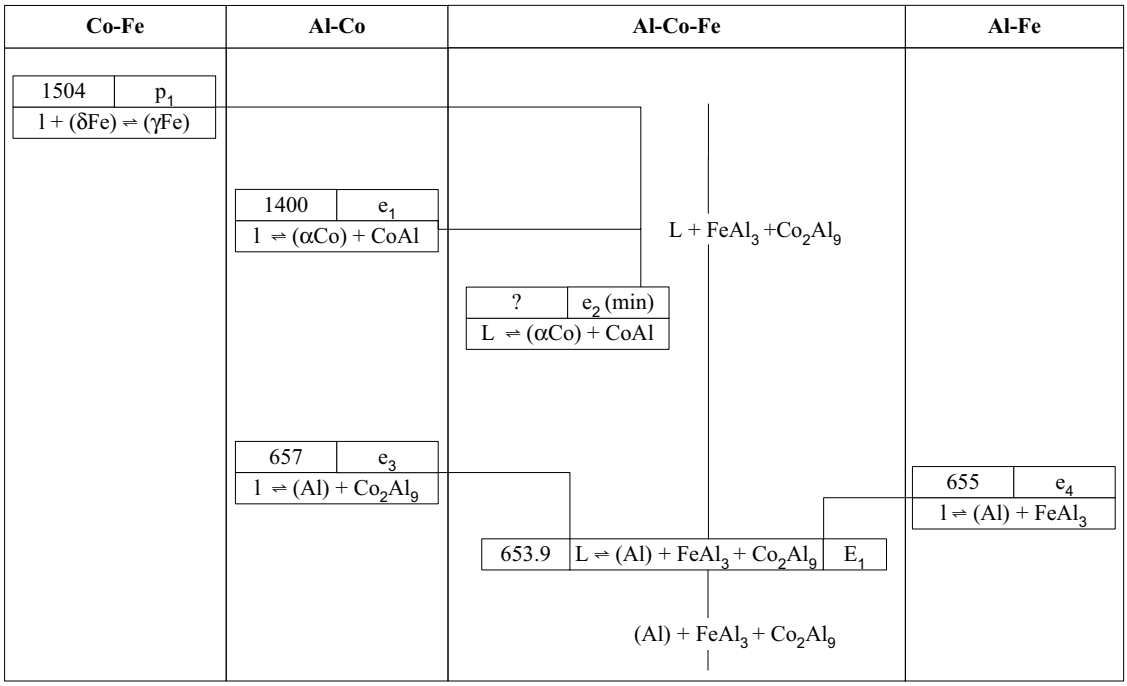

Fig. 1: Al-Co-Fe. Partial reaction scheme

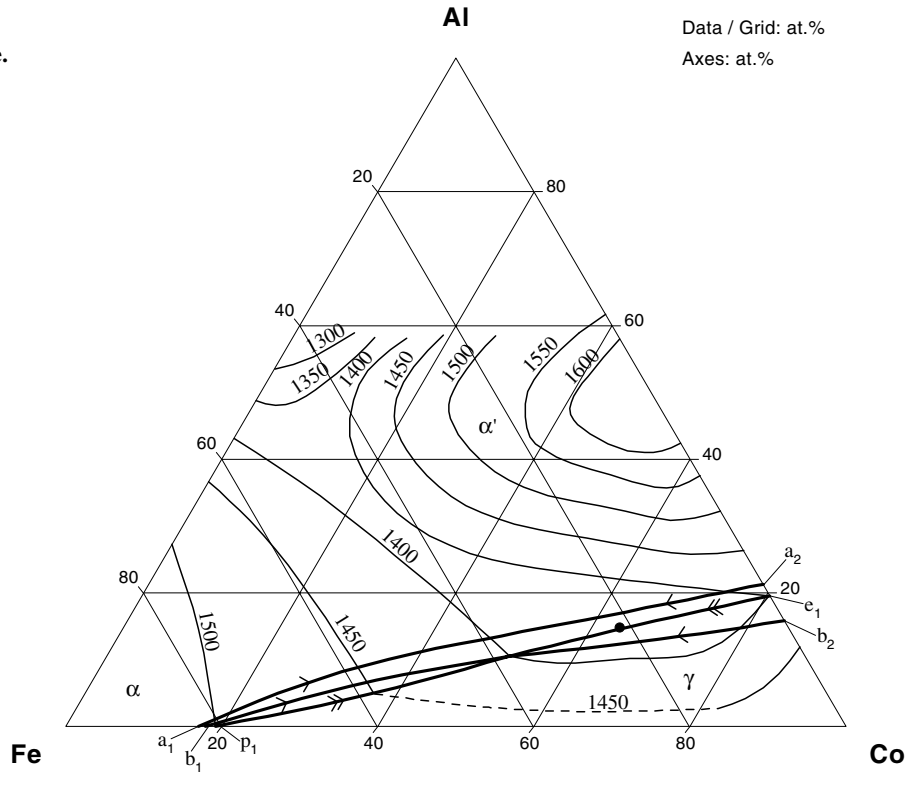

Fig. 2: Al-Co-Fe. Part of the liquidus surface

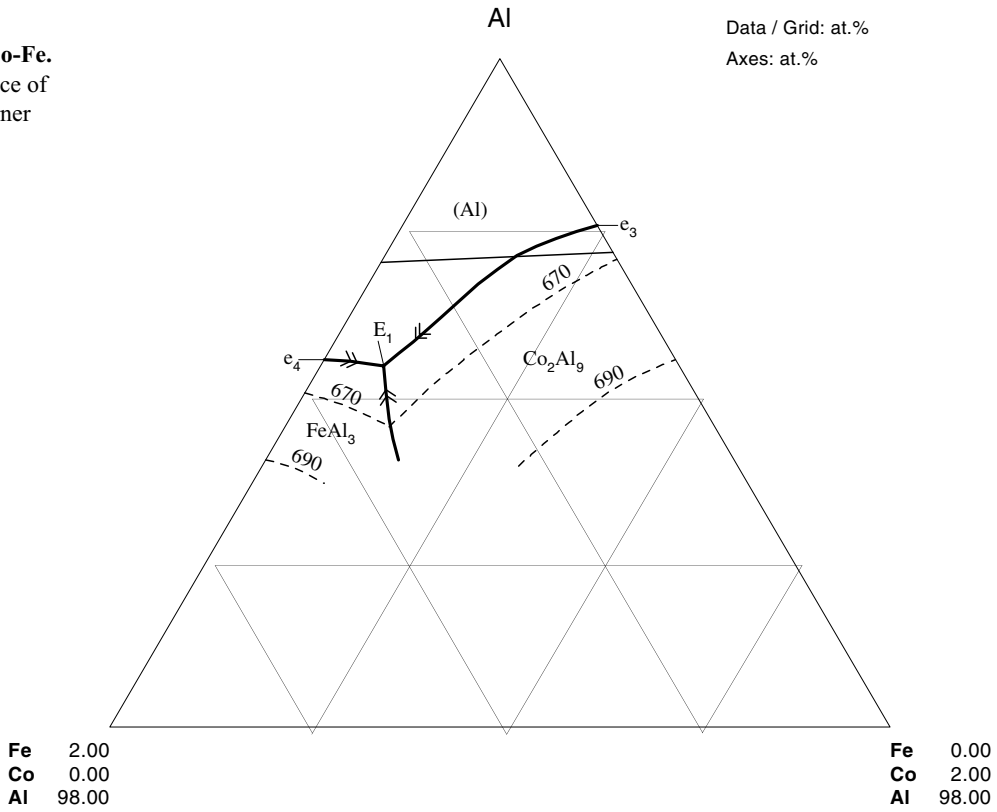

Fig. 3: Al-Co-Fe. Liquidus surface of the Al rich corner

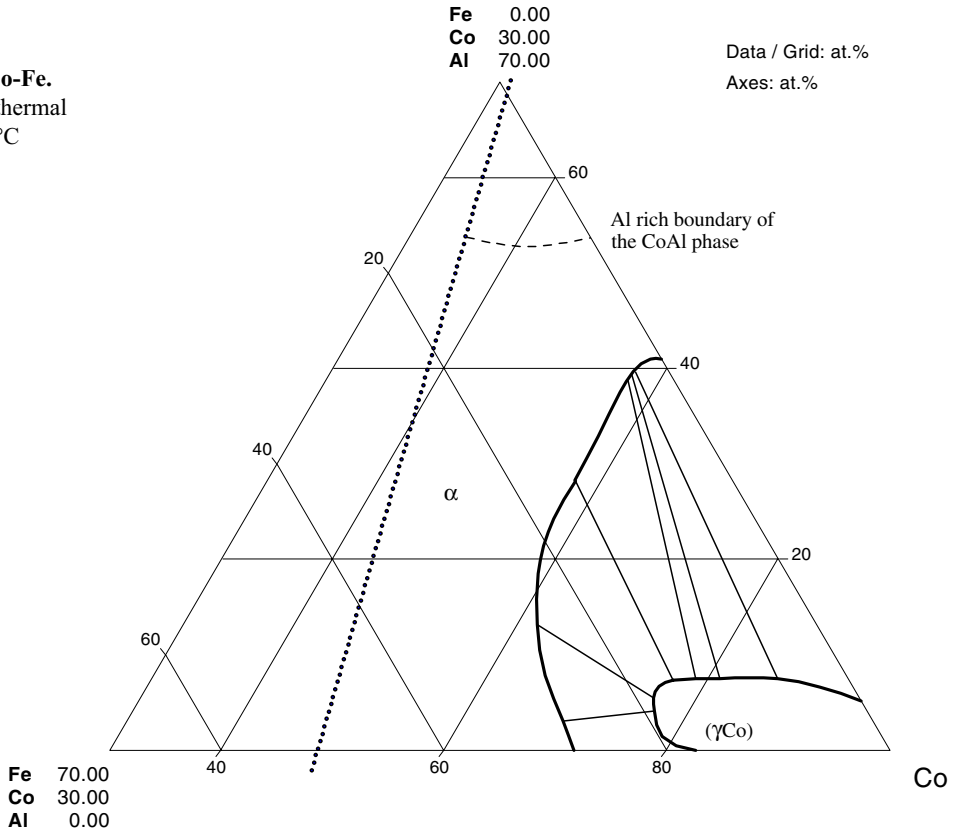

Fig. 4: Al-Co-Fe. Part of the isothermal section at 800°C

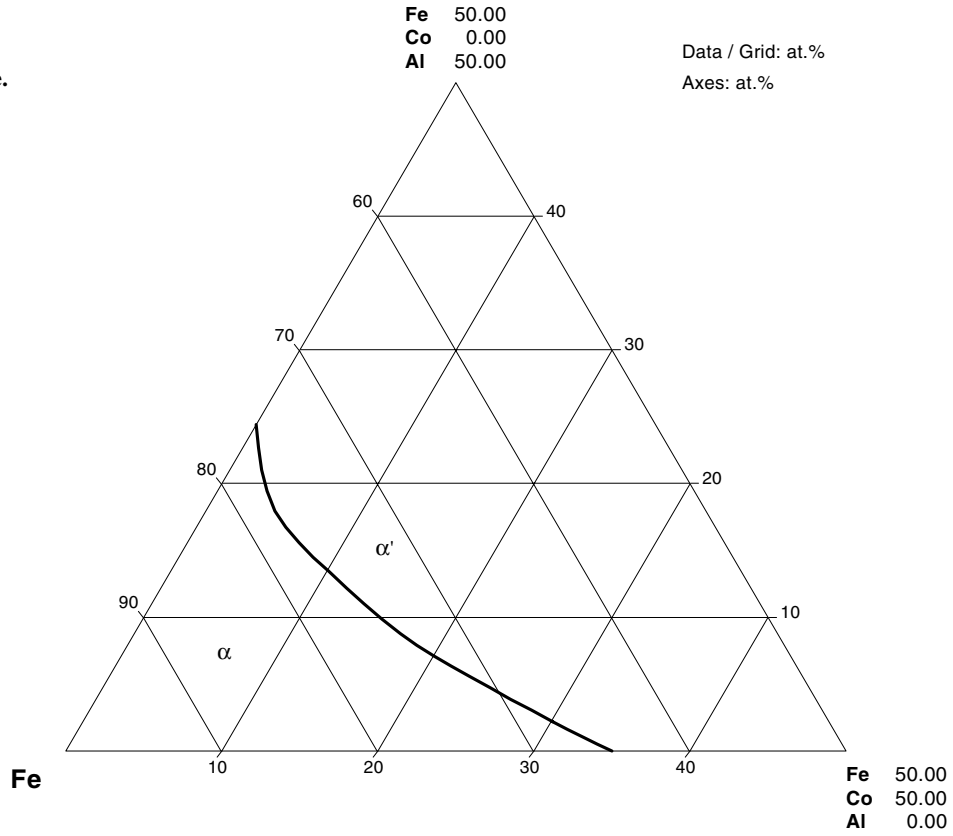

Fig. 5: Al-Co-Fe. Isothermal section (Fe-rich part) at 700°C

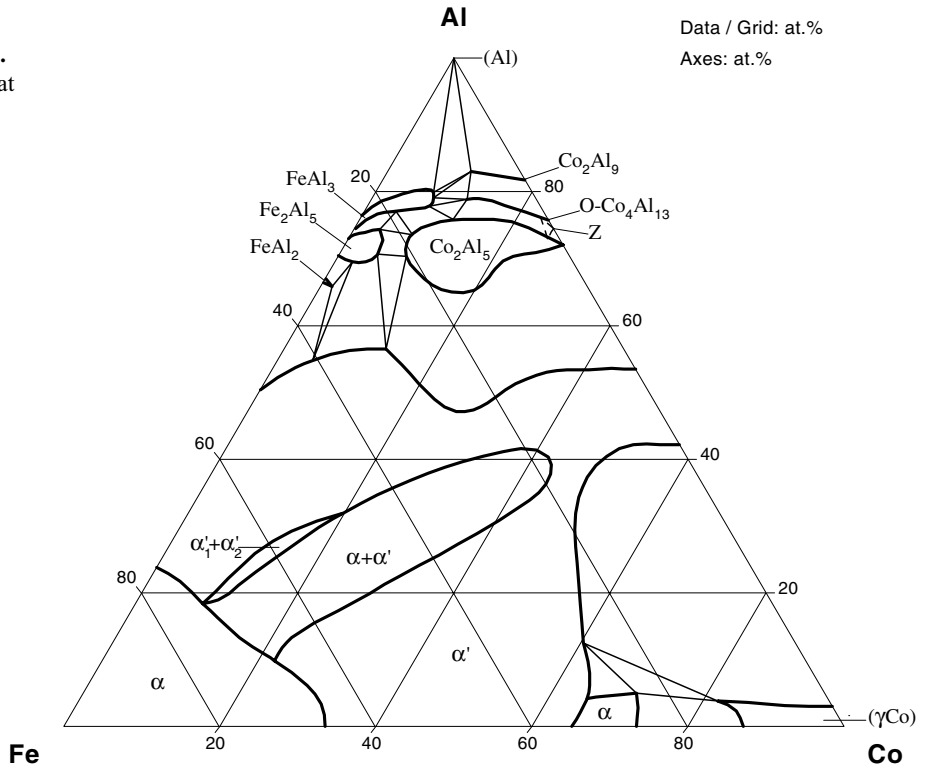

Fig. 6: Al-Co-Fe. Isothermal section at 650°C

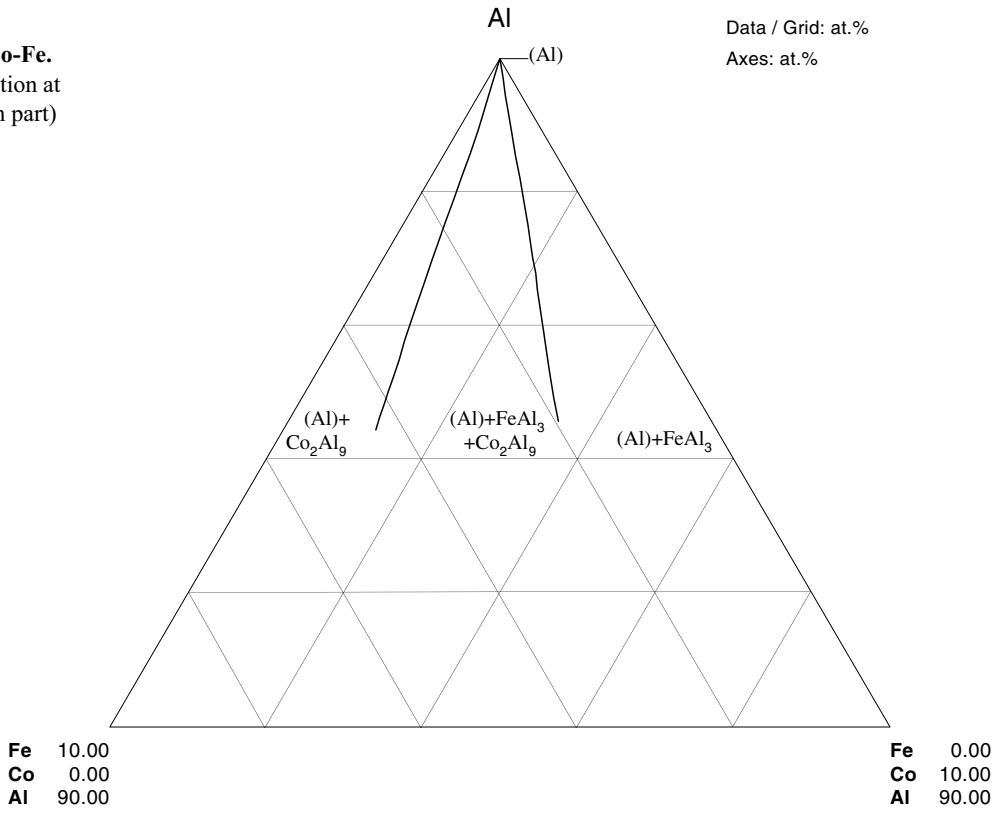

Fig. 7: Al-Co-Fe. Isothermal section at 640°C (Al-rich part)

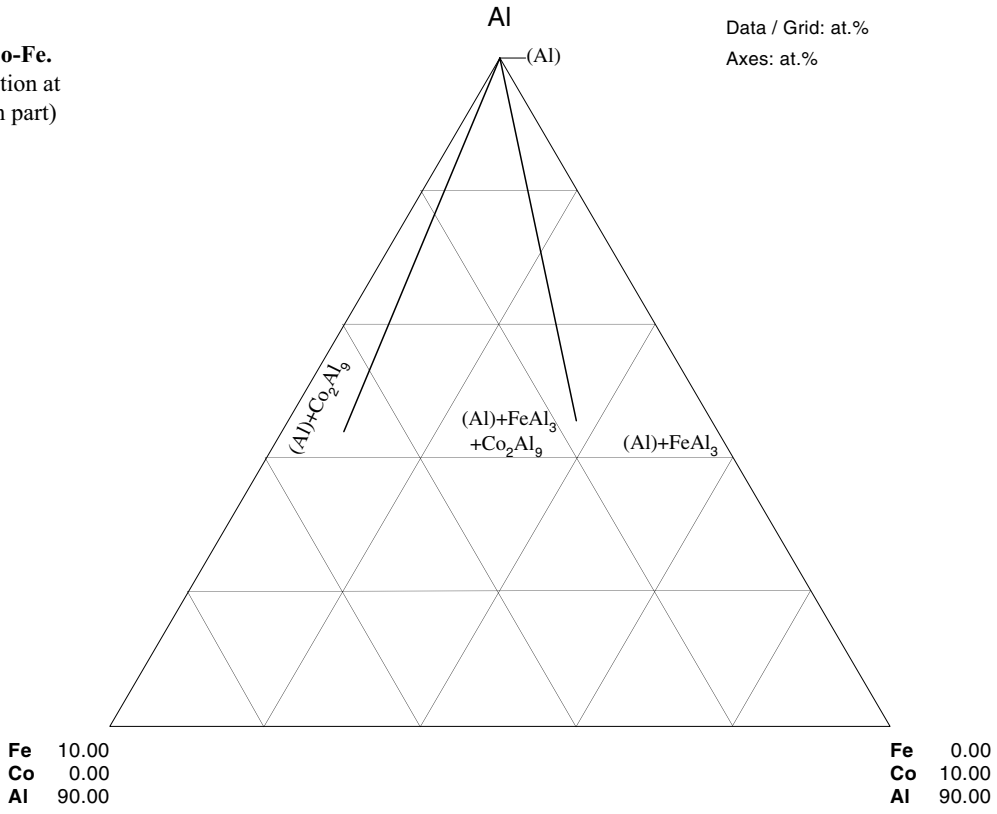

Fig. 8: Al-Co-Fe. Isothermal section at 600°C (Al-rich part)

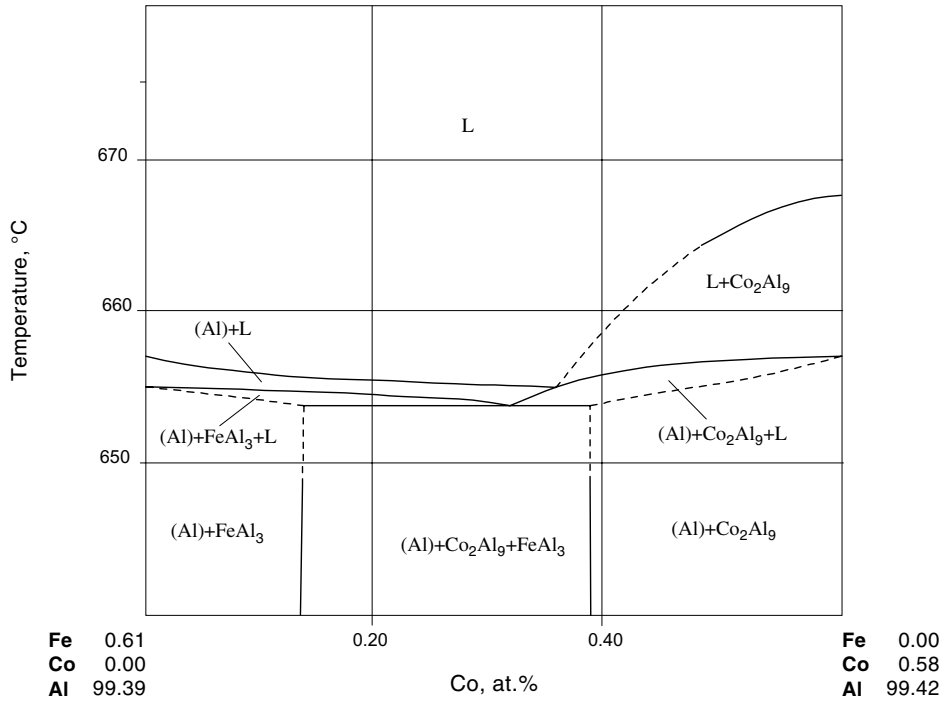

Fig. 9: Al-Co-Fe. Isopleth at 98.75 mass% Al

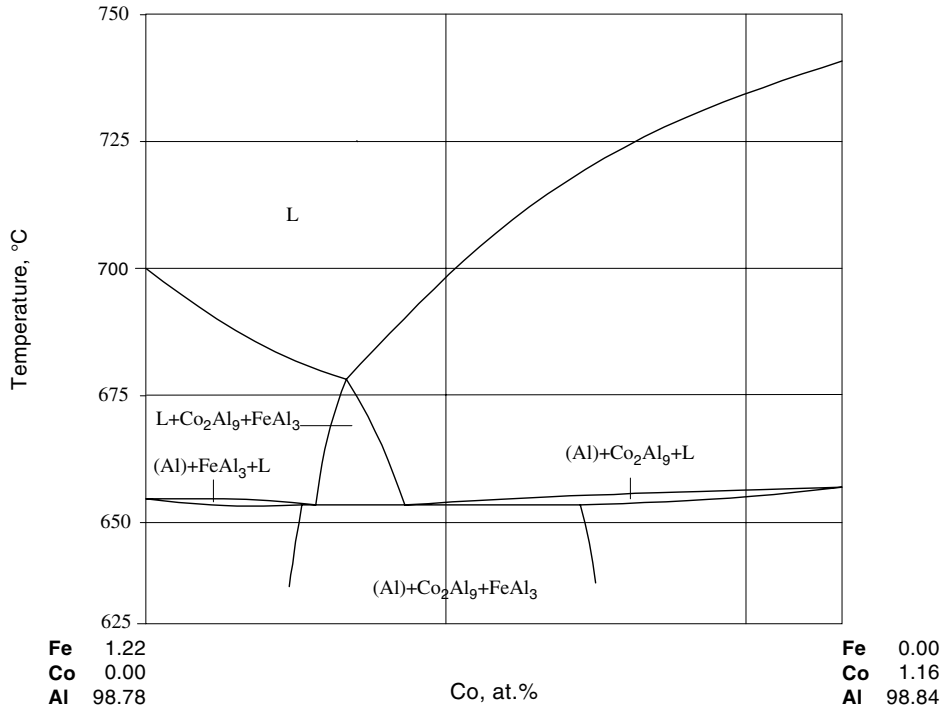

Fig. 10: Al-Co-Fe. Isopleth at 97.5 mass% Al

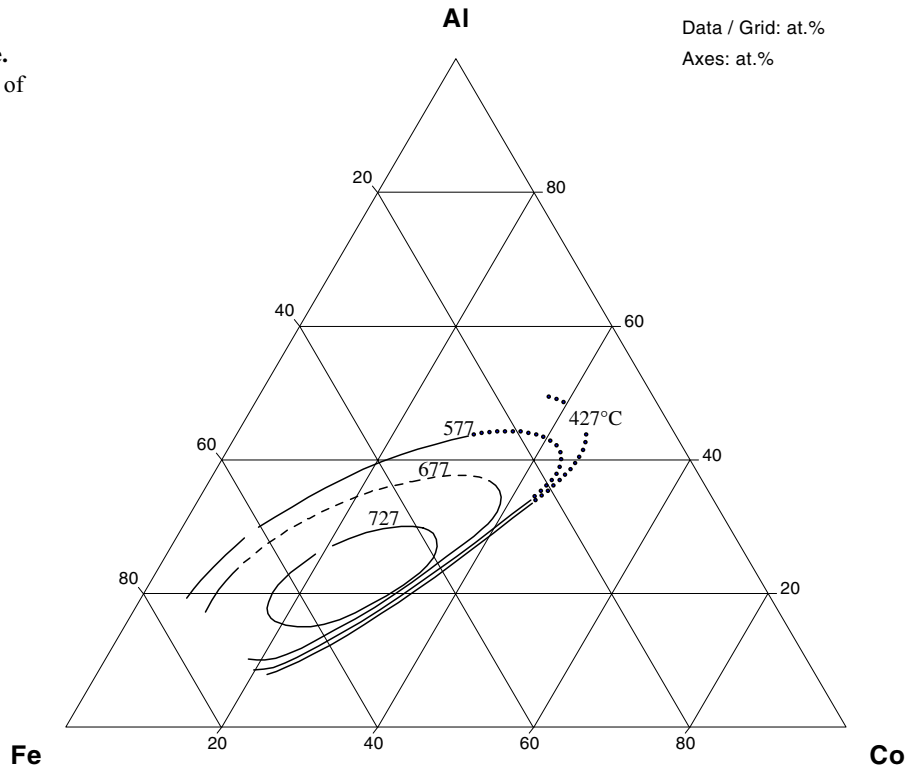

Fig. 11: Al-Co-Fe. Temperature limits of the A2 + B2 phase field