Aluminium – Cobalt – Manganese

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Literature Data

The Al-Co-Mn system was first investigated by Köster and Gebhardt [1938Koe1]. They determined seven temperature-concentration sections and constructed the liquidus surface projection as well as the reaction scheme in the region between 0 and 50 mass% Al by thermal analysis and microstructural observation. The materials they used were of technical purities: Co with 1.4 mass% Fe, Mn with 1.4 mass% Si and 0.24 mass% (S+P) and Al with 0.4 mass% (Fe+Si). The solubility limits of Mn in (Mn,Co)Al were determined by the same authors by magnetic measurement [1938Koe2]. [1942Ven] used the same methods as [1938Koe1], but with purer materials (Al 99.99%, Mn 99.9% and Co 99.1%) and established liquidus isotherms and the liquidus surface projection in the Al-corner at compositions of more than 90 mass% Al. [1944Ray] reported small solubility of Co in $MnAl_6$ by microstructural analysis. [1947Ray] presented the results of thermal analysis and metallographic observation along three vertical sections and three isothermal sections, which are in the composition range 0 to 5.6 mass% Mn and 0 to 4.0 mass% Co. The alloys were prepared from superpure aluminium, aluminium manganese master alloy and aluminium cobalt master alloy; the impurity levels of the last two alloys being about 0.01 to 0.02 mass%. Using electrolytic Mn and Co (both 99.9%) and pure Al, [1962Tsu] constructed a partial isothermal section at 900°C using the results of magnetic measurements but the concentration scale was uncertain. Based on earlier work, using newer versions of the binary boundary systems and pure materials (99.9% Co, 99.99% Mn and 99.99% Al), Gödecke and Köster [1972Goe] performed a comprehensive study of the system using thermal analysis and metallography. The experimental details were not given. Apart from [1938Koe1] and [1942Ven], the above works agree well or complement each other. However, more recent studies by [1998Kai] indicate that the phase equilibria in the ternary system are more complex. Previous studies had assumed a continuous solid solution between the CoAl (B2) phase and the (δMn) (A2) phase. [1998Kai] prepared diffusion couples that were annealed in sealed quartz tubes at temperatures between 1000 and 1200°C. Using EDS, the critical compositions of the A2/B2ordering transition between the two phases were determined from concentration-penetration curves. They found that both a continuous and a discontinuous transition from A2 to B2 exists between the two phases, resulting in the presence of an A2+B2 region at certain compositions and temperatures. Isothermal sections for Al contents less than 50 mole % at 1000, 1050, 1100 and 1200°C and an isopleth between CoAl-Mn were presented. Several works [1962Tsu, 1971Web, 1981Sol1, 1981Sol2, 1983Kue] contributed to the crystal structure of the Heusler alloy $MnCo_2Al$.

Binary Systems

The Al-Co and Al-Mn binary systems were taken from the MSIT binary evaluation programme, [2003Gru, 2003Pis]. The Co-Mn system was accepted from [Mas2].

Solid Phases

Solid phases are presented in Table 1. These include a ternary phase $Mn_2Co_4Al_{62}$ (τ) having a small homogeneity range [1972Goe]. [1972Goe] had suggested a continuous solid solution between CoAl, γ and (δMn) at temperatures greater than 1000°C. However, as CoAl is ordered there must be an order/disorder transition between CoAl and MnAl and (δMn) somewhere in the ternary. Such a reaction was discovered by [1998Kai], between CoAl and (δMn), but there should also be one between CoAl and MnAl. [1981Sol2] reports the occurrence of order-disorder transformations in the Heusler alloy $MnCo_2Al$:
*cF*16 --- (990°C) --- *cP*2 ----(1250°C) ---- *cI*2
However, this would not be consistent with the work of [1972Goe] and [1998Kai], where it is suggested that this composition would most likely result in a two-phase mixture of (γCo) and the *cP*2 β phase. The

Curie temperature of the $MnCo_2Al$ alloy was measured to be ~422°C [1983Kue, 1971Web]. A small solubility of Co in $MnAl_6$ was reported by [1944Ray].

Pseudobinary Systems

The CoAl-Mn section was reported to be pseudobinary by [1938Koe1]. However, this was found not to be the case by [1972Goe] and [1998Kai].

Invariant Equilibria

A reaction scheme was constructed by [1972Goe] (Fig. 1). Details of the invariant points are listed in Table 2. In order to distinguish between the ordered and disordered variants of the δ phase, the ordered CoAl based phase is given as δ'. Also, in order to differentiate between the reactions involving the (δMn) and $Mn_{55}Al_{45}$ phases in the Al-Mn binary, these phases have been designated as δ_1 and δ_2, respectively.

Liquidus Surface

A liquidus surface was constructed by [1972Goe] and is given in Fig. 2. Figure 3 shows an enlarged Al-rich portion of the liquidus surface.

Isothermal Sections

Isothermal sections for 500, 800 and 900°C are given in Figs. 4-6 taken from [1972Goe]. Figures 7 and 9 show composite isothermal sections for 1000 and 1100°C taken from the work of [1972Goe] for Al contents greater than 50 mole%, and from [1998Kai] for Al contents less than 50 mole%. Figures 8 and 10 show partial isothermal sections for 1050 and 1200°C, respectively, for Al contents less than 50 mole%, taken from [1998Kai]. In all cases, slight adjustments have been made to make the sections consistent with the accepted binary phase diagrams. It should be noted that [1972Goe] did not distinguish between the M- and O- modifications of Co_4Al_{13}, and hence they appear in the diagrams as the same phase.

Temperature – Composition Sections

Figures 11-15 show isopleths for 25, 40, 70, 85 and 95 mass% Al, respectively, taken from [1972Goe]. A section at 45 mass% Mn was also presented by [1972Goe], but was found to be incompatible with [1998Kai], hence, it is omitted here. Figure 16 shows the vertical section from CoAl-Mn taken from [1998Kai]. Vertical sections were presented in [1938Koe1, 1947Ray, 1978Urs] but were found to be incompatible with the above.

Notes on Materials Properties and Applications

On investigating the use of thin films of $Mn_{60}Al_{40}$ as a recording medium, it was found that substituting Mn with Co increased the saturation magnetization by a factor of up to 2 for $Mn_{55}Co_5Al_{40}$ [1991Mat].

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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
(αAl) < 660.452	*cF*4 $Fm\bar{3}m$ Cu	a = 404.96	at 25°C [Mas2] Dissolves 0.62 at.% Mn at 658.5°C
(βAl)	*hP*2 $P6_3/mmc$ Mg	a = 269.3 c = 439.8	at 25°C, 20.5 GPa [Mas2]
(γCo)(h) 1495-422	*cF*4 $Fm\bar{3}m$ Cu	a = 354.46	[V-C2]. Dissolves 59.4 at.% Mn at 1161°C and ~17 at.% Al at 1400°C
(εCo)(r) < 422	*hP*2 $P6_3/mmc$ Mg	a = 250.71 c = 406.95	[V-C2, Mas2]
(γMn) 1138-1100	*cF*4 $Fm\bar{3}m$ Cu	a = 386.2	[Mas2]. Dissolves ~4.5 at.% Co 1145°C and 9.33 at.% Al at 1073°C.
(βMn) 1100-727	*cP*20 $P4_132$ βMn	a = 631.52	[Mas2]. Dissolves 45 at.% Co at 546°C and 41.79 at.% Al at 840°C
(αMn) < 727	*cI*58 $I\bar{3}m$ αMn	a = 891.26	at 25°C [Mas2].
δ, $(Mn_{1-y},Co_y)_{1-x}Al_x$			
(δMn) 1246-840 $Mn_{55}Al_{45}$ < 1177	*cI*2 $Im\bar{3}m$ W	a = 308.0 a = 306.3	[Mas2]. Dissolves ~8 at.% Co at 1188°C and 31.91 at.% Al at 1275°C [V-C2]. Dissolves 65 at.% Al at 1048°C, 46 at.% Al at 870°C. ~0.2 < x < 0.537 for y = 1
δ', CoAl < 1640°C	*cP*2 $Pm\bar{3}m$ CsCl	a = 286.2	at x = 0.5, y = 1 [1966Rid]
Co_2Al_5 <1188	*hP*28 $P6_3/mmc$ Co_2Al_5	a = 767.2 c = 760.5	[1996Gru] [1996Bur]
O-Co_4Al_{13} < 1080	*oP*102 $Pmn2_1$ O-Co_4Al_{13}	a = 815.8 b = 1234.7 c = 1445.2	[1996Gru] [1996Bur]
M-Co_4Al_{13} 1093-?	*mC*102 *C*2/*m* Fe_4Al_{13}	a = 1517.3 b = 810.9 c = 1234.9 β = 107.84°	[1996Fre]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Z, $CoAl_3$ < 1158	*mC**	*a* = 3984.0 *b* = 814.8 *c* = 3223.0 β = 107.97°	[1998Mo] often designated τ_2-Co_4Al_{13}.
Co_2Al_9	*mP*22 $P12_1/c1$ Co_2Al_9	*a* = 855.65 *b* = 629.0 *c* = 621.3 β = 94.76°	[V-C2]
$MnAl_{12}$	*cI*26 $Im\bar{3}$ Wal_{12}	*a* = 747	[V-C2]
$MnAl_6$ < 705	*oC*28 *Cmcm* $MnAl_6$	*a* = 755.51 *b* = 649.94 *c* = 887.24	[V-C2]
λ, $MnAl_4$ < 693	*hP*586 $P6_3/m$	*a* = 2838.2 *c* = 1238.9	[2003Pis] space group does not fit 100%, probably $P6_3$
μ, $MnAl_4$ < 923	*hP*574 $P6_3/mmc$ $MnAl_4$	*a* = 1998 *b* = 2467.3 *c* = 1389.7	[2003Pis]
Mn_4Al_{11}(h) 1002 - 916	*oP*160 *Pnma*	?	[2003Pis]
Mn_4Al_{11}(r) < 916	*aP*30 $P\bar{1}$ Mn_4Al_{11}	*a* = 509.5 ± 0.4 *b* = 887.9 ± 0.8 *c* = 505.1 ± 0.4 α = 89.35 ± 4° β = 100.47 ± 5° γ = 105.08 ± 6°	[V-C2]
γ_1, ≈$MnAl_2$ < 1048		?	[2003Pis]
γ_2, Mn_5Al_8 < 991	*hR*26 $R\bar{3}m$ Cr_5Al_8	*a* = 1273.9 *c* = 1586.1	at 58 at.% Al [V-C2]
ε, Mn_3Al_2 < 1312	*hP*2 $P6_3/mmc$ Mg	*a* = 270.5 to 270.5 *c* = 436.1 to 438	44.2 - 44.9 at.% Al [2003Pis]
MnCo < 545°C	*cI*58 $I\bar{3}m$ αMn	*a* = 628.1	[V-C2]
*τ, $Mn_{12}Co_4Al_{62}$	*oC*156 *Cmcm* $Mn_{12}Ni_4Al_{62}$	?	[1972Goe]

Table 2: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Al	Co	Mn
L + (γCo) ⇌ δ' + (βMn)	1152	U_1	L	8.0	32.2	59.8
			(γCo)	3.1	39.2	57.7
			δ'	12.7	36.8	50.5
			(βMn)	2.5	36.7	60.8
L + Z ⇌ Co_2Al_5 + Co_4Al_{13}	~1090	U_2	L	78.5	15.4	6.1
			Z	74.3	25.1	0.6
			Co_2Al_5	71.8	26.2	2.0
			Co_4Al_{13}	76.5	21.9	1.6
L + δ ⇌ Co_2Al_5 + Mn_4Al_{11}(h)	1038	U_3	L	69.1	6.7	24.2
			δ	53.0	18.7	28.3
			Co_2Al_5	66.9	15.0	18.1
			Mn_4Al_{11}(h)	62.0	9.7	28.3
L + $MnAl_2$ ⇌ Mn_4Al_{11}(h)+ Co_2Al_5	990	U_4	L	78.8	1.1	20.1
			$MnAl_2$	69.8	2.1	28.1
			Mn_4Al_{11}(h)	73.0	0.3	26.7
			Co_2Al_5	72.3	3.6	24.1
δ + Mn_4Al_{11}(h) ⇌ Co_2Al_5 + Mn_4Al_{11}(r)	980	U_5	δ	50.8	20.1	29.1
			Mn_4Al_{11}(h)	62.9	8.0	29.1
			Co_2Al_5	67.8	15.5	16.7
			Mn_4Al_{11}(r)	59.0	10.9	30.1
$MnAl_2$ ⇌ Mn_4Al_{11}(h) + Mn_4Al_{11}(r) + Co_2Al_5	~935	E_1	$MnAl_2$	68.5	2.1	29.4
			Mn_4Al_{11}(h)	72.2	0.6	27.2
			Mn_4Al_{11}(r)	66.3	1.8	31.9
			Co_2Al_5	71.2	6.3	22.5
L + Mn_4Al_{11}(h) ⇌ μ$MnAl_4$ + Co_2Al_5	920	U_6	L	85.3	0.5	14.2
			Mn_4Al_{11}(h)	76.1	0.4	23.5
			μ$MnAl_4$	79.5	0.3	20.2
			Co_2Al_5	78.8	1.3	19.9
Mn_4Al_{11}(h) + μ$MnAl_4$ ⇌ Co_2Al_5 + Mn_4Al_{11}(r)	908	U_7	Mn_4Al_{11}(h)	74.2	0.9	24.9
			μ$MnAl_4$	79.1	0.1	20.8
			Co_2Al_5	77.3	1.4	21.3
			Mn_4Al_{11}(r)	73.8	0.3	25.9
L + Co_2Al_5 + μ$MnAl_4$ ⇌ τ	895	P_1	L	89.1	0.7	10.2
			Co_2Al_5	78.4	1.7	19.9
			μ$MnAl_4$	79.6	0.2	20.2
			τ	79.5	1.1	19.4
L + Co_2Al_5 ⇌ τ + Co_4Al_{13}	877	U_8	L	90.6	1.3	8.1
			Co_2Al_5	76.4	4.6	19.0
			τ	78.9	2.2	18.9
			Co_4Al_{13}	76.9	7.7	15.4
Mn_4Al_{11}(h) ⇌ Co_2Al_5 + Mn_4Al_{11}(r) + Mn_5Al_8	868	E_2	Mn_4Al_{11}(h)	73.0	0.6	26.4
			Co_2Al_5	73.1	3.5	23.3
			Mn_4Al_{11}(r)	73.8	0.2	26.0
			Mn_5Al_8	68.0	0.4	31.6

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Al	Co	Mn
$L + Co_4Al_{13} \rightleftharpoons \tau + Co_2Al_9$	770	U_9	L	96.2	1.0	2.8
			Co_4Al_{13}	76.0	12.8	11.2
			τ	78.9	2.8	18.3
			Co_2Al_9	81.5	17.6	0.9
$L + \mu MnAl_4 \rightleftharpoons \tau + MnAl_6$	698	U_{10}	L	98.0	0.3	1.7
			$\mu MnAl_4$	79.8	0.6	19.6
			τ	78.9	3.4	17.7
			$MnAl_6$	85.3	0.2	14.5
$L + \tau \rightleftharpoons MnAl_6 + Co_2Al_9$	680	U_{11}	L	98.3	0.5	1.2
			τ	78.6	3.9	17.5
			$MnAl_6$	85.3	0.2	14.5
			Co_2Al_9	81.9	17.2	0.9
$L \rightleftharpoons (Al) + MnAl_6 + Co_2Al_9$	652	E_3	L	98.5	0.7	0.8
			(Al)	99.4	0.2	0.4
			$MnAl_6$	85.3	0.2	14.5
			Co_2Al_9	81.5	17.6	0.9

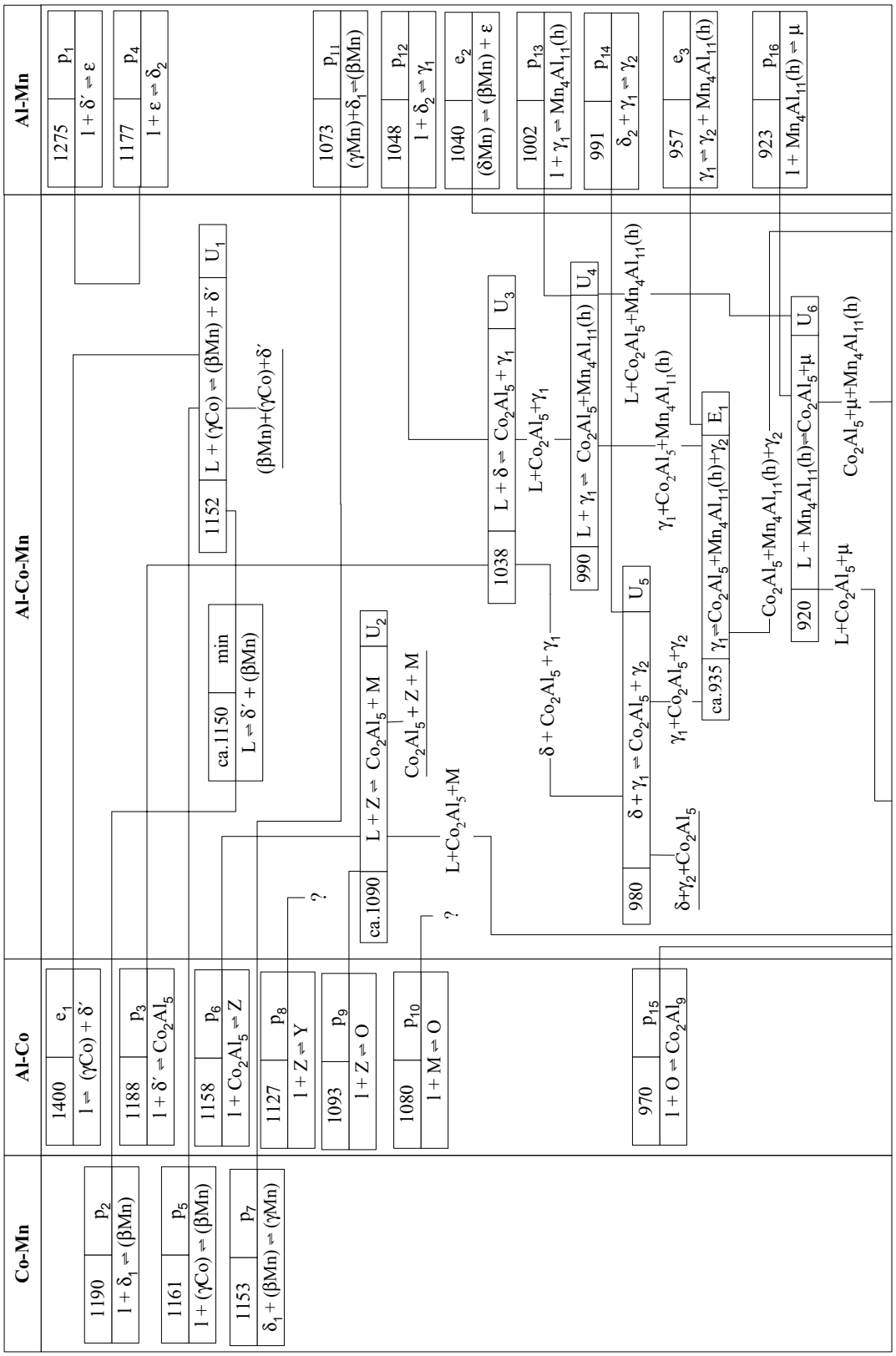

Fig. 1a: Al-Co-Mn. Reaction scheme, part 1

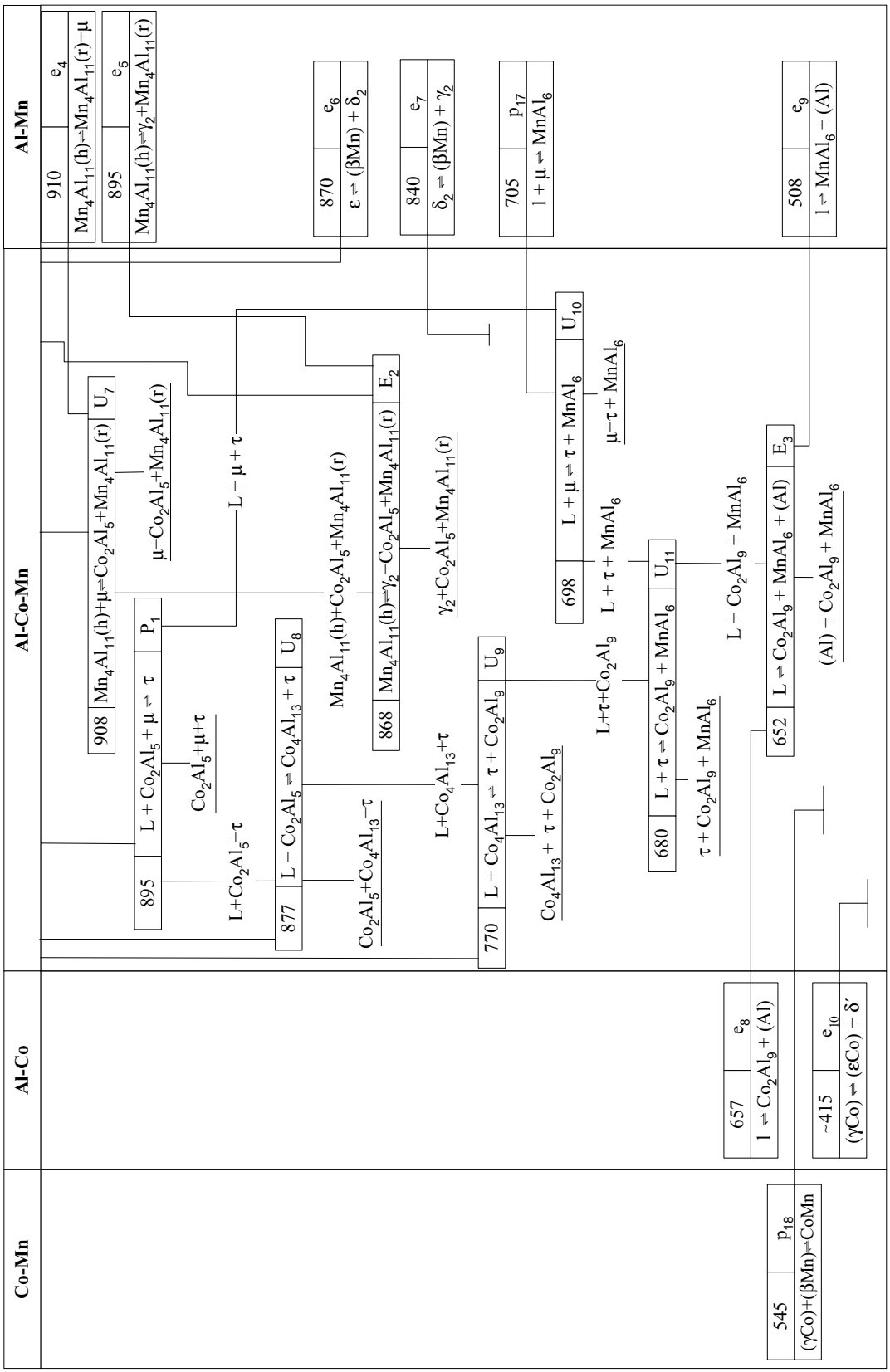

Fig. 1b: Al-Co-Mn. Reaction scheme, part 2

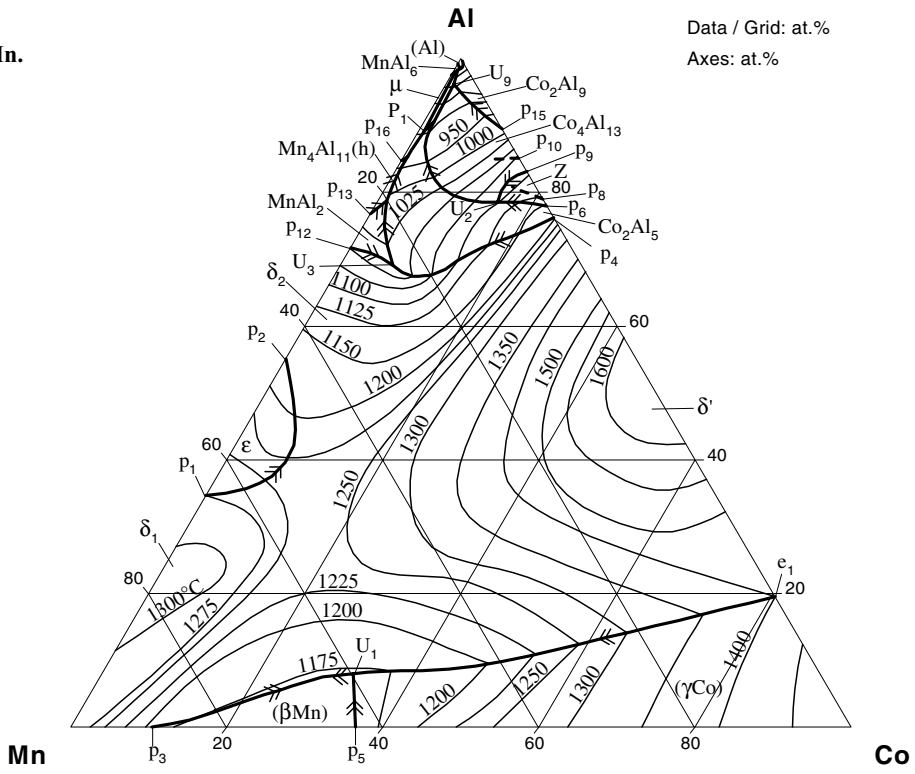

Fig. 2: Al-Co-Mn. Liquidus surface

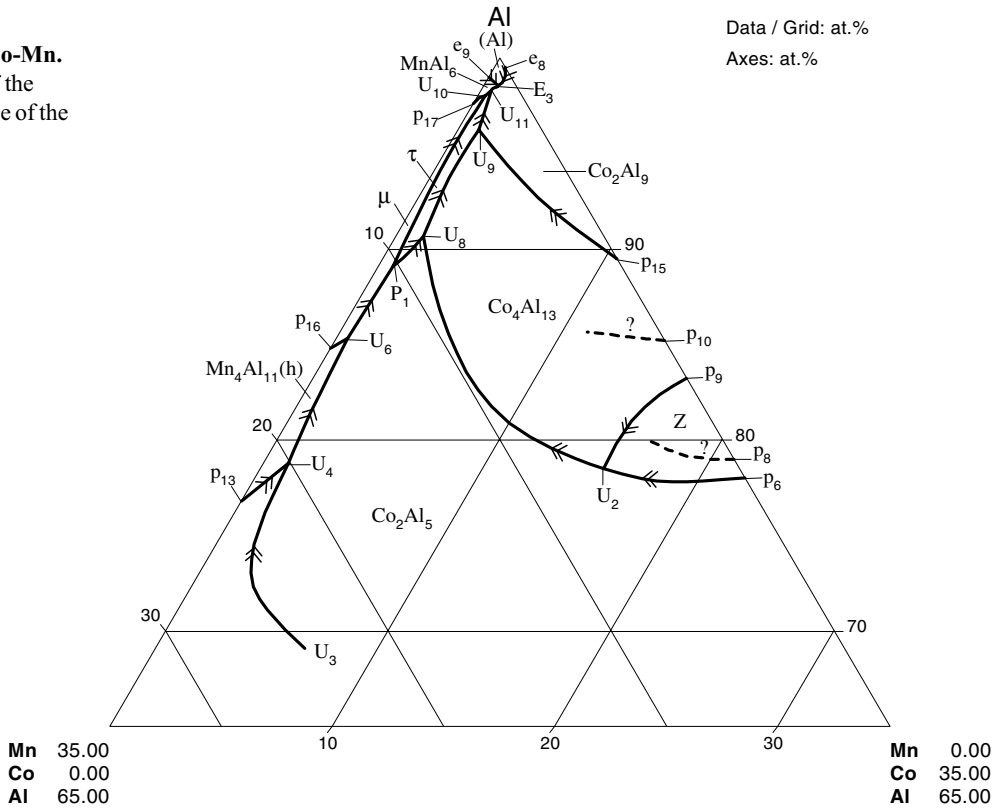

Fig. 3: Al-Co-Mn. Enlargment of the liquidus surface of the Al-rich corner

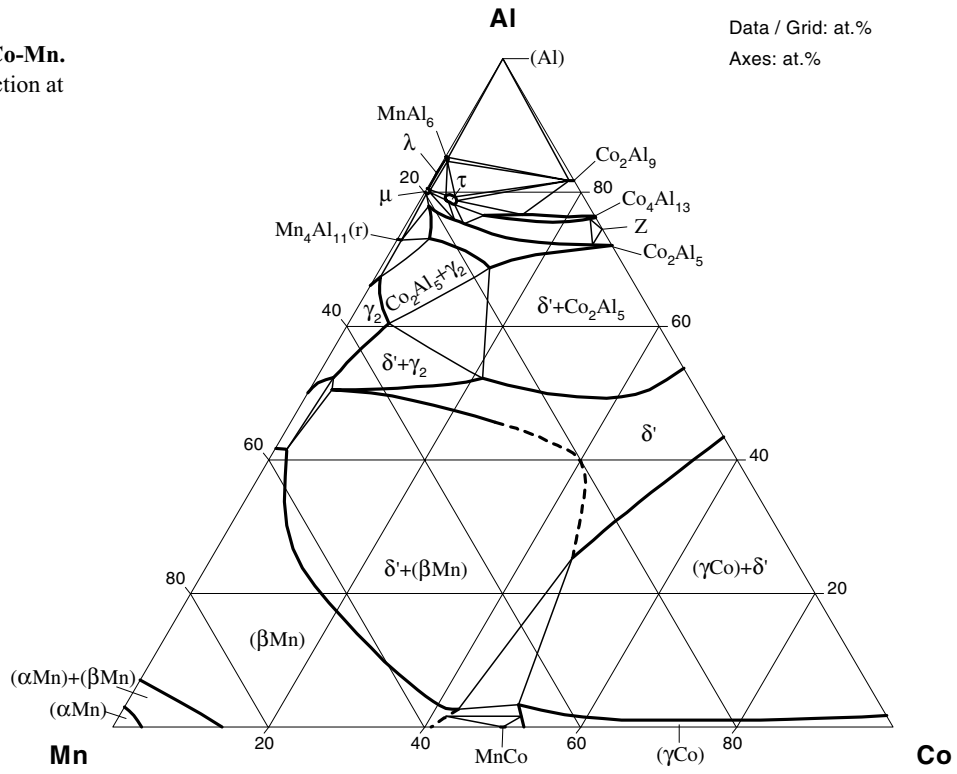

Fig. 4: Al-Co-Mn. Isothermal section at 500°C

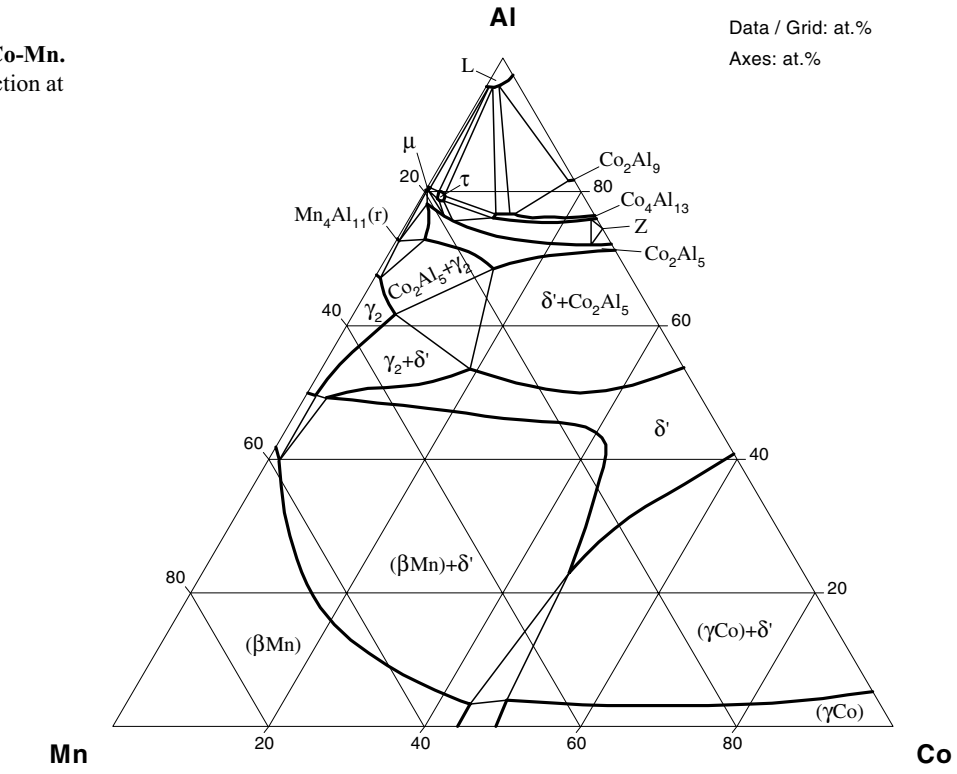

Fig. 5: Al-Co-Mn. Isothermal section at 800°C

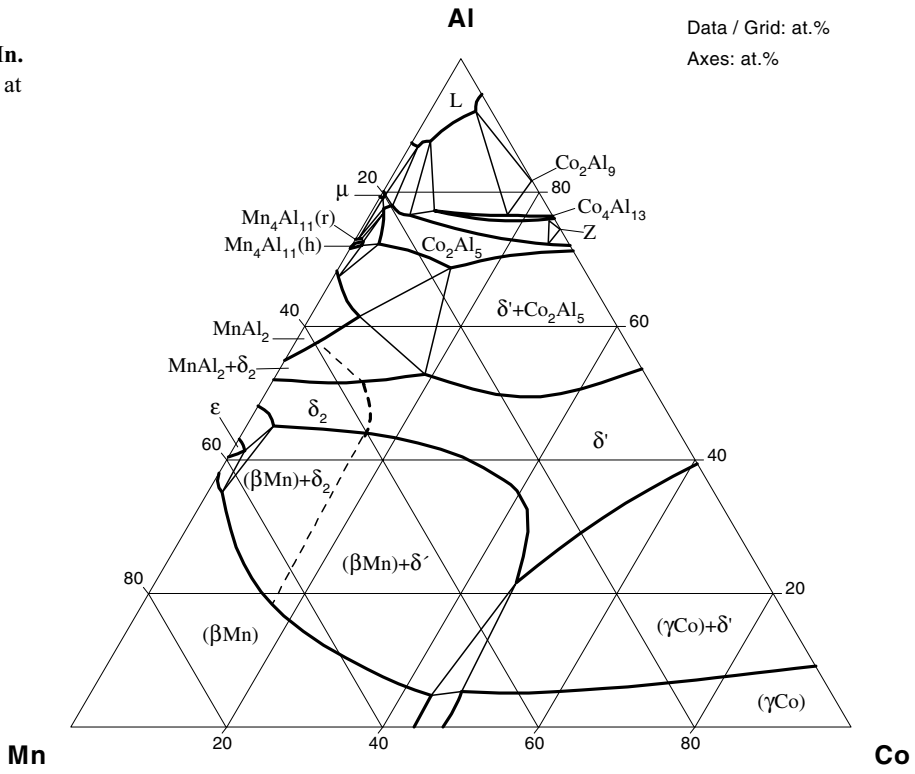

Fig. 6: Al-Co-Mn. Isothermal section at 900°C

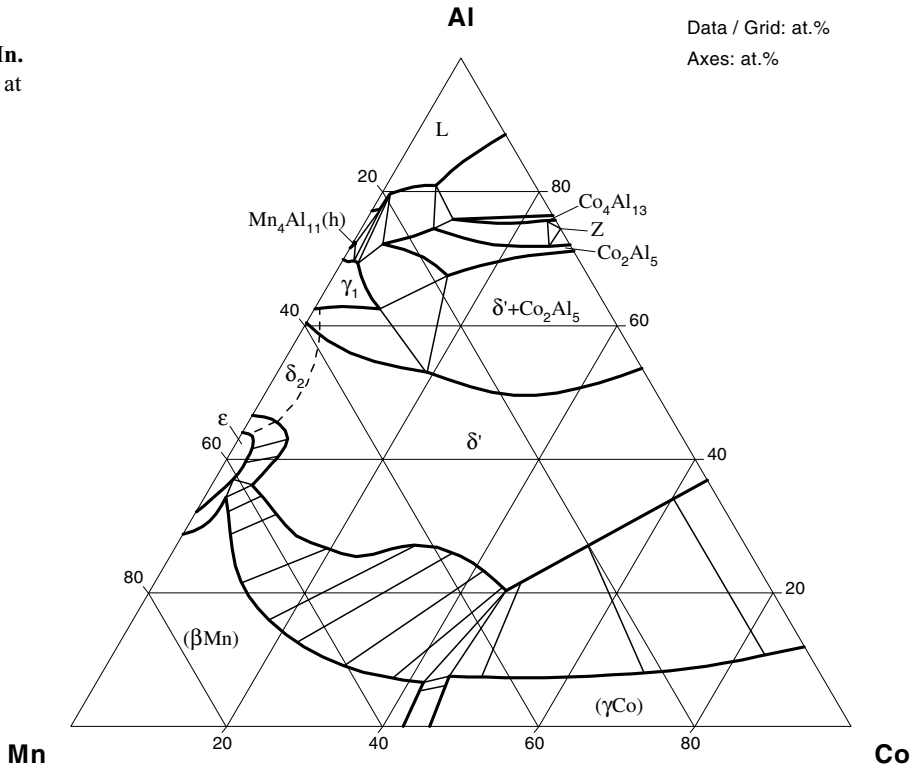

Fig. 7: Al-Co-Mn. Isothermal section at 1000°C

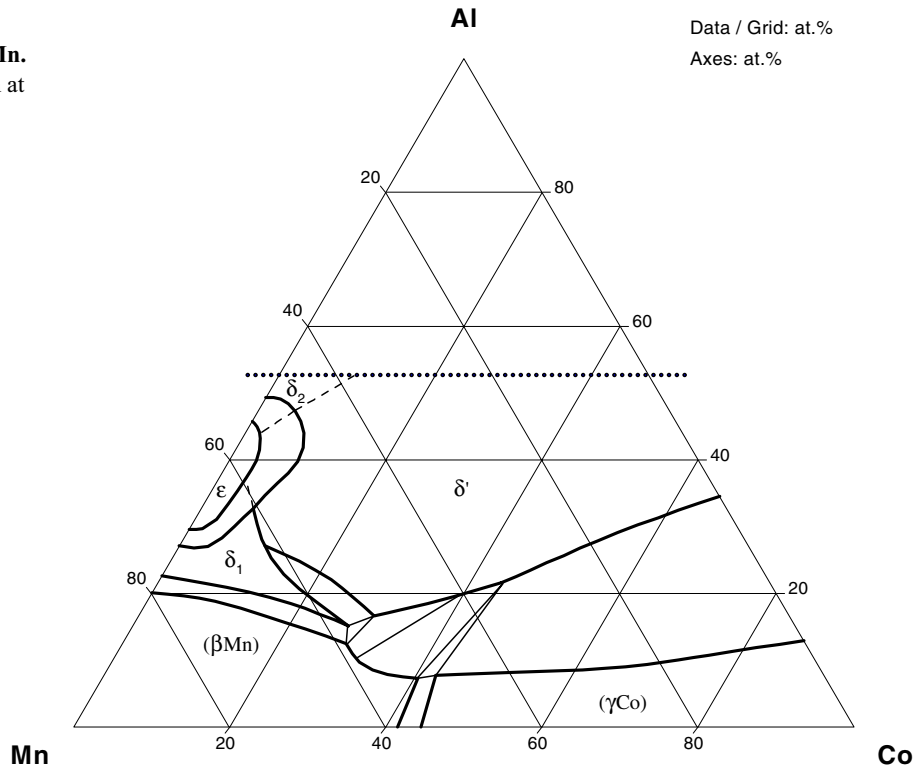

Fig. 8: Al-Co-Mn. Isothermal section at 1050°C

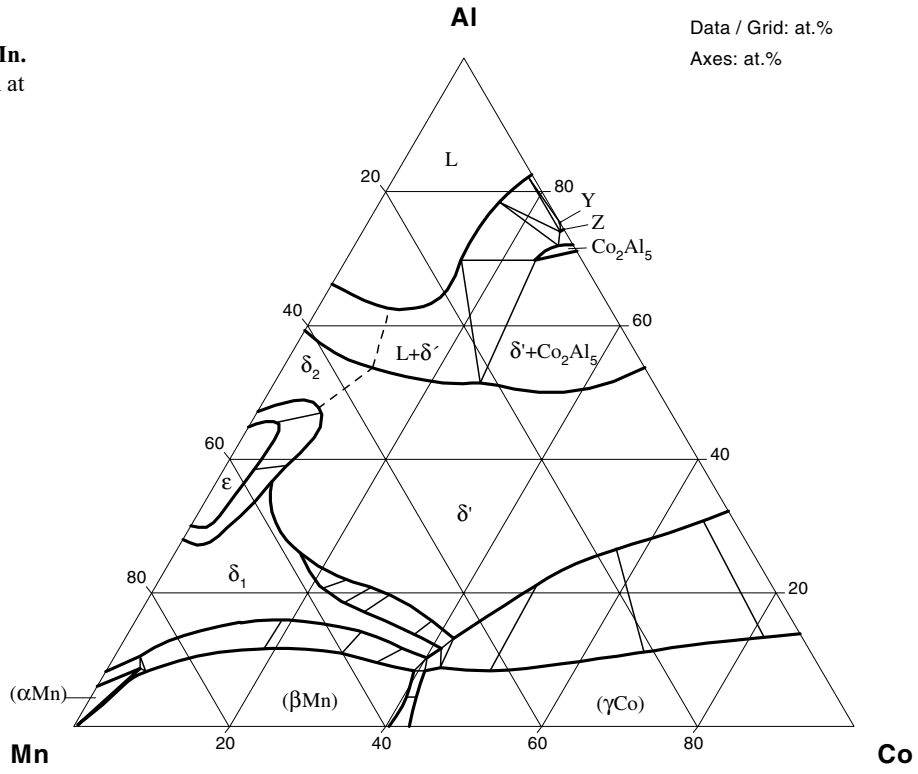

Fig. 9: Al-Co-Mn. Isothermal section at 1100°C

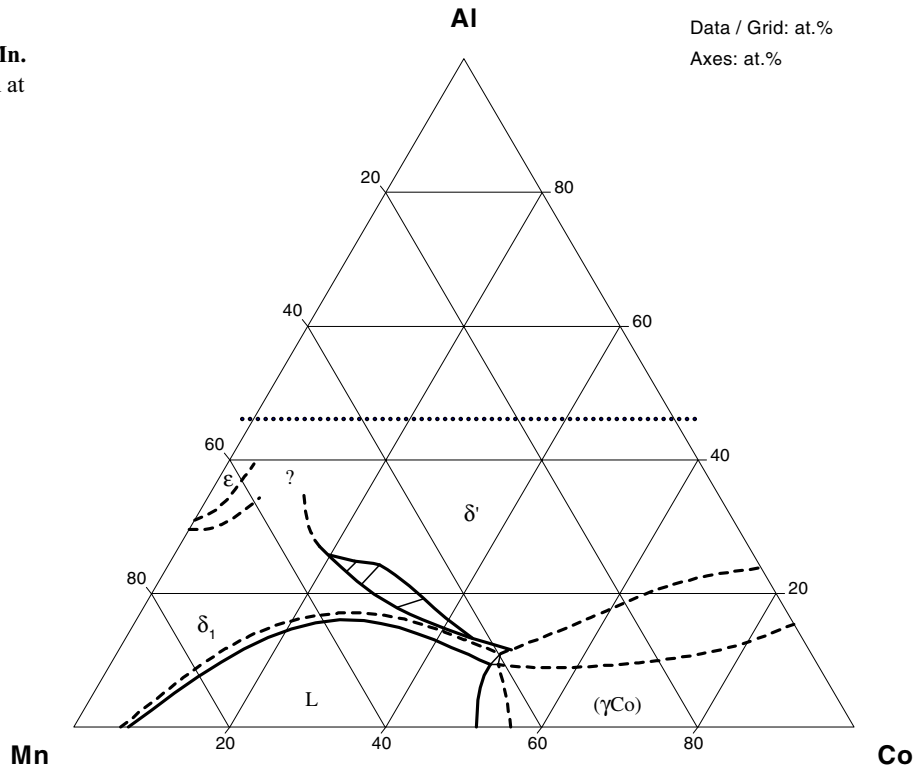

Fig. 10: Al-Co-Mn. Isothermal section at 1200°C

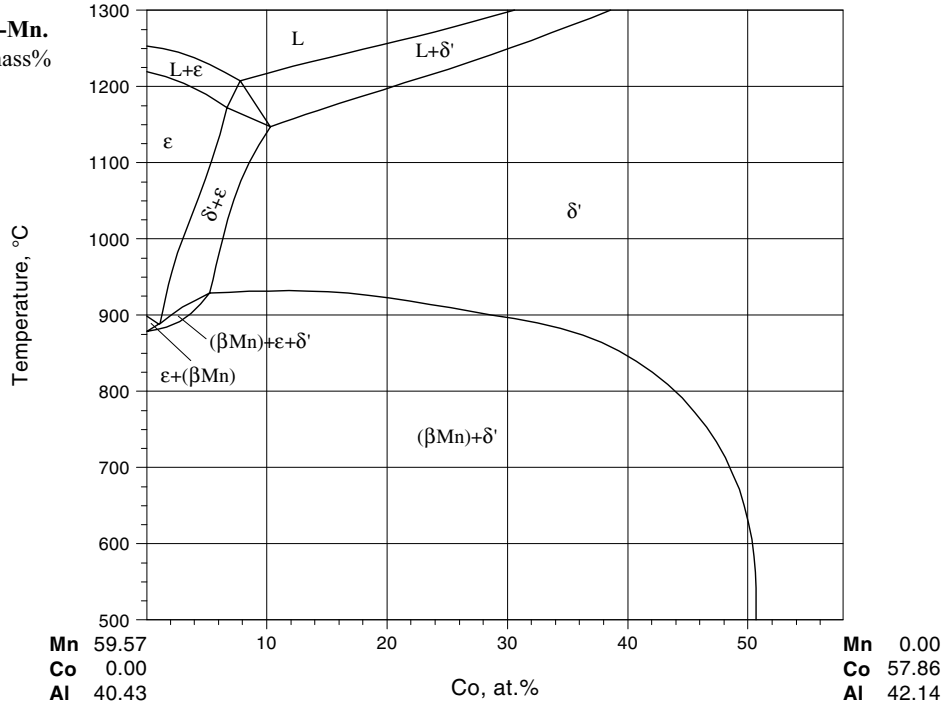

Fig. 11: Al-Co-Mn. Isopleth at 25 mass% Al

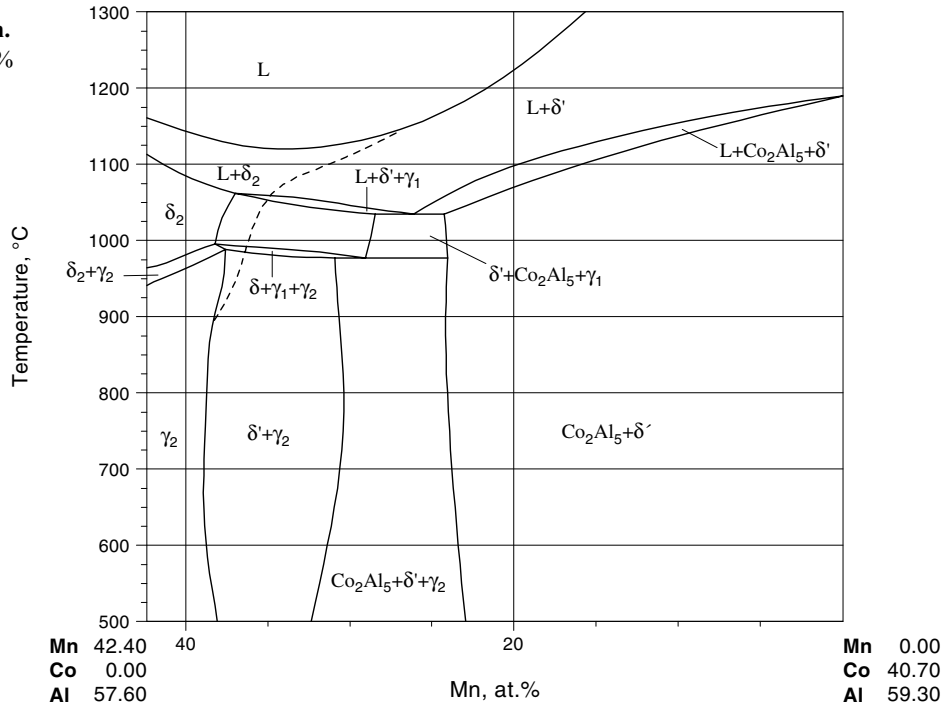

Fig. 12: Al-Co-Mn. Isopleth at 40 mass% Al

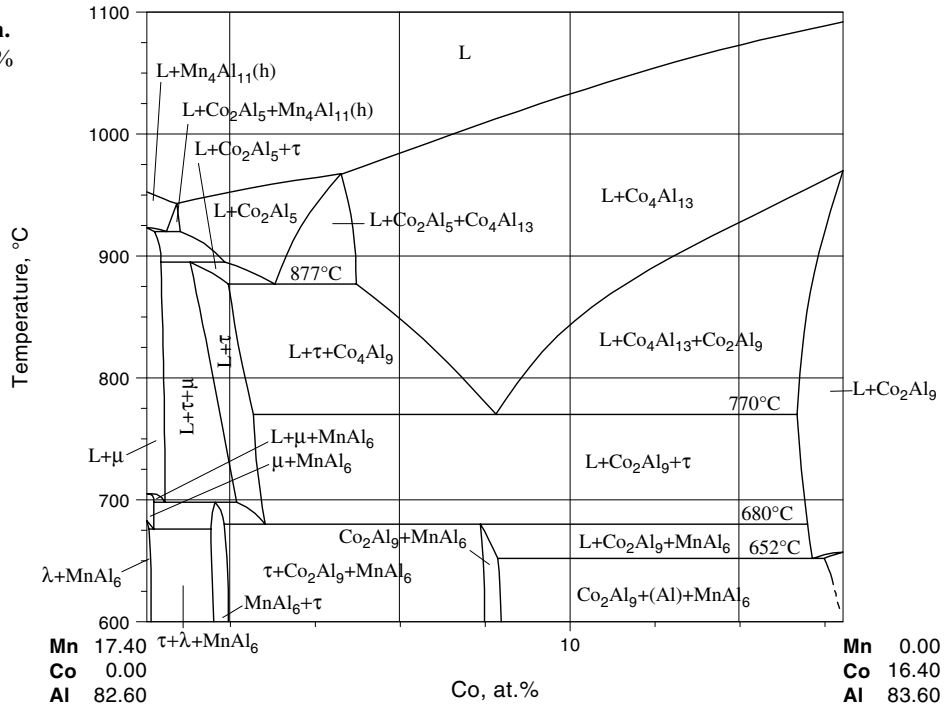

Fig. 13: Al-Co-Mn. Isopleth at 70 mass% Al

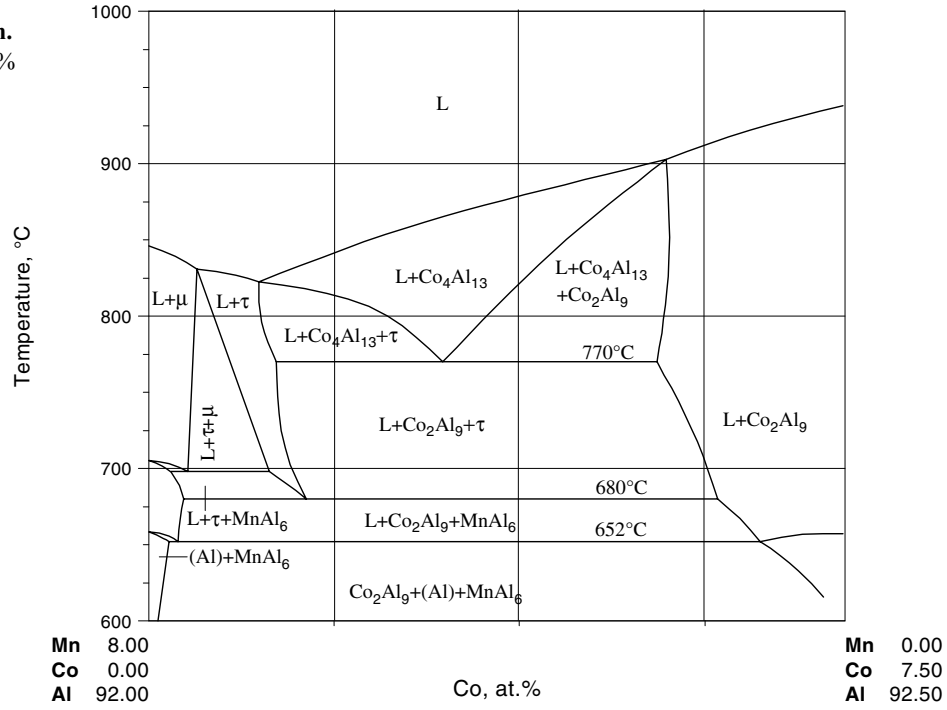

Fig. 14: Al-Co-Mn. Isopleth at 85 mass% Al

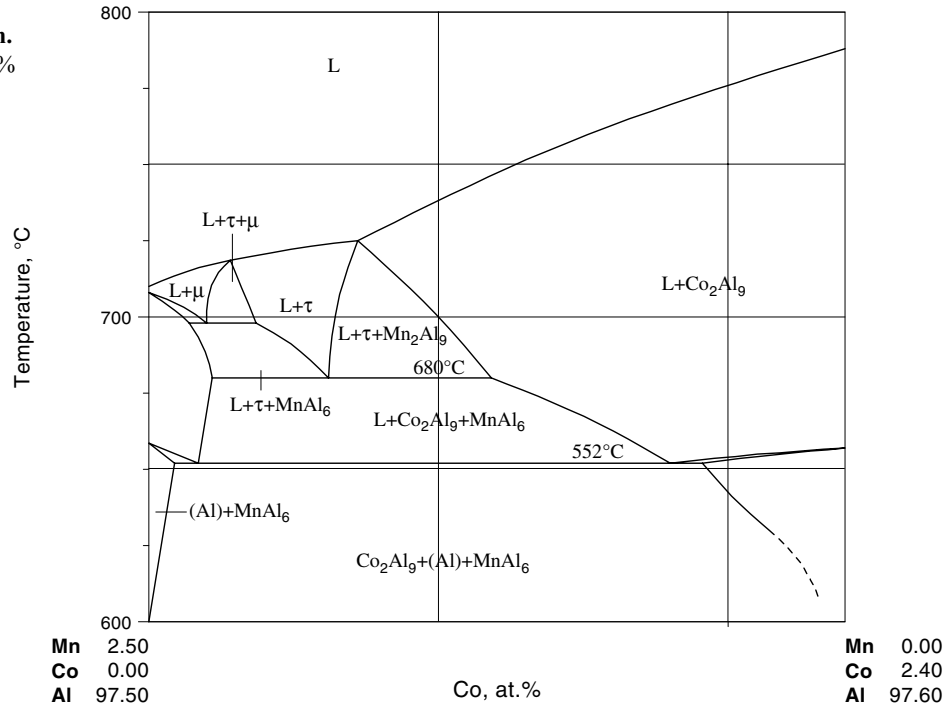

Fig. 15: Al-Co-Mn. Isopleth at 95 mass% Al

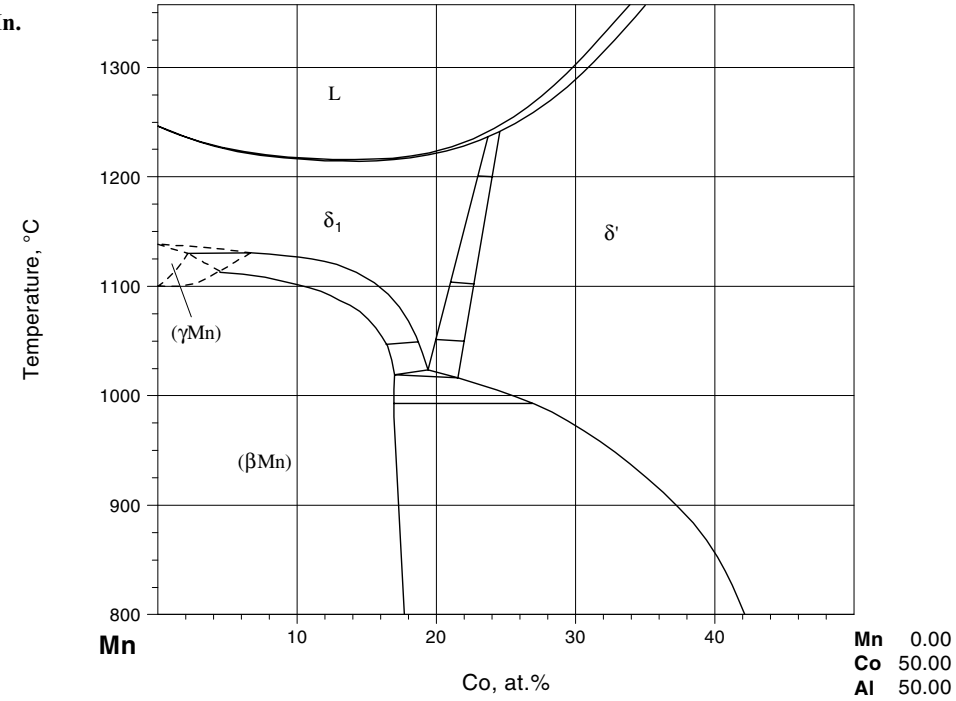

Fig. 16: Al-Co-Mn. Vertical section at Mn-CoAl