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Al-Co-Ni (Aluminum-Cobalt-Nickel)

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The previous review of this system by [1991Hub] gave partial liquidus projections for Al-poor alloys from [1941Sch] and for Al-rich alloys from [1947Ray], four isothermal sections at 1300, 1100, 900, and 25 °C from [1941Sch] and two vertical sections. The compilation by [1995Vil] gave isothermal sections for Al-poor alloys at 1350, 1300, 1200, 1000, 900, and 800 °C from [1941Sch], two computed isothermal sections at 1327 and 527 °C from [1975Kau] and several vertical sections. Recently, in a series of papers [1996God, 1997God1, 1997God2, 1997God3, 1998God, 1998Sch, 1999Luc], Godecke et al. investigated in detail the phase equilibria in Al-rich alloys and presented a liquidus projection, isothermal sections at 1170, 1100, 1050, 900, 850, 730, and 600 °C, and a number of vertical sections. They ignored the structural variations of the decagonal quasi-crystalline phase and marked the region of their existence as a single phase D in their sections. More information is now available regarding the nature and the interrelationships between the modifications of the decagonal phase.

Binary Systems

The Al-rich region of the Al-Co phase diagram reinvestigated by [1996God] is shown in Fig. 1. Differential thermal analysis, metallography, x-ray powder diffraction, and magnetic susceptibility measurements were used by [1996God]. The main difference between Fig. 1 and the diagram listed in [Massalski2] is the presence of three modifications of Co_4Al_{13} in Fig. 1, all occurring in a narrow range of composition between 24 and 24.7 at. % Co. The high-temperature Co_4Al_{13} (HT) (Os_4Al_{13}-type, denoted Y_1) is stable below 1127 °C. It decomposes eutectoidally at 1083 °C to the orthorhombic form Co_4Al_{13} (o) and the monoclinic form Co_4Al_{13} (m). [1997God4] attributed the differences between the diagram in Fig. 1 and that published by [1996Gru] to the existence of metastable states even at relatively slow rates of cooling. The other phases on the Al-rich side are: Co_2Al_9 ($D8_d$-type monoclinic), $CoAl_3$ ($D0_{11}$, Fe_3C-type orthorhombic), and Co_2Al_5 ($D8_{11}$-type hexagonal). Quenching of compositions close to 25 at.% Co from the liquid state yielded a metastable decagonal form of $CoAl_3$ [1996God]. On the Co-rich side (not shown in Fig. 1), CoAl ($B2$, CsCl-type cubic) has a wide range of homogeneity from 48 to 78.5 at.% Co. The structural details of the Al-Co phases are listed in Table 1 [1997God1, Pearson3]. For a recent thermodynamic description of the Co-Al system, see [2004Oht].

The Al-Ni phase diagram [1993Oka] shows five intermediate phases: $NiAl_3$ (Fe_3C-type orthorhombic), Ni_2Al_3 ($D5_{13}$-type hexagonal), NiAl ($B2$, CsCl-type cubic), Ni_5Al_3 (Ga_3Pt_5-type orthorhombic), and Ni_3Al ($L1_2$, $AuCu_3$-type cubic; also denoted γ'). Recently, [2004Oht] gave a thermodynamic description of the Al-Ni system. The Co-Ni alloys solidify as a continuous face-centered-cubic (fcc) solid solution that is stable over a wide temperature range. The fcc → close-packed-hexagonal (cph) transition temperature in pure Co is lowered by the addition of Ni.

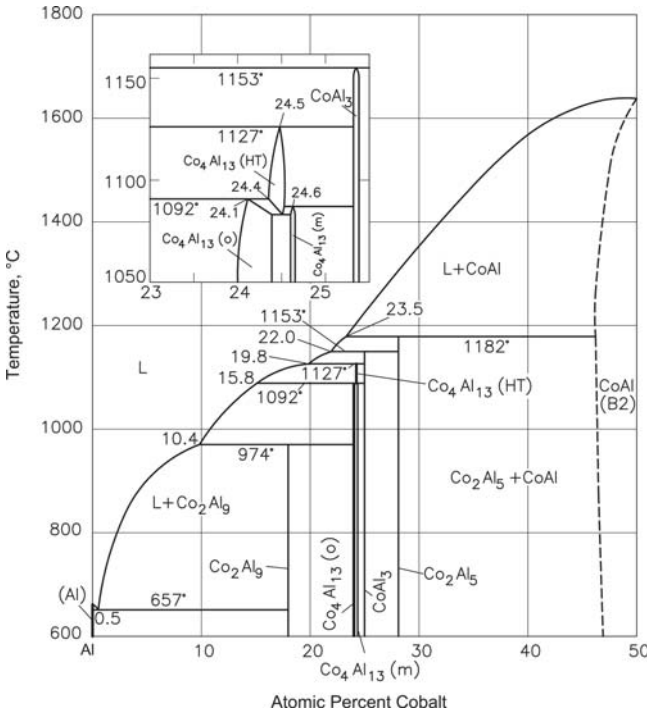

Fig. 1 Al-Co phase diagram for the Al-rich region [1998God]

Ternary Phases

The main ternary phase of this system is the decagonal, quasi-crystalline phase [1989Tsa] denoted D. It forms at an upper critical point of 1175 °C through the reaction: L + $B2$ → D and is stable down to room temperature [1998God]. Its homogeneity range in at.% extends from 4.3Ni-72Al to 12.4Ni-70.2Al at 1100 °C. The range increases with decreasing temperature, extending from ~5.5Ni-73.5Al to ~22.5Ni-70.3Al at 900 °C. The structure determination of D and its variants has been the subject of many recent publications, for example, [1995Rit], [1999Luc], [1999Tsa], [2002Yam], [2003Sol], and [2004Sai]. For a complete listing of the key papers on this subject, see the above references. Based on the selected-area-electron-diffraction studies of an $Al_{70}Co_{17}Ni_{13}$ alloy, Edagawa et al. [1994Eda] first reported the existence of two distinct sets of superlattice reflections labeled as S1 and S2 reflections, in addition to the reflections of the basic decagonal structure. [2003Sol]

Table 1 Al-Co crystal structure and lattice parameter data

Phase	Composition, at.%	Pearson symbol	Space group	Prototype	Lattice parameter, nm
Co_2Al_9	18.2 Co	*mP*22	$P2_1/c$	Co_2Al_9	$a = 0.62130$ $b = 0.6290$ $c = 0.85565$ $\beta = 94.76°$
$Co_4Al_{13}(m)$	24.6-24.7 Co	*mP*99	*C*2/*m*	$Co_4Al_{13}(m)$	$a = 1.5173$ $b = 0.81090$ $c = 1.2349$ $\beta = 107.84°$
Co_4Al_{13} (*o*)	24-24.4 Co	*oP*102	$Pmn2_1$	$Co_4Al_{13}(o)$	$a = 0.8158$ $b = 1.2342$ $c = 1.4452$
Co_4Al_{13} (HT) (Y_1)	24.3-24.5 Co	*mC*32	*C*2/*m*	Os_4Al_{13}	$a = 1.7071$ $b = 0.40993$ $c = 0.74911$ $\beta = 116.17°$
$CoAl_3$	25.3-25.4 Co	*oP*16	*Pnma*	Fe_3C	$a = 0.65982$ $b = 0.73515$ $c = 0.48021$
Co_2Al_5	28.6 Co	*hP*28	$P6_3/mmc$	Co_2Al_5	$a = 0.76715$ $b = 0.76085$
CoAl (*B*2)	~48-78.5 Co	*cP*3	$Pm\bar{3}m$	CsCl	$a = 0.28611$(a)

(a) At 50 at.% Co

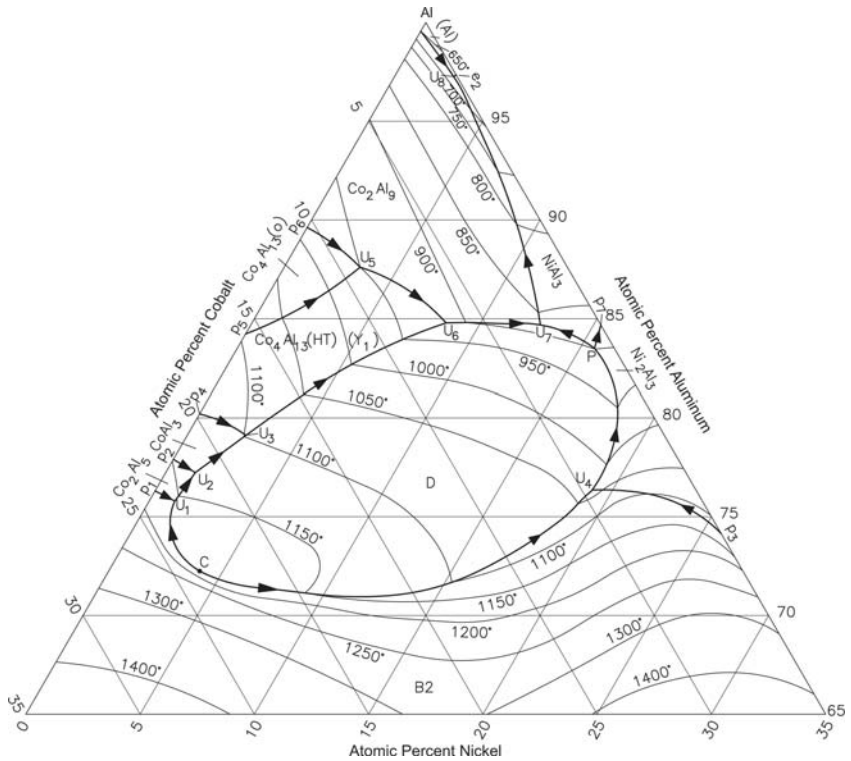

Fig. 2 Al-Co-Ni liquidus projection for Al-rich alloys [1997God2]

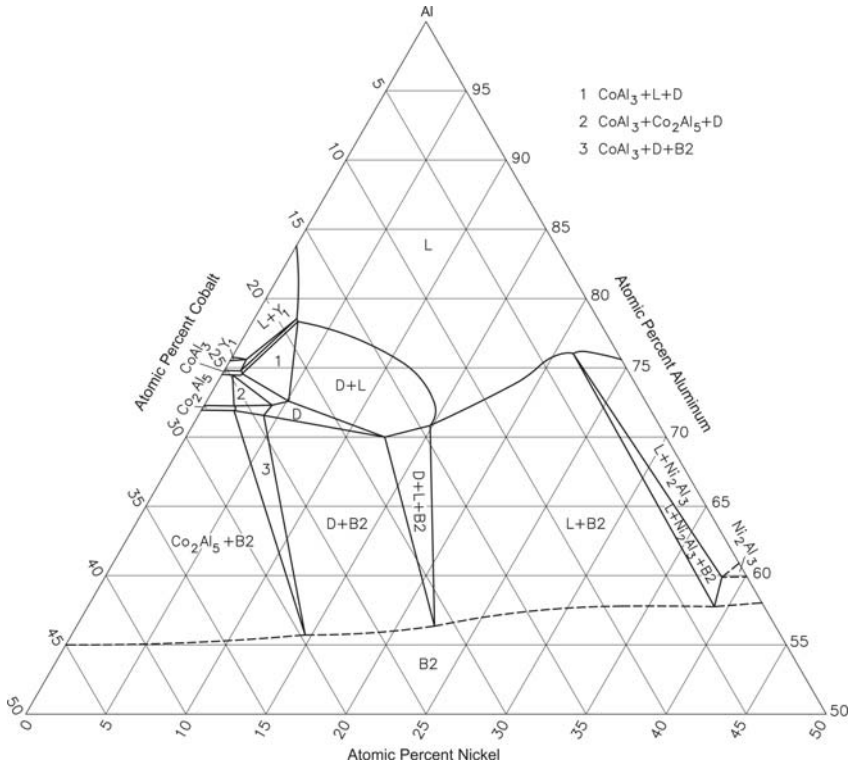

Fig. 3 Al-Co-Ni isothermal section at 1100 °C [1998God]

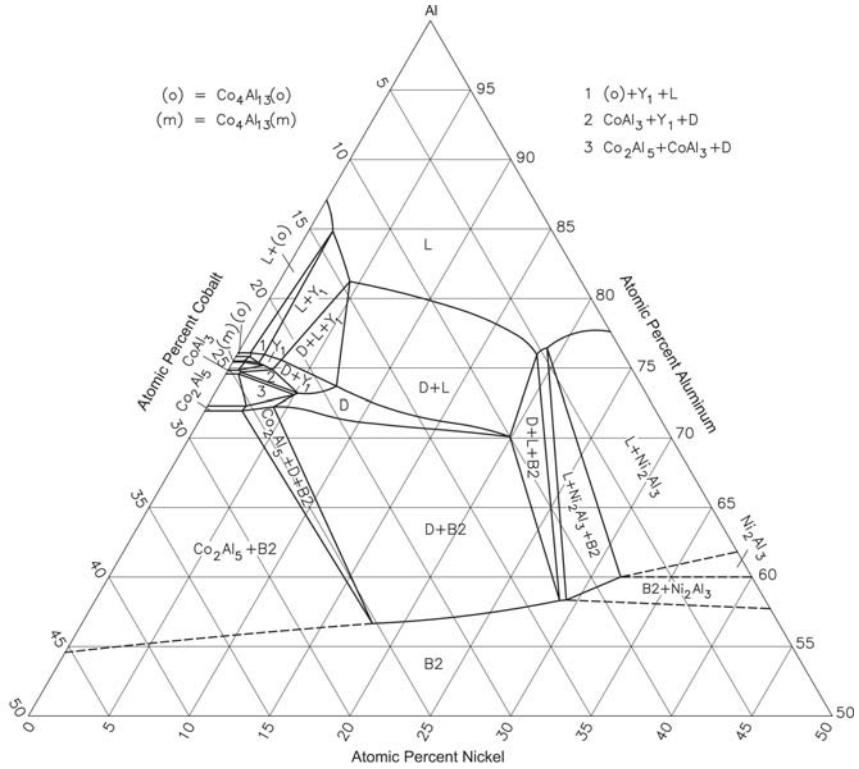

Fig. 4 Al-Co-Ni isothermal section at 1050 °C [1998God]

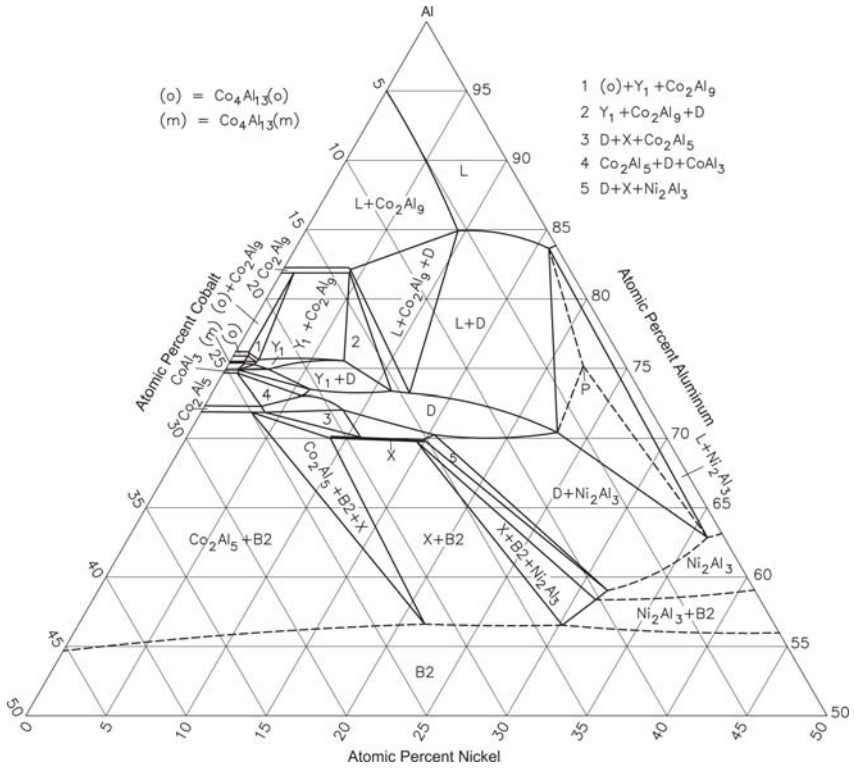

Fig. 5 Al-Co-Ni isothermal section at 900 °C [1998God]

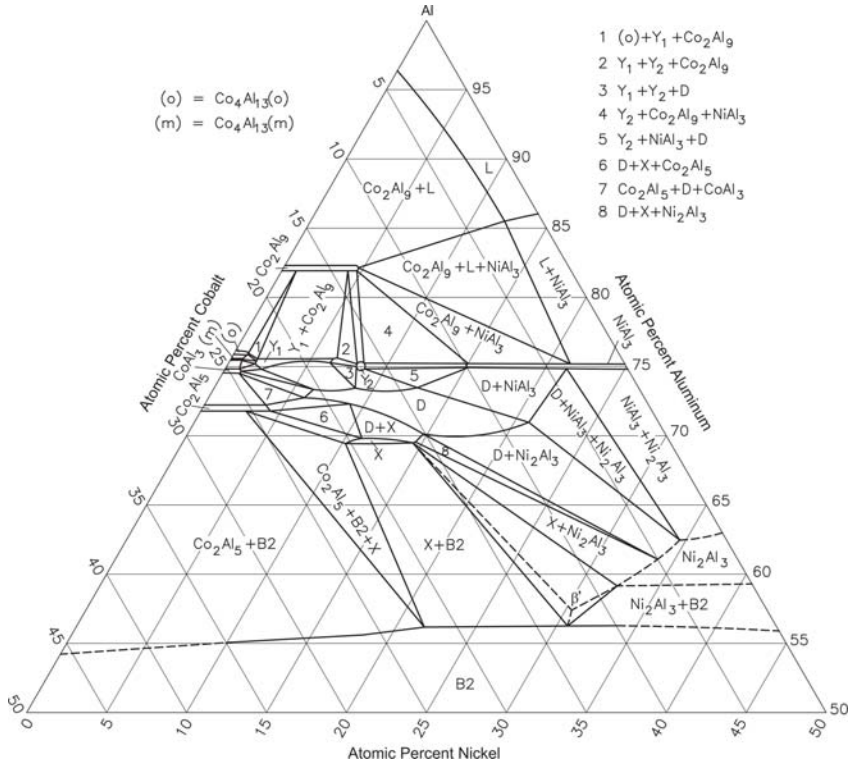

Fig. 6 Al-Co-Ni isothermal section at 850 °C [1998God]

studied an $Al_{71.2}Co_{12.8}Ni_{16}$ alloy and reported that the type I superstructure (the most ordered state) stable at low temperatures changes by a second-order transition on heating to a S1 superstructure, where the S2 reflections disappear. On further heating, the S1 superstructure changes to the basic decagonal structure. The transition characteristics and

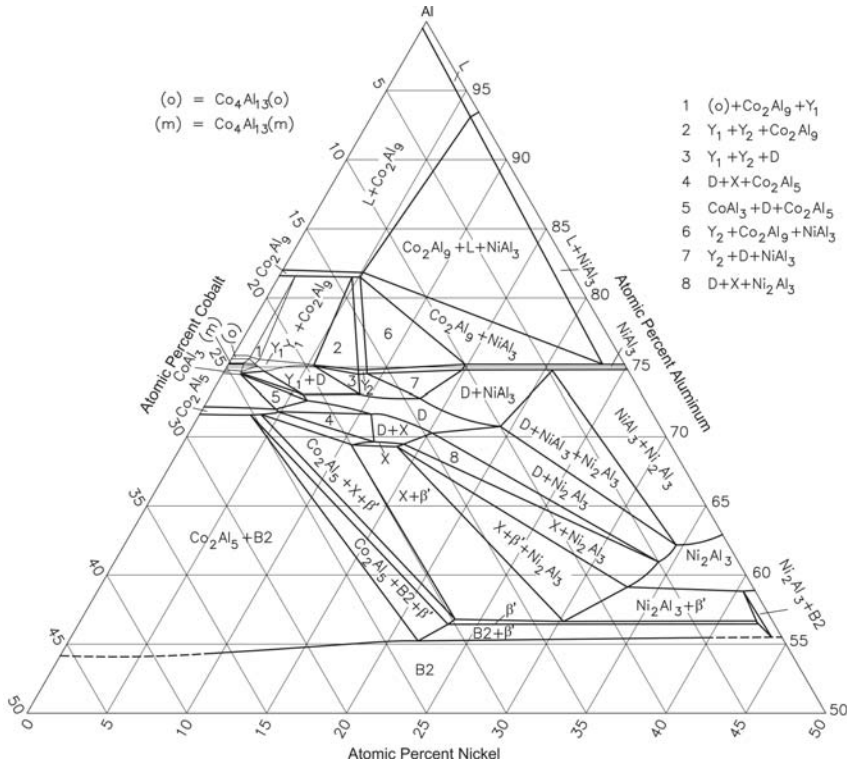

Fig. 7 Al-Co-Ni isothermal section at 730 °C [1998God]

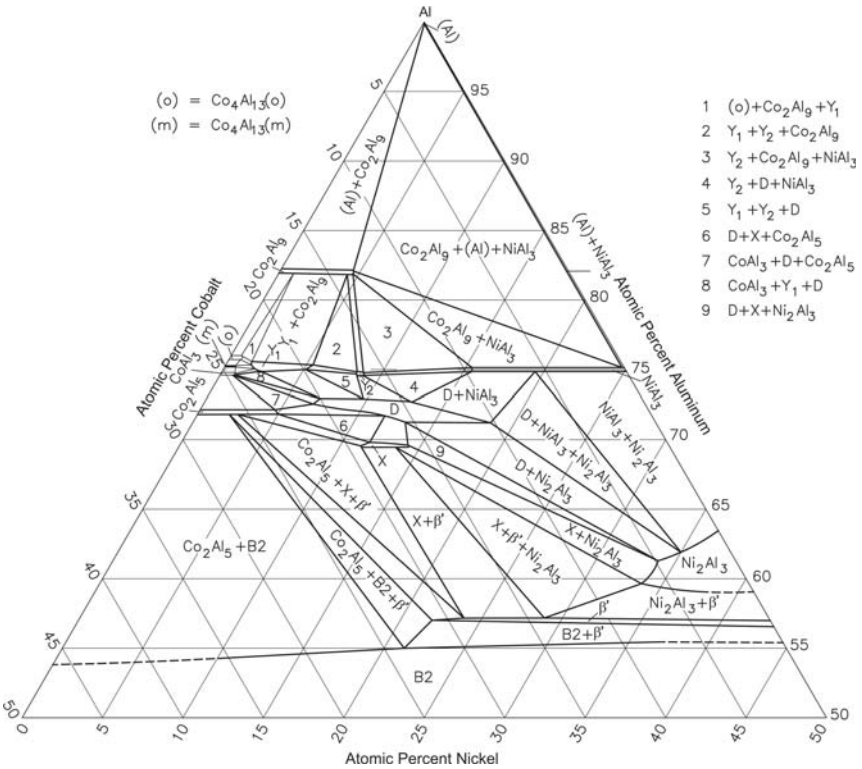

Fig. 8 Al-Co-Ni isothermal section at 600 °C [1998God]

temperatures are very sensitive to variations in the composition of the alloys. On a vertical section along the $Al_{74}Co_{26}$-$Al_{69}Ni_{31}$ join, [2003Sol] sketched the tentative phase relationships between different structural forms within the stability region of the decagonal phase.

Among the other known ternary phases, the phase de-

noted Y_1 [1997God1] is the binary phase Co_4Al_{13} (HT) stabilized by the addition of Ni. The binary phase decomposes at 1083 °C, whereas in the ternary region the phase is stable down to room temperature. The ternary phase denoted X forms by the ternary peritectoid reaction Pd_1: *B*2 + Co_2Al_5 + D → X at 1002 °C. At 900 °C, it has a Ni range of 9.2 to 14.5 at.% at constant Al of 70 at.%. [1991Kek] assigned an orthorhombic unit cell for X, but [1997God3] found it to be triclinic. The ternary phase Co_2NiAl_9 (denoted Y_2) forms by the ternary peritectoid reaction Pd_2: Y_1 + D + Co_2Al_9 → Y_2 at 880 °C. It has orthorhombic symmetry, space group *Immm*, with the lattice parameters *a* = 1.20646 nm, *b* = 0.75553 nm and *c* = 1.5353 nm [1998Gri]. The ternary phase β′ has a vacancy-ordered Ga_4Ni_3-type cubic structure with *a* = 1.15 nm [1997God3]. It forms through the ternary peritectoid reaction Pd_3: *B*2 + X + Ni_2Al_3 → β′ at 850 °C.

The isostructural phases CoAl and NiAl with the CsCl-type structure form a continuous solid solution *B*2. Ni and αCo (both fcc) form a continuous solid solution, dissolving about 5 at.% Al.

The Liquidus Projection

With starting metals of 99.999% Al, 99.98% Co, and 99.99% Ni, [1997God2] melted a number of Al-rich alloys in an induction furnace under Ar atmosphere. The phase equilibria were studied by differential thermal analysis, magneto-thermal analysis (susceptibility measurements as a function of temperature), light microscopy, and x-ray diffraction. The heating/cooling rate used in the thermal analysis experiments was 2 to 10 °C/min. The liquidus surface constructed by [1997God2] for Al-rich alloys is redrawn in Fig. 2. The primary phases of crystallization marked in the figure are (Al), Co_2Al_9, Co_4Al_{13}(HT) (Y_1), Co_4Al_{13} (o), $CoAl_3$, Co_2Al_5, D, $NiAl_3$, Ni_2Al_3 and *B*2. The prominent primary areas are those of D and *B*2. Eight U-type transition reactions U_1 to U_8 occur during solidification. The decagonal phase forms at 1175 °C (the upper critical point *C* in Fig. 2). The binary phase $NiAl_3$ nucleates in the ternary region through the peritectic reaction *P*: L + Ni_2Al_3 + D → $NiAl_3$ at 900 °C. Isothermal contour lines at intervals of 50 °C are shown in Fig. 2 [1997God2].

Isothermal Sections

Four isothermal sections for Al-rich alloys at 1000, 850, 700, and 600 °C were determined by [1991Kek]. Later, Godecke et al., in their comprehensive investigations of this system, extended this work and presented seven isothermal sections at 1170, 1100, 1050, 900, 850, 730, and 600 °C [1998God]. Six of these are redrawn in Fig. 3 through 8. At 1170 °C (not shown), the D phase has just nucleated on a critical tie-line between L and *B*2. At 1100 °C (Fig. 3), $CoAl_3$, Y_1 and Ni_2Al_3 appear in the equilibrium and the extent of the D phase has increased. At 1050 °C (Fig. 4), the Y_1 phase has receded into the ternary region. Co_4Al_{13} (m) and Co_4Al_{13} (o) have nucleated and the region of stability of

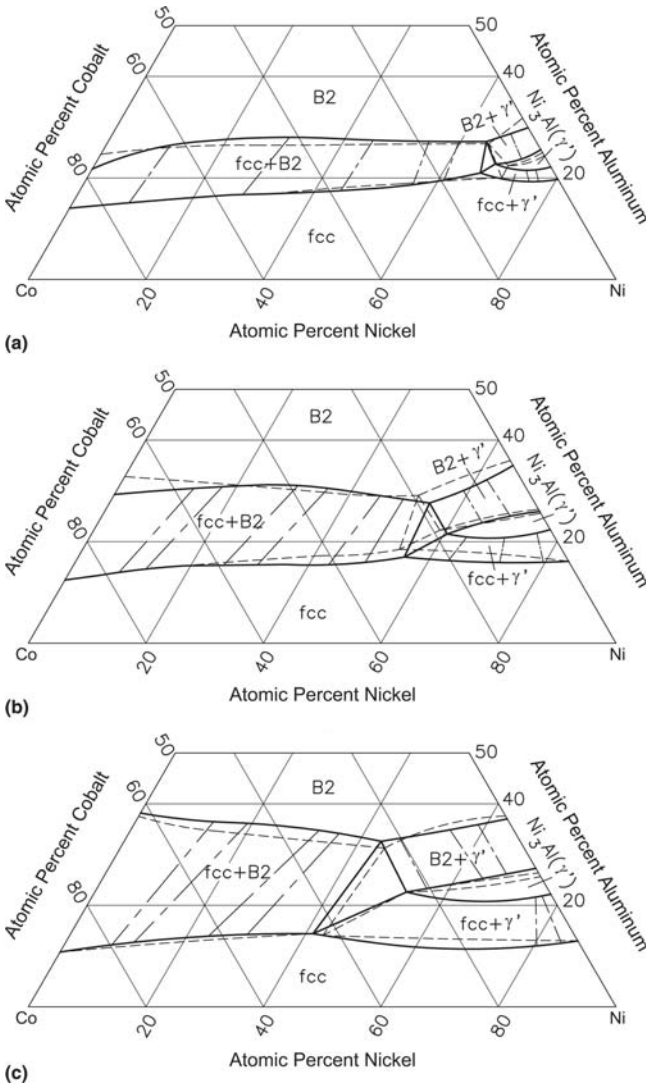

Fig. 9 Al-Co-Ni isothermal sections at (a) 1300, (b) 1100, and (c) 900 °C [1996Kai]. Dotted phase boundaries are from [1941Sch]

D continues to grow. At 900 °C (Fig. 5), Co_2Al_9 and the ternary phase X have appeared and extend along lines of constant Al content. This is also the temperature of the ternary peritectic reaction P, through which $NiAl_3$ nucleates in the ternary region. At 850 °C (Fig. 6), the Y_2 phase is already in existence. $NiAl_3$ has extended up to the binary side at constant Al content. β′ nucleates peritectoidally at this temperature. At 730 °C (Fig. 7), β′ extends from ~24 to ~43 at.% Ni at a constant Al content of 57.1 at.%. At 600 °C (Fig. 8), the Al-rich liquid has solidified. The β′ phase is shown by [1998God] to extend up to Al-Ni binary side at 600 °C, even though this phase is not seen in the Al-Ni binary diagram. The reaction table of [1998God] (see Fig. 10) postulates a peritectoid reaction *B*2 + Ni_2Al_3 → β′ at 702 °C in the Al-Ni system. The section in Fig. 8 was found to be valid also for 400 °C by [1998God].

At all the temperatures illustrated above, the phase equilibria in the Al-poor region were not included, to preserve the clarity of the details in the Al-rich region. The isother-

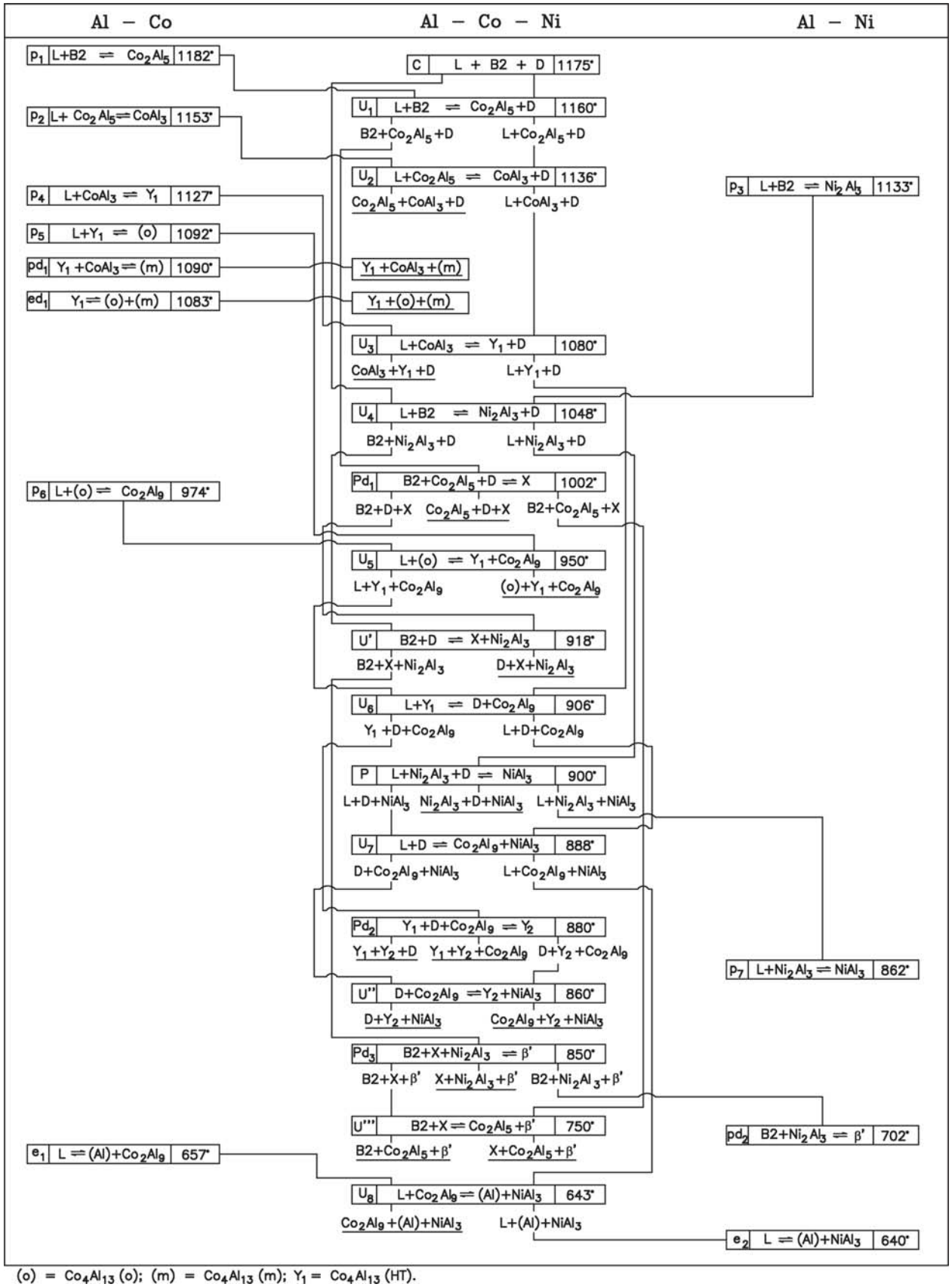

Fig. 10 Al-Co-Ni reaction sequence for the Al-AlCo-AlNi region [1998God]

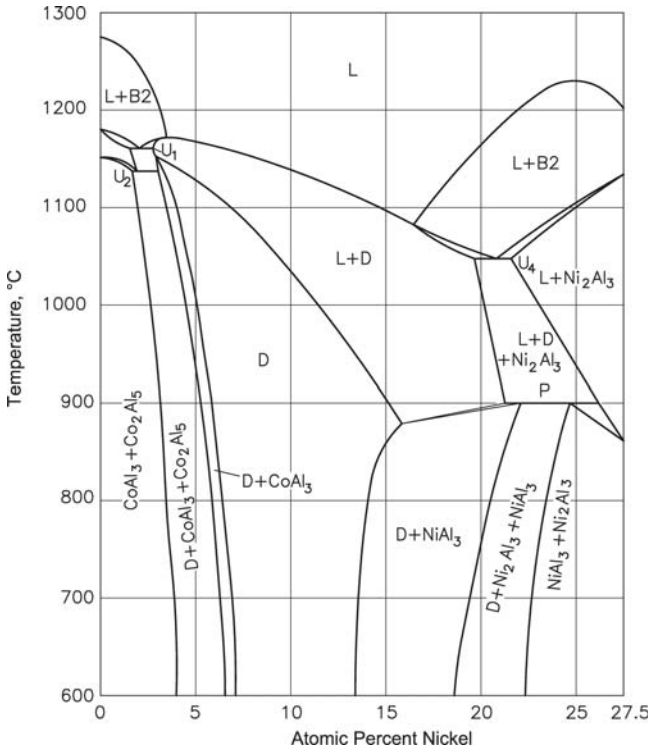

Fig. 11 Al-Co-Ni vertical section at 72.5 at.% Al [1998Sch]

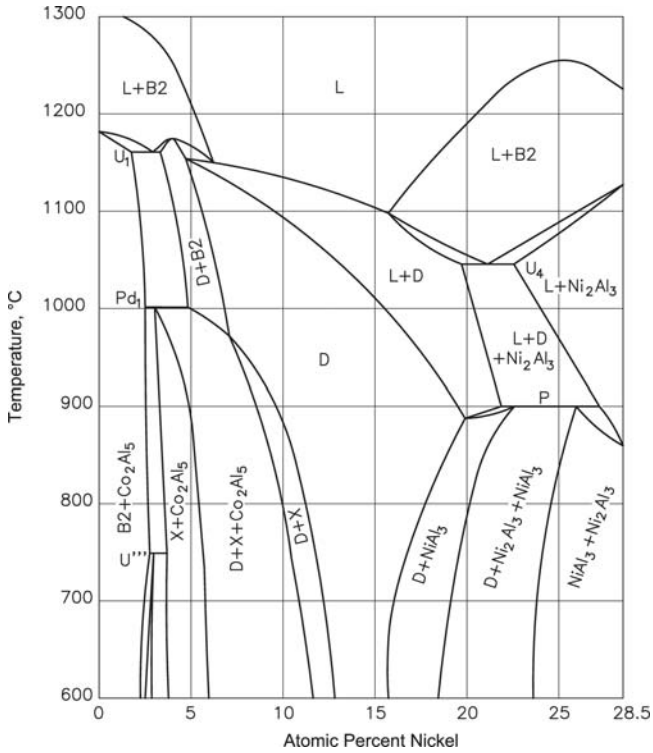

Fig. 12 Al-Co-Ni vertical section at 71.5 at.% Al [1998Sch]

mal sections between 1350 and 527 °C compiled by [1995Vil] depict the Al-poor region. At these temperatures, the continuous solid solutions CoAl-NiAl (*B*2) and Ni-αCo (fcc) coexist with Ni_3Al (γ′) [1941Sch, 1993Pov]. Recently, [1996Kai] redetermined the phase relationships in the Al-poor region and presented isothermal sections at 1300, 1100, and 900 °C. The tie-lines between *B*2 and γ′ and between *B*2 and fcc were determined, with energy-dispersive x-ray spectroscopy. Earlier, the tie-lines between γ (fcc) and γ′ were measured by [1994Jia]. Comparison of the isothermal sections of [1996Kai] with those determined by [1941Sch] (who used only metallography) shows good agreement (Fig. 9).

A reaction scheme written by [1998God] covering the liquid-solid and the solid-solid reactions of this system is given in Fig. 10. The invariant reactions on the liquidus surface are denoted in the same way as in Fig. 2. Solid-state transition reactions are denoted U′, U″, and U‴, and the ternary peritectoid reactions are labeled Pd_1, Pd_2, and Pd_3. Underlined three-phase equilibria are stable down to room temperature. The three-phase fields at room temperature are the same as seen in Fig. 8 at 600 °C. The reaction scheme is consistent with the liquidus projection (Fig. 2) and the isothermal sections (Fig. 3-8).

Vertical Sections

A number of vertical sections have been reported for this system: at constant contents of 75 and 78 at.% Al [1997God1], 80, 85, 92.5, and 97 at.% Al [1997God2], 57.5, 65, and 70 at.% Al [1997God3], 70, 71.5, and 72.5 at.% Al [1998Sch], 19 at.% Ni [1997God3], and 10 and 13 at.% Ni [1998Sch]. Here, the sections at constant Al contents of 72.5 and 71.5 at.% are redrawn from [1998Sch] in Fig. 11 and 12, respectively, to illustrate the large region of stability of the decagonal phase D. Figure 11 depicts the horizontals corresponding to the invariant reactions U_1, U_2, U_4, and P. Figure 12 depicts the invariant horizontals at U_1, U_4, Pd_1, P, and U‴.

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