

## Aluminium – Cobalt – Nickel

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### Literature Data

This system is of pronounced industrial and scientific interest because of the mechanical properties of its alloys [1995Mis, 1998Che, 2000Eda] and the formation of quasicrystalline phases. The relevant literature has drastically increased by a factor of 8 since [1991Hub] has made the first critical evaluation of this system under the MSIT Evaluation Program.

Phase equilibria in the range of aluminium content up to 50 at.% were studied by [1941Sch] using thermal analysis, metallography, X-ray and magnetic techniques. The starting components were Al (99.9 mass%), Co (97.6 mass%) and Ni (99.9 mass%). The alloys for investigation were prepared using high frequency induction melting in Fe moulds. The partial liquidus surface, temperature-composition sections at constant Ni/Co ratios of 9/8, 8/2, 5/5, and 2/8 as well as isothermal sections at 1300, 1200, 1100, 1000, 900 and 25°C for the compositional range up to 50 at.% Al were presented. The major result of this work was the verification of a continuous range of solid solutions between the congruent isostructural CoAl and NiAl phases ( $\beta$ ), which divides the ternary system to Co-CoAl-NiAl-Ni and Al-CoAl-NiAl. [1966Rid] confirmed the  $\beta$  phase by X-ray analysis of alloys along Ni/Co ratios of 8/2, 5/5, and 3/7. The Al-poor boundary of the  $\beta$  phase was determined at room temperature on slowly cooled alloys; its position agrees well with that of [1941Sch]. The Al-rich corner of the Al-Co-Ni system was studied first by [1947Ray] who determined the melting points of alloys with more than 95 at.% Al at constant 97.5 mass% (98.8 at.%) Al, the thermal effects were measured whilst cooling the melts at a rate of 1–2°C·min<sup>-1</sup> under simultaneous stirring. Alloys annealed at 638–639.9, 643, 648.5 and 655°C and quenched were examined by their micrographs, which established the three-phase solid state equilibrium (Al)+(Co<sub>2</sub>Al<sub>9</sub>)+(NiAl<sub>3</sub>). The temperature of the ternary eutectic  $L \rightleftharpoons (Al)+(Co_2Al_9)+(NiAl_3)$  has been determined in [1976Kov].

The data published up to 1985 have been evaluated by [1991Hub] who presented a number of isothermal sections, temperature-concentration cuts and the liquidus projection. [1993Pov] investigated phase equilibria and presented isothermal sections at 1100 and 900°C at the content of Al up to 70 at.%. Aluminium 99.99, cobalt 99.99, and nickel 99.97 mass% purities were used. The alloys were prepared by arc melting in argon atmosphere. Specimens containing more than 50 at.% Al were sealed in quartz ampoules and annealed at 1100°C for 300 h. Preliminary homogenization of other alloys was conducted in an induction furnace under helium atmosphere at 1300°C for 100 h. Then the specimens were annealed at 1100 and 900°C in the quartz ampoules for 100 and 300 h, respectively, followed by water quenching and investigated by X-ray diffraction and EMPA. Phase equilibria between  $\gamma$ (Ni),  $\gamma'$ (Ni<sub>3</sub>Al) and  $\beta$  phases were investigated by [1994Jia, 1996Kai, 2001Kai] and [2001Oik1]. The alloys were prepared by induction melting of appropriate mixtures of pure aluminium (99.7 mass%), cobalt (99.9 mass%) and nickel (99.9 mass%) under an argon atmosphere. Then diffusion couples were made, sealed in evacuated transparent quartz capsules and annealed at 627 to 1300°C for 1 to 1000 h [2001Kai] or at 800 to 1300°C for 10 to 1000 h [1994Jia]. Microstructures of the annealed diffusion couples were examined by optical microscopy and the concentration profiles across the  $\gamma'/\beta$  interface determined by EMPA. [1996Kai] fabricated the melted ingots by hot-rolling at 1250 to ~1300°C into sheets. The specimens were studied by optical microscopy, energy dispersion X-ray spectroscopy, transmission electron microscopy as well as differential scanning calorimetry. [2001Oik1] took small specimens from the ingots and sealed them in quartz capsules filled with argon. Solution heat treatment at 1300°C for 24 h, and subsequent equilibrating treatments were carried out at 1100, 1200 and 1300°C for 1 to 24 h before the samples were quenched in ice water. The samples were examined by metallography, EDX and X-ray diffraction. The tie lines and phase boundaries at 1300, 1200, 1100, 900 and 800°C by [1994Jia, 2001Oik1], as well as isothermal sections at 1300, 1100 and 900°C by [1996Kai] in the range of compositions 0–50 at.% Al are reported. The influence of alloying elements on the morphological stability of the interface between the  $\gamma'$  and  $\beta$  phases was studied at temperatures ranging from 900 to 1300°C [2001Kai].

The structure and properties of the ternary compounds in the system have been reported starting from [1989Tsa1, 1989Tsa2] in more than 90 publications. Most of them are dedicated to the structure of the decagonal phase and its modifications. A great number of results on the investigations of the structure of the decagonal phase and its modifications were published by [1990Yam, 1991Bur, 1991Hir1, 1991Hir2, 1991Zha, 1992Eda, 1992Eib, 1992Tsa, 1992Zha, 1993Bur, 1993Eda, 1993Fre, 1993Lue, 1993Ste1, 1993Ste2, 1994Est, 1994Gru, 1994Rey, 1995Hra, 1995Qin, 1995Rit, 1995Wue, 1996Rit1, 1996Sch, 1996Tsa, 1996Tsu, 1996Yam, 1997Che, 1997Dug, 1997Feu, 1997Gru1, 1997Gru2, 1997Hra, 1997Kal, 1997Qin, 1997Gru2, 1997Hra, 1997Qin, 1997Sai2, 1997Sai1, 1997Yam, 1997Yok, 1997Zha, 1998Hon, 1998Rit, 1998Sai, 1998Sat, 1998Wid, 1999Fis, 1999Gil, 1999Rit, 1999Wit, 2000Abe, 2000Bee, 2000Cer, 2000Dam, 2000Dro, 2000Doe, 2000Elh, 2000Fre, 2000Gra, 2000Hai, 2000Hra, 2000Kra1, 2000Kra2, 2000Liu, 2000Pra, 2000Rit, 2000Sai, 2000Shi, 2000Ste1, 2000Ste2, 2000Wei, 2000Yan, 2000Yur, 2001Hir1, 2001Hir2, 2001Hir3, 2001Hir4, 2001Hir5, 2001Hir6, 2001Hir7, 2001Tak, 2002Cer, 2002Hir1, 2002Hir2, 2002Kup, 2003Ebe]. The main experimental methods were TEM and HREM. They were applied to rapidly cooled, as-cast, and annealed alloys. Information concerning the phase composition, phase transformations, compositional ranges of ternary phases stability is reported by [1991Kek, 1994Eda, 1995Kal, 1995Wue, 1996Gru1, 1996Gru2, 1996Kai, 1997Bau, 1997Gru1].

Four isothermal sections of the Al-CoAl-NiAl subsystem at 1000, 850, 700 and 600°C were suggested by [1991Kek] based on X-ray diffraction and light optical microscopy data for heat-treated samples. The re-investigated phase equilibria in the Al-corner of ternary system is given by [1996Goe, 1997Goe1, 1997Goe2, 1997Goe3, 1997Yok, 1998Goe] and [1998Sch]. As starting components, they mostly used 99.999 pure aluminium from Heraeus, 99.9 pure cobalt from Johnson Matthey and 99.98 pure nickel from Good fellow. The alloys were prepared by melting mixtures of the components in corundum crucibles, put them into silica ampoules which were closed, evacuated and refilled with argon. The specimens were heat treated under different conditions and investigated by microstructural and X-ray diffraction techniques as well as by magneto-thermal analysis (MTA) [1996Goe, 1997Goe1, 1997Goe2, 1997Goe3, 1998Goe, 1998Sch]; differential thermal analysis [1996Goe, 1997Goe1, 1997Goe2, 1997Goe3, 1998Sch], TEM [1997Goe3, 1998Goe] and selected for selected areas by electron diffraction (SED) [1997Goe3]. Liquidus surface projection of the ternary system in the range of 50-100 at.% Al was plotted by [1997Goe2, 1997Goe3] and [1998Goe]. Reaction scheme of the partial Al-CoAl-NiAl system was reported by [1997Goe2, 1998Goe]. Isothermal sections at 1050°C in the range of compositions 0-9 at.% Ni and 72-87 at.% Al [1996Goe] as well as at 1150 and 1110°C in the range of cobalt content up to 35 at.% and aluminium content from 55 to 100 at.% were plotted by [1997Goe2]. Isothermal sections of the Al-CoAl-NiAl subsystem at 1170, 1100, 1050, 900, 850, 730, and 600°C (also valid for 400°C) are presented by [1998Goe]. Temperature - composition sections were plotted: at constant Al contents of 57.5, 65, 70, 71.5, 72.5, 75, 78, 80, 85, 92.5, and 97 at.% as well as at constant Ni concentrations of 10, 13, and 19 at.% [1996Goe, 1997Goe1, 1997Goe2, 1997Goe3] and [1998Sch]. Partial isothermal sections at 927 and 1027°C including the decagonal  $\tau_1$  phase as well as isopleth along the Co:Ni = 1:1 were determined by [1997Yok]. [1997Yok] prepared alloys in the composition range 3 to 20 at.% Ni or Co by arc-melting in argon atmosphere followed by annealing in vacuum for 48h just below melting temperature. Pre-alloyed ingots were heated under flowing argon protection for 1 h at 1123°C, which is about 100 to 200°C above their melting temperatures. Solidification process from a perfect liquid was examined by DTA and the specimens were investigated by X-ray diffraction and LOM techniques.

## Binary Systems

The Co-Ni system is accepted from [Mas2], Al-Ni from [2003Sal], Al-Co from [2003Gru]. In the Al-Co phase diagram, according to [2003Gru], two alternative views [1996Goe, 1996Gru1] do exist in the range of 12 to 34 at.% Co. The results of [1996Goe] are preferred because of the better agreement with the constitution of the ternary system.

### Solid Phases

Crystallographic data on unary and binary phases as well as recently reported ternary ones are listed in Table 1. Two continuous ranges of solid solutions exist in the system,  $\beta$  (between the isostructural NiAl and CoAl phases of the CsCl type) and  $\gamma$  (between the  $(\gamma\text{Co})$  and  $(\text{Ni})$  phases) [1941Sch, 1996Kai]. [1998Tia] clarified the crystallographic properties of strengthening precipitates in the  $\beta$  phase which are supersaturated with Co and Ni. Precipitation was observed in specimens which have been aged at different aging temperatures. The precipitates was the  $(\text{Co})$  phase, but with different crystal structures depending on the aging temperature. The Co phase has a face centered cubic structure at aging temperature higher than 700°C and its shape was rod-like, with the long axis parallel to the  $\langle 111 \rangle$  direction of the matrix. At aging temperatures below 600°C the precipitates of the  $(\text{Co})$  phase take a hexagonal close packed structure, again of rod-like shape with the long axis parallel to the  $\langle 111 \rangle$  direction of the matrix. More recently [2001Tan] confirmed the continuity of the  $\beta$  solid solution by the measurements of its hardness and lattice parameter. [1985Mor2] have shown that estimation of Al solubility in the fcc Co-Ni alloys based on semi-empirical approach of [1985Mor1] developing the method of Darken and Gurry [1953Dar] does not lead to a satisfactory result. The solubility of Co in  $\text{Ni}_3\text{Al}$  increases from 8 at.% at 1300°C to 24 at.% at 900°C [1996Kai]. The lattice parameter depends weakly on the Co content [1985Mis].

The  $\beta'$  compound considered in [1980Lu] to be a ternary phase has been concluded in [1997Goe3, 1998Goe] to be the extension of binary  $\text{Ni}_3\text{Al}_4$ . Its structure is described as a superlattice built up by stacking together of 54 CsCl type fundamental structural units.

The Co addition stabilizes the  $\varepsilon$   $\text{NiAl}_3$  solid solution up to 900°C. The  $(\text{Ni},\text{Co})_3\text{Al}_4$  solid solution demonstrates a similar behavior. On the other hand, for the Y phase, dissolved Ni decreases the temperature range of existence compared with the binary Al-Co system. So this phase exists in ternary system, as a ternary phase below 1083°C. Moreover the ternary  $\tau_2$  phase, which possesses a crystal structure close to that of Y phase, appears at lower temperature when Ni is increased, at constant Al content.

Three ternary phases with crystal structure different from that of the binary intermetallics are reported in the Al-CoAl-NiAl subsystem. Their structure and specifications as well as their role in various phase reactions has been subject of many studies in the last two decades.

The stable decagonal  $\tau_1$  phase, usually designated as D in the literature, was first reported by [1989Tsa1, 1989Tsa2] in the  $\text{Co}_{15}\text{Ni}_{15}\text{Al}_{70}$  alloy. The  $\tau_1$  phase is formed below 1175°C [1997Goe3, 1998Sch, 1998Goe] and is stable in a wide composition range from about 5 to 24 at.% Ni and 70 to 73 at.% Al) [1998Goe, 1996Gru3]. The stability range of D significantly depends on temperature. Several structural variants of the decagonal phase were reported depending on composition and annealing temperatures [1992Eda, 1994Eda, 1994Gru1, 1994Hir, 1996Gru1, 1996Gru2, 1996Rit2, 1996Rit3, 1996Tsa, 1997Goe1, 1997Goe2, 1997Goe3, 1997Yam, 1997Zha, 2000Hir, 2001Hir1, 2001Hir2, 2001Hir3, 2001Hir4, 2001Hir5, 2001Hir6, 2001Hir7, 2002Hir2, 2002Hir1, 2002Hir2].

In addition, metastable or stable periodic structures with pseudo-decagonal (PD) symmetry [1998Gru2] and monoclinic [1990Yam] or orthorhombic [1995Kal, 2002Sug] structures, closely related to the decagonal phase were observed, too. Such structures commonly are addressed as “approximants”. In a number of works the alloy phase transformations in the decagonal composition range were studied using in some cases DTA or DSC methods supported by TEM [1995Kal, 1997Bau, 1998Gru2, 2000Doe, 2002Kup] and others. The structural relationships in decagonal phase ranges are still not firmly established, in spite of the great amount of information that has been generated.

The  $\tau_2$  ternary phase based on  $\text{Co}_2\text{NiAl}_9$  composition forms at 880°C [1997Goe1]. Its crystal structure was studied by [1998Gri] on single crystals and by [1999Got] using X-ray powder diffraction technique. It was concluded that it cannot be considered as an approximant for the decagonal or icosahedral phases because of the small size of the structural segments with pentagonal antiprisms and because of the absence of atoms with icosahedral atomic environment.

[1997Goe3] found the ternary  $\tau_3$  phase with composition of  $\text{Co}_{18.5}\text{Ni}_{14.0}\text{Al}_{67.5}$  which forms in the solid state through the ternary peritectoid reaction at 1002°C. The single phase region of the  $\tau_3$  phase shifts with decreasing temperature to higher Ni contents. That happens between 1002 and 918°C where the transition

plane in the ternary diagram is. The composition of this phase at low temperatures is far away from its initial peritectoid composition.

### Pseudobinary Sections

There is the pseudobinary CoAl–NiAl section, which triangulates the ternary diagram into the Co–CoAl–NiAl–Ni and Al–CoAl–NiAl subsystems.

### Invariant Equilibria

The reaction scheme in the Co–CoAl–NiAl–Ni subsystem is given in Fig. 1. The invariant quaternary equilibrium of transition type  $L+(Ni) \rightleftharpoons Ni_3Al+NiAl$  proposed initially by [1941Sch] is more consistent with the updated Al–Ni phase diagram [2003Sal] than that in [1991Hub]. The reaction scheme in the Al–CoAl–NiAl subsystem is presented in Figs. 2a, 2b according to [1997Goe2, 1997Goe3, 1998Goe], the temperature of the  $p_5$  reaction in the Al–Ni system is corrected after [2003Sal].

[1976Kov] confirmed the ternary eutectic by the experiments on directional solidification of the alloy, but the melting temperature was determined to be 637.4°C. That is lower than that accepted in the present assessment. Table 2 specifies the invariant equilibria in the investigated range of compositions according to the data by [1997Goe2] and [1997Goe3] and taking the above corrections into account.

### Liquidus Surface

The projection of the liquidus surface of the Co–CoAl–NiAl–Ni subsystem given in Fig. 3 takes into account the data of [1941Sch, 1991Hub] with minor corrections applied to achieve consistency with the accepted binary systems. The projection of the liquidus surface of the Al–CoAl–NiAl subsystem is presented in Fig. 4 and as enlargement in Fig. 5. It is based on [1997Goe2], [1997Goe3] and complemented with data from [1947Ray] for composition range with more than 95 at.% Al.

### Isothermal Sections

[1941Sch] published isothermal sections at 1300, 1200, 1100, 1000, 900 and 25°C. Thermodynamic calculations of isothermal sections of the Al–Co–Ni system have been presented for 1327 and 527°C [1975Kau], as well as for 1527, 1427, 1327 and 1277°C [1985Bar]. Both calculations are considered as approximations by their authors. As they deviate from experimental points, the experimental data should be preferred. The calculated sections at 1327 and 527°C [1975Kau] show identical features. The calculated isothermal sections from 1527 to 1277°C [1985Bar] also reproduce the general features of the isotherms of [1941Sch] and confirm the presence of a stable  $\beta, Al(Co, Ni)$  solid solution. The 1427°C section of [1985Bar] implies that the critical tie line joining the phases (Co, Ni), liquid and  $\beta, Al(Co, Ni)$  forms at a temperature above 1427°C, which contradicts the experimentally verified liquidus surface.

The isothermal sections of the phase diagram in the vicinity of the Co–Ni edge at 900 and 1100°C were reinvestigated by [1993Pov, 1996Kai], and at 1300°C by [1996Kai]. The results for the microanalysis of phase compositions in the above works are in agreement with the metallography data of [1941Sch] and the data on  $\gamma/\gamma'$  equilibria reported by [1994Jia].

Isothermal sections at 1300, 1100, 900°C are presented in Figs. 6, 7, 8 after [1996Kai], whose data are also consistent with previous results included in [1941Sch, 1994Jia, 1993Pov]. The 25°C isothermal section published in [1941Sch] is reproduced in Fig. 9. The data are corrected in accordance with the updated binary phase diagrams.

The isothermal sections in the Al-rich part of the system at 1170, 1100, 1050, 900, 850, 730 and 600°C (the latter is also valid for 400°C) are given in Figs. 10, 11, 12, 13, 14, 15, 16 after [1998Goe].

Figures 10, 11 exhibit phase equilibria at temperatures close to that of the ternary decagonal phase formation in result of the quasibinary peritectic reaction at 1175°C. This phase is shown to be in equilibria only with binary solid phases and liquid up to 1002°C, the temperature of the peritectoid formation of  $\tau_3$ . At 900°C the peritectic melting of the  $\epsilon$  phase, a  $NiAl_3$  based solid solution phase, occurs. At that temperature the maximum solubility of Ni in  $\tau_1$  is observed at 70 at.% Al and corresponding to a Ni:Co ratio of 74:26

(atomic ratio) (Fig. 13) [1998Goe], while [1996Gru3] at the practically same aluminium content (71 at.%) and the same temperature indicates the higher solubility corresponding to the 83:17 Ni:Co ratio. The addition of Cr stabilizes the  $\epsilon$  solid solution phase in the ternary towards higher temperatures, compared with the stability in binary alloys.  $(\text{Ni,Co})_3\text{Al}_4$  solid solution demonstrates similar behavior as one can see in Figs. 14, 15, 16. On the other hand, for the Y phase, dissolved Ni decreases the temperature range of existence compared with the binary Al-Co system, as one can see in Figs. 12, 13, 14, 15, 16. So this phase exists in the ternary system, as a ternary phase below 1083°C. Moreover, the ternary  $\tau_2$  phase, which possesses crystal structure close to that of Y phase, appears at lower temperature when Ni is increased, at constant Al content (Figs. 14, 15, 16 and Fig. 2).

### Temperature – Composition Sections

In Fig. 17 the  $\text{Co}_{20}\text{Ni}_{80}$ - $\text{Co}_{11}\text{Ni}_{44}\text{Al}_{45}$  isopleth is reproduced from [1991Hub] based on the data for the liquidus surface and the 1300, 1100, 900 and 25°C isothermal sections from [1941Sch], binaries and the data from [1966Rid]. The Figs. 18, 19, 20, 21, 22 and 23 after [1997Goe2, 1998Sch] demonstrate the complicated constitution of the Al-rich part of the Al-Co-Ni phase diagram.

### Thermodynamics

[1991Kek] measured partial thermodynamic properties with emphasis on chemical potentials for the first time for the ordered intermetallic  $\text{Ni}_3\text{Al}$  phase with different additions of cobalt. The investigation was carried out by vaporization measurements using Knudsen effusion mass spectrometry.

[1992Tso] developed a thermodynamic model based on the cluster variation method for the description of solid phases for ternary systems, with emphasis on the characterizations of ternary ordered phases and order-disorder transformations in alloys. The model is applied to study the equilibrium between  $\gamma$  (*cF4* disordered phase) and  $\gamma'$  (*cP4* ordered phase). It is shown that the present model is valid to describe accurately the degree of long-range order, thermochemical potentials and phase diagram data within the same free energy formalism and the same order of approximation.

[1998Bia] determined experimentally the specific heat  $C_p$  in the temperature interval from 1.5 to 36 K of the decagonal  $\text{Co}_{13}\text{Ni}_{16}\text{Al}_{71}$  quasicrystal, which was cut from the  $\text{Co}_{15}\text{Ni}_{15}\text{Al}_{70}$  alloy, rapidly cooled to room temperature after annealing at 1030°C for 5 d. A conventional relaxation method was used. Graphical dependence is presented in Fig. 24.

[1998Gru1] measured the enthalpies of formation  $\Delta H^f$  of the ordered  $\beta$  phase of compositions  $(\text{Co}_{1-x}\text{Ni}_x)_{0.50}\text{Al}_{0.50}$ ,  $(\text{Co}_{1-x}\text{Ni}_x)_{0.58}\text{Al}_{0.42}$  with  $0 \leq x \leq 1$  and  $\text{Co}_{0.15}\text{Ni}_{0.30}\text{Al}_{0.55}$  with B2 (*cP2*) structure at 1073 K using differential solution calorimetry. The values of the enthalpy of formation are given in Table 3. The authors noted that the composition dependence of the  $\Delta H^f$  can be described by the disorder model by Wagner and Schottky.

The melting enthalpies  $\Delta H_{\text{fus}}$ , temperatures  $T_{\text{fus}}$  and entropies  $\Delta S_{\text{fus}}$  of quasiperiodic and periodic phases are presented in Table 4 after [1999Hol] (DTA data).

The Bragg-Williams model for describing the composition and temperature dependence of thermodynamic properties of ternary B2 (*cP2*) phase has been applied successfully by [2001Bre] for the  $\beta$  phase in the Al-Co-Ni system and boundary binaries Al-Ni and Al-Co. With the activities and the integral enthalpies of formation as input data, values for the enthalpy and entropy of bonds between atoms were obtained. An analytical expression was derived for the dependence of the concentration of point defects (vacancies and antistructure atoms) on the composition and temperature.

### Notes on Materials Properties and Applications

Mechanical properties of the Al-Co-Ni alloys are investigated from the end of fifties, in particular, [1959Gua] investigated the influence of cobalt addition on the structure and hardness of the  $\gamma'$ ,  $\text{Ni}_3\text{Al}$  phase. The martensitic transformations in the  $\beta$ ,  $\text{Al}(\text{Co,Ni})$  phase in the alloys with aluminium content from 32 to 36 at.% quenched from high temperatures were studied by [1977Lit]. It was shown that introduction of cobalt at constant aluminium content influences on morphology of martensite like decreasing of aluminium

content, but to a much less degree. [1995Mis] obtained the dependence of the tensile flow stress on the strain for the  $\text{Co}_{14}\text{Ni}_{56}\text{Al}_{30}$  (at.%). Hot-workability of  $\beta$  phase is shown by [1996Kai] to be drastically improved by the introduction of the  $\gamma$  phase i.e. the hot workability is significantly related to the phase diagram. It was established that the temperature of the  $\beta$  phase martensitic transformation in the  $\beta + \gamma$  two-phase alloys increases with increasing of the annealing temperature. Planar interfaces between  $\gamma'$  and  $\beta$  phases in the ternary Al-Co-Ni diffusional couples annealed at temperatures ranging from 900 to 1300°C were observed by [2001Kai]. Interdiffusion in the  $\gamma'$  phase alloyed by up to 19 at.% Co was studied by [2002Gaz] in the sections corresponding to 22 at.% Al, 3.5 or 16 at.% Co at temperatures between 900 and 1200°C. The relations between the measured interdiffusion coefficients in the ordered  $\gamma'$  phase agree well with literature data for both the ordered  $\gamma'$  phases and also for the disordered Al-Ni and Co-Ni solid solutions.

Mechanical, electronic, magnetic properties of the decagonal phase, point and other defects and diffusion in this phase has been extensively studied. The reports are included in a number of monographs and text books.

The single quasicrystal elastic moduli  $c_{ij}$  of a decagonal  $\tau_1$  phase were determined by [1998Che] using resonance ultrasound spectroscopy at selected temperatures in the range between 5 and 290 K. It has been found to be transversely elastically isotropic to  $(0.02 \pm 0.04)$  %. There are weak temperature dependences of elastic moduli. The elastic Debye temperature calculated from  $c_{ij}$  measured at 5 K agrees well with the thermodynamic Debye temperature obtained from a low-temperature specific-heat experiment.

Compression experiments were performed by [2000Eda] on an Al-Co-Ni decagonal single quasicrystals grown by the floating zone method with different orientations of the compression axes: the tenfold direction ( $c_{\parallel}$ ), the twofold direction perpendicular to it ( $c_{\perp}$ ) and the direction inclined from the tenfold direction by about 45° ( $c_{45^\circ}$ ). For the samples inclined from the tenfold direction by about 45° a slip deformation was observed on the twofold prismatic slip plane and in the tenfold slip direction. Long straight screw dislocations were observed by TEM in the  $c_{45^\circ}$  compressed samples, indicating the existence of deep Peierls-potential valleys for the dislocation glide. The  $c_{\parallel}$  and  $c_{\perp}$  compressed samples showed slip deformations along more than two types of pyramidal slip planes.

Data on electrical properties and magnetic behavior of the Al-Co-Ni alloys were obtained by [1991Mar, 1992Poo, 1992Sch, 1993Wan, 1997Goe3, 1998Sch, 1999Cal, 2001Oik1, 2001Oik2, 2002Liu, 2002Mor] and [2002Mur]. In particular, while investigating phase equilibria in the Al-CoAl-NiAl subsystem [1997Goe3] and [1998Sch], performed the magneto-thermal analysis (MTA) by recording magnetic susceptibility versus temperature using a Faraday type magnetic balance. From the magnetic behavior of the alloys, the character of order-disorder transformations and the solid state formation of the  $\beta$ ,  $\text{Ni}_3\text{Al}_4$  phase was determined and the position of the  $\beta$  phase homogeneity region could be clarified. In the homogeneous region of the  $\tau_1$  phase no simple relationship of magnetic properties and composition is found. [2001Oik1, 2001Oik2] investigated magnetic properties of the  $\beta$  phase, which possesses ferromagnetism.

Diffusion in the Al-Co-Ni alloys was studied by [2000Kho, 2000Zum, 2001Kai] and [2002Gaz]. Self-diffusion of  $^{57}\text{Co}$  in decagonal quasicrystals was investigated as a function of the temperature by means of the radioactive tracer method [2000Kho]. In combination with serial sectioning, diffusivities were measured over a large temperature range from 459 to 1000°C. Using the same method, [2000Zum] measured the diffusion coefficient of  $^{60}\text{Co}$  in a single decagonal  $\text{Co}_{16.0}\text{Ni}_{11.8}\text{Al}_{72.2}$  quasicrystal. The results are discussed together with data on similar diffusion investigations on icosahedral quasicrystals, and a diffusion mechanism via vacancies is suggested.

### Miscellaneous

Partitioning of Co between the  $\gamma$ ,  $\gamma'$  and  $\beta$  phases at 800 to 1300°C were studied by [1994Jia] using diffusion couples. The compositional dependence of the partition coefficients between  $\gamma$  and  $\gamma'$  phases at 1100°C is shown in Fig. 25 after [1994Jia].

Dependences of the lattice parameters of the  $\beta$ , Al(Co,Ni) solid solutions on the aluminium content is presented in Fig. 26 after [1966Rid]. The density measurements reveal that the steep drops in lattice

parameters which take place when the aluminium content exceeds ~50 at.%, are accompanied by the omission of atoms from the lattice.

[2000Wid] extended the generalized pseudo-potential theory of interatomic potentials in binary transition-metal aluminides to the ternary system, and applied the first-principle pair potential calculation to the aluminium-rich corner for Al-Co-Ni alloys. The results reproduce many features of the known phase diagram, placing known stable and metastable structures on or near the convex hills of the energy-composition plots.

The generalized vibrational density of states (GVDOS) was determined by [1996Mih] for decagonal  $\text{Co}_{15}\text{Ni}_{15}\text{Al}_{70}$  using cold neutron inelastic scattering techniques. A computer modeling of the GVDOS was proposed using realistic pair potentials. [1999Yam] studied the relation between the electron concentration and anomalous dip appearing on the  $[110]\text{TA}_1$  phonon branch of the  $\beta_1$  phase with B2 (cP2) structure in Ni-Al and established that by substituting Ni by Co, the dip-positions shifts toward the Brillouin zone center. The obtained results indicate clearly that the dip is not any precursor of the martensitic transition but a reflection of the electronic property in the  $\beta_1$  phase

[2000Elh] analyzed the experimentally measured temperature dependence of the phonon density of states (DOS) in the decagonal phase obtained by [1997Dug] in the range 27 to 827°C, assuming that the relationship between the DOS at different temperatures can be expressed in terms of frequency shifts of the phonon modes. It was concluded that the temperature-dependent frequency shifts are anomalously large at high temperatures, increasing significantly the vibrational entropy. The authors expect that this contribution can not be neglected in the competition between quasicrystals and related crystalline phases.

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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	<i>cF4</i> <i>Fm<math>\bar{3}m</math></i> Cu	$a = 404.88$	pure Al, $T = 24^{\circ}\text{C}$ [V-C]
$\text{Co}_x\text{Ni}_y\text{Al}_{1-x-y}$			$x = 0, y = 0$ to 0.004 [2003Sal]
$\gamma, (\text{Co}_{1-x}\text{Ni}_x)$  ( $\gamma\text{Co}$ ) (h) 1495 - 422	<i>cF4</i> <i>Fm<math>\bar{3}m</math></i> Cu	$a = 354.46$	$0 < x < 1$  pure Co [V-C]
(Ni) < 1455		$a = 352.40$ $a = 352.32$	pure Ni, $T = 25^{\circ}\text{C}$ [1984Och, Mas2] [V-C]
$\epsilon, (\text{Co}) (\text{r})$ ≤ 422	<i>hP2</i> <i>P6<math>_3</math>/mmc</i> Mg	$a = 250.71$ $c = 406.95$	[V-C]
$\text{Co}_2\text{Al}_9$ < 970	<i>mP22</i> <i>P2<math>_1</math>/a</i>	$a = 855.6$ $b = 629.0$ $c = 621.3$ $\beta = 94.76^{\circ}$	[1950Dou]
$(\text{Co}_{1-x}\text{Ni}_x)_2\text{Al}_9$			5 at.% Ni, $T = 850$ to $750^{\circ}\text{C}$ [1998Goe]
O- $\text{Co}_4\text{Al}_{13}$ < 1092	<i>oP102</i> <i>Pnm2<math>_1</math></i>	$a = 815.8$ $b = 1234.7$	[1996Gru1, 1996Bur] ~1.5 at.% Ni, $T = 600$ to $900^{\circ}\text{C}$
O- $(\text{Co}_{1-x}\text{Ni}_x)_4\text{Al}_{13}$	O- $\text{Co}_4\text{Al}_{13}$	$c = 1445.2$	
M- $\text{Co}_4\text{Al}_{13}$ < 1090	<i>mC102</i> <i>C2/m</i> $\text{Fe}_4\text{Al}_{13}$	$a = 1517.3$ $b = 810.9$ $c = 1234.9$ $\beta = 107.84^{\circ}$	[1996Fre]  ~1.5 at.% Ni, $T = 600$ to $900^{\circ}\text{C}$ [1998Goe]
Y 1083 < $T$ < 1127	<i>oI96</i> <i>Immm</i>	$a = 1531.0$ $b = 1235.0$ $c = 758.0$	[1998Ma] [1996Gru1]
	<i>mC34</i> <i>C2/m</i> $\text{Os}_4\text{Al}_{13}$	$a = 1707.1$ $b = 409.9$ $c = 749.1$ $\beta = 116.17^{\circ}$ $a = 1704.0$ $b = 409.0$ $c = 758.0$ $\beta = 116.0^{\circ}$	[1995Zha]  [1998Ma]
Y, solid solution			Maximum solubility of Ni is 6.5 at.% at $850^{\circ}\text{C}$ [1998Goe]
Z < 1153	C-centred monoclinic	$a = 3984.0$ $b = 814.8$ $c = 3223.0$ $\beta = 107.97^{\circ}$	[1998Mo]
Z, solid solution			~1.5 at.% Ni, $T = 600$ to $1100^{\circ}\text{C}$ [1998Goe] 4-5 at.% Ni [2003Gru]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Co <sub>2</sub> Al <sub>5</sub> < 1182	<i>hP</i> 28 <i>P</i> 6 <sub>3</sub> / <i>mmc</i> Co <sub>2</sub> Al <sub>5</sub>	<i>a</i> = 767.2 <i>c</i> = 760.5	[1996Gru1, 1996Bur]
(Co <sub>1-x</sub> Ni <sub>x</sub> ) <sub>2</sub> Al <sub>5</sub>			~5.5 at.% Ni, 750°C [1998Goe]
D <sub>2</sub> (Al-Co)	decagonal	n* = 800	~Co <sub>27</sub> Al <sub>73</sub> , metastable [1997Gru1]
β, CoAl < 1640	<i>cP</i> 2 <i>Pm</i> $\bar{3}$ <i>m</i> CsCl	<i>a</i> = 285.7 <i>a</i> = 286.2 <i>a</i> = 285.9	20 to 54 at.% Al [2003Gru] 52 at.% Al [1966Rid] 50 at.% Al [1966Rid] 43 at.% Al [1966Rid]
β, NiAl < 1676		<i>a</i> = 287.04 <i>a</i> = 287.26 <i>a</i> = 286.0 <i>a</i> = 287.0 <i>a</i> = 288.72(2) <i>a</i> = 287.98(2) <i>a</i> = 289.0 <i>a</i> = 289.7 <i>a</i> = 290.4 <i>a</i> = 291.2 <i>a</i> = 291.9 <i>a</i> = 293.2	42 to 69.2 at.% Ni [Mas2] 57.7 at.% Ni [L-B] 46.6 at.% Ni [L-B] [1987Kha] 63 at.% Ni [1993Kha] 50 at.% Ni [1996Pau] 54 at.% Ni [1996Pau]; <i>T</i> = 0°C [1971Cli] <i>T</i> = 200°C [1971Cli] <i>T</i> = 400°C [1971Cli] <i>T</i> = 600°C [1971Cli] <i>T</i> = 800°C [1971Cli] <i>T</i> = 1000°C [1971Cli]
β, (Co <sub>1-x</sub> Ni <sub>x</sub> )Al			<i>x</i> = 0 to 1; in the alloys annealed at <i>T</i> = 1000°C to 1200°C (7 d), slowly cooled to 300°C and quenched [1966Rid]: <i>a</i> = 286.4 Co <sub>12</sub> Ni <sub>48</sub> Al <sub>40</sub> <i>a</i> = 287.3 Co <sub>11</sub> Ni <sub>44</sub> Al <sub>45</sub> <i>a</i> = 288.1 Co <sub>10</sub> Ni <sub>40</sub> Al <sub>50</sub> <i>a</i> = 288.2 Co <sub>9.8</sub> Ni <sub>39.2</sub> Al <sub>51</sub> <i>a</i> = 287.5 Co <sub>9.6</sub> Ni <sub>38.4</sub> Al <sub>52</sub> <i>a</i> = 286.8 Co <sub>9.4</sub> Ni <sub>37.6</sub> Al <sub>53</sub> <i>a</i> = 286.5 Co <sub>29</sub> Ni <sub>29</sub> Al <sub>42</sub> <i>a</i> = 286.4 Co <sub>12</sub> Ni <sub>48</sub> Al <sub>40</sub> <i>a</i> = 287.1 Co <sub>27</sub> Ni <sub>27</sub> Al <sub>46</sub> <i>a</i> = 287.5 Co <sub>25</sub> Ni <sub>25</sub> Al <sub>50</sub> <i>a</i> = 286.6 Co <sub>23</sub> Ni <sub>23</sub> Al <sub>52</sub> <i>a</i> = 285.6 Co <sub>22.5</sub> Ni <sub>22.5</sub> Al <sub>55</sub> <i>a</i> = 286.3 Co <sub>39.2</sub> Ni <sub>16.8</sub> Al <sub>44</sub> <i>a</i> = 286.7 Co <sub>36.4</sub> Ni <sub>15.6</sub> Al <sub>48</sub> <i>a</i> = 287.1 Co <sub>35</sub> Ni <sub>15</sub> Al <sub>50</sub> <i>a</i> = 287.0 Co <sub>34.65</sub> Ni <sub>14.85</sub> Al <sub>50.5</sub> <i>a</i> = 285.9 Co <sub>32.9</sub> Ni <sub>14.1</sub> Al <sub>53</sub> <i>a</i> = 285.5 Co <sub>32.2</sub> Ni <sub>13.8</sub> Al <sub>54</sub> <i>a</i> = 285.0 Co <sub>31.15</sub> Ni <sub>13.35</sub> Al <sub>55.5</sub> <i>a</i> = 290.2 33 at.% Co, <i>T</i> = 600°C [1971Cli] <i>a</i> = 290.9 33 at.% Co, <i>T</i> = 800°C [1971Cli]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\epsilon$ , NiAl <sub>3</sub> < 856	<i>oP16</i> <i>Pnma</i> NiAl <sub>3</sub>	$a = 661.15$ $b = 736.64$ $c = 481.18$	[L-B]
		$a = 661.3(1)$ $b = 736.7(1)$ $c = 481.1(1)$	[1996Vik]
	<i>oP16</i> <i>Pnma</i> CFe <sub>3</sub>	$a = 659.8$ $b = 735.1$ $c = 480.2$	[1997Bou, V-C]
$\epsilon$ , (Ni <sub>1-x</sub> Co <sub>x</sub> )Al <sub>3</sub>			Maximum solubility of Co is ~10 at.%, at $T = 850^\circ\text{C}$ [1998Goe]
$\delta$ , Ni <sub>2</sub> Al <sub>3</sub> < 1138	<i>hP5</i> <i>Pm\bar{3}m1</i> Ni <sub>2</sub> Al <sub>3</sub>	$a = 403.63$ $c = 490.65$	36.8 to 40.5 at.% Ni [Mas2] [L-B]
		$a = 402.8$ $c = 489.1$	[1997Bou, V-C]
$\delta$ , (Ni <sub>x</sub> Co <sub>1-x</sub> ) <sub>2</sub> Al <sub>3</sub>			4.6 at.% Co, $T = 1050^\circ\text{C}$ [1998Goe]; 20 at.% Co, $T = 900^\circ\text{C}$ [1993Pov, 1998Goe]; 18 at.% Co, $T = 600$ to $730^\circ\text{C}$ [1998Goe]
$\beta'$ , Ni <sub>3</sub> Al <sub>4</sub> < 702	<i>cI112</i> <i>Ia\bar{3}d</i> Ni <sub>3</sub> Ga <sub>4</sub>	$a = 1140.8(1)$	[1989Ell, V-C]
$\beta'$ , (Ni <sub>x</sub> Co <sub>1-x</sub> ) <sub>3</sub> Al <sub>4</sub>			Maximum solubility of Co is 22 at.% at 57 at.% Al [1998Goe]
Ni <sub>5</sub> Al <sub>3</sub> < 723	<i>oC16</i> <i>Cmmm</i> Pt <sub>5</sub> Ga <sub>3</sub>	$a = 753$ $b = 661$ $c = 376$	63 to 68 at.% Ni [1993Kha, Mas2]; at 63 at.% Ni [1993Kha]
$\gamma'$ , Ni <sub>3</sub> Al < 1372	<i>cP4</i> <i>Pm\bar{3}m</i> Cu <sub>3</sub> Au	$a = 356.6$ $a = 357.0$ $a = 356.77$ $a = 356.32$ $a = 357.92$ $a = 357.1$	73 to 76 at.% Ni [Mas2]; [1952Tay], [1984Och, 1959Gua], [1986Hua], disordered [1998Rav], ordered [1998Rav]; 15 at.% Co [1959Gua] [1996Kai]: 8 at.% Co, $T = 1300^\circ\text{C}$ , 20 at.% Co, $T = 1100^\circ\text{C}$ , 24 at.% Co, $T = 900^\circ\text{C}$
(Ni <sub>1-x</sub> Co <sub>x</sub> ) <sub>3</sub> Al			
Ni <sub>2</sub> Al <sub>9</sub>	<i>mP22</i> <i>P2<sub>1</sub>/c</i> Ni <sub>2</sub> Al <sub>9</sub>	$a = 868.5(6)$ $b = 623.2(4)$ $c = 618.5(4)$ $\beta = 96.50(5)^\circ$	Metastable; [1988Li, 1997Poh]:

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\text{Ni}_x\text{Al}_{1-x}$ $0.60 < x < 0.68$	$tP4$ $P4/mmm$ AuCu	$a = 383.0$	Martensite, metastable [1993Kha]
		$c = 320.5$	
		$a = 379.5$	
		$c = 325.6$	
		$a = 379.5$	
		$c = 325.6$	
		$a = 379.5$	
		$c = 325.6$	
		$a = 379.9$ to $380.4$	
		$c = 322.6$ to $323.3$	
		$a = 371.7$ to $376.8$	
		$c = 335.3$ to $339.9$	
		$a = 378.00$	
		$c = 328.00$	
	$m^{**}$	$a = 418$	[1992Mur]
		$b = 271$	
		$c = 1448$	
		$\alpha = 90^\circ$	
		$\beta = 93.4^\circ$	
		$\gamma = 90^\circ$	
$\text{Ni}_2\text{Al}$	$hP3$ $P\bar{3}m1$ $\text{CdI}_2$	$a = 407$	Metastable [1993Kha]
		$b = 499$	
	$a^*126$ $P\bar{1}$	$a = 1252$	[1994Mur]
		$b = 802$	
		$c = 1526$	
		$\alpha = 90^\circ$	
		$\beta = 109.7^\circ$	
		$\gamma = 90^\circ$	
$\text{D}_1(\text{Al-Ni})$	decagonal	$n \approx 400$	Metastable [1988He, 1988Li], $\text{Ni}_{31}\text{Al}_{69}$ [1997Gru1]
$\text{D}_4(\text{Al-Ni})$	decagonal	$n \approx 400$	Metastable [1988He, 1988Li]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* $\tau_1$ , $\leq 1175$	decagonal		In $\text{Co}_{15}\text{Ni}_{15}\text{Al}_{70}$ , called as D [1989Tsa1] $\text{Co}_{20}\text{Ni}_{10}\text{Al}_{70}$ , single-crystal [1990Yam]; the overall composition range $\text{Co}_{22}\text{Ni}_5\text{Al}_{73}$ to $\text{Co}_{5.5}\text{Ni}_{24.5}\text{Al}_{70}$ [1997Gru1];
	$P10/mmm$ , decagonal $P10_5/mmc$ , decagonal	$d_i = 339.3$ $d_5 = 408.07$ $\alpha_{ij} = 60^\circ$ $\alpha_{i5} = 90^\circ$ $i, j = 1 \text{ to } 4$	$\text{Co}_{15}\text{Ni}_{15}\text{Al}_{70}$ , single-crystal cut from annealed at $850^\circ\text{C}$ 1 d ingot, five-dimensional unit-cell parameters [1993Ste1];
	$D_1$	$n \approx 400$	$\text{Co}_{5.5}\text{Ni}_{24.5}\text{Al}_{70}$ , perfect structure of the single crystal, 900 to $1100^\circ\text{C}$ [1997Gru1]
		$n \approx 410$	Ni-rich, perfect structure of high temperature modification [1998Rit]
	$P\overline{10}$ decagonal ( $D_1?$ )	$d_1 = 475$ $d_2 = 336$ $d_3 = 336$ $d_4 = 475$ $d_5 = 817.1$ $\alpha_{12} = 69.295^\circ$ $\alpha_{13} = 45^\circ$ $\alpha_{14} = 41.410^\circ$ $\alpha_{23} = 90^\circ$ $\alpha_{24} = 45^\circ$ $\alpha_{34} = 69.295^\circ$ $\alpha_{i5} = 90^\circ$ ( $i = 1 \text{ to } 4$ )	in $\text{Co}_{6.7}\text{Ni}_{22.7}\text{Al}_{70.6}$ alloy, at room temperature, five-dimensional unit cell parameters [2002Cer];
	$D_2$	$n \approx 820$	Co-rich modification [1998Rit]
	SI SII		Superstructures of $D_2(?)$ [1998Rit]
			in $\text{Co}_{12}\text{Ni}_{18}\text{Al}_{70}$ alloy, annealed at $900^\circ\text{C}$ 48 h [2002Hir1], and in $\text{Co}_{11}\text{Ni}_{16.5}\text{Al}_{72.5}$ alloy, annealed at $900^\circ\text{C}$ (40 h) [2002Hir1]; in $\text{Co}_{14.5}\text{Ni}_{14.5}\text{Al}_{71}$ alloy, annealed at $1000^\circ\text{C}$ 65 h [2002Hir2]; in $\text{Co}_{14.5}\text{Ni}_{14.5}\text{Al}_{71}$ alloy, annealed at $900^\circ\text{C}$ 72 h [2002Hir1];
	$D_{bf}$ $D_{cf}$ $D_{bg}$ $D_{ag}$ $D_{cg}$	(Ordered decagonal) (Disordered decagonal Co-rich)	stable variants of decagonal phase in range 9.5 to 16 at.% Ni, 11 to 20 at.% Co, 70 to 72.5 at.% Al, in as-cast and annealed at 800 to $1000^\circ\text{C}$ alloys

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
< 900°C	1D	$n = 3070$	one-dimensional quasicrystal, in range 18 to 22 at.% Co, 70-71.5 at.% Al;
	PD <sub>1</sub>	pseudo-decagonal $a = 3900$ $b = 800$ $c = 3800$	in range 9.5 to 16 at.% Ni, 11 to 20 at.% Co, 70 to 72.5 at.% Al in as-cast and annealed at 800 to 1000°C alloys [1998Gru2]
	PD <sub>2</sub>	$a = 3900$ $b = 800$ $c = 3800$	
	PD <sub>3</sub>	$a = 3900$ $b = 800$ $c = 3800$	
	PD <sub>4</sub>	$a = 3900$ $b = 800$ $c = 3800$	
	PD <sub>5</sub>	$a = 3900$ $b = 800$ $c = 3800$	
* $\tau_2$ , < 880	<i>oI96</i> Immm	$a = 1206.46$ $b = 755.53$ $c = 1535.3$ $a = 1252$ $b = 802$ $c = 1526$	Co <sub>2</sub> NiAl <sub>9</sub> , called as Y <sub>2</sub> [1998Gri]; 6 to 8.5 at.% Ni, 75 at.% Al [1998Goe]; Co <sub>17</sub> Ni <sub>8.2</sub> Al <sub>74.8</sub> , quenched after annealing at 850°C 3 d [1998Gri]  Co <sub>19</sub> Ni <sub>6</sub> Al <sub>75</sub> , quenched after annealing at 600°C (30 d) [1998Gri]
* $\tau_3$ , < 1002	orthorhombic (?) triclinic	$d_1 = 735$ $d_2 = 583$ $d_3 = 364$ $d_1 \wedge d_2 = 74.3^\circ$ $d_2 \wedge d_3 = 80.5^\circ$	Co <sub>18.5</sub> Ni <sub>14.0</sub> Al <sub>67.5</sub> , called as X [1991Kek], the overall composition range: 7 to 16 at.% Ni, 69 to 69.5 at.% Al [1998Goe]; [1991Kek]; [1997Goe3]
“W-CoNiAl”	Cm	$a = 3966.8$ $b = 815.8$ $c = 2339.2$ $\beta = 90.05^\circ$	in Co <sub>20</sub> Ni <sub>7.5</sub> Al <sub>72.5</sub> alloy annealed at 950°C 20 d [2002Sug]

\* $n$  is a parameter of periodicity

**Table 2:** Invariant Equilibria in the Al-CoAl-NiAl Subsystem

Reaction	$T$ [°C]	Type	Phase	Composition (at.%)		
				Al	Co	Ni
$L + \beta \rightleftharpoons \tau_1$	1175	$P_{3(\max)}$	L	72	25	~3
			$\beta$	55	35	10
			$\tau_1$	71	26	~3
$L + \beta \rightleftharpoons \text{Co}_2\text{Al}_5 + \tau_1$	1160	$U_2$	L	76.0	23.5	1.5
			$\beta$	55.0	35.5	9.5
			$\text{Co}_2\text{Al}_5$	72.0	26.0	2.0
			$\tau_1$	71.5	25.0	3.5
$L + \text{Co}_2\text{Al}_5 \rightleftharpoons Z + \tau_1$	1136	$U_3$	L	77.5	21.5	1.0
			$\text{Co}_2\text{Al}_5$	72.0	26.0	2.0
			Z	74.8	24.5	0.7
			$\tau_1$	73.0	22.5	4.5
$L + Z \rightleftharpoons Y + \tau_1$	1080	$U_4$	L	79.0	18.0	3.0
			Z	74.5	24	1.5
			Y	75.0	23.5	1.3
			$\tau_1$	73.0	22.0	5.0
$L + \beta \rightleftharpoons \delta + \tau_1$	1048	$U_5$	L	76.0	5.0	19.0
			$\beta$	56.5	12.5	31.0
			$\delta$	59.5	10.0	30.5
			$\tau_1$	69.5	9.5	21.0
$\beta + \text{Co}_2\text{Al}_5 + \tau_1 \rightleftharpoons \tau_3$	1002	$P_1$	$\beta$	55	22.5	22.5
			$\text{Co}_2\text{Al}_5$	72.0	26.0	2
			$\tau_1$	71.5	23.0	5.5
			$\tau_3$	69.5	23.5	7.0
$L + \text{O-Co}_4\text{Al}_{13} \rightleftharpoons Y + \text{Co}_2\text{Al}_9$	950	$U_6$	L	87.5	9.5	3
			O-Co <sub>4</sub> Al <sub>13</sub>	76.0	22.5	1.5
			Y	75.5	22.0	2.5
			$\text{Co}_2\text{Al}_9$	82.0	16.5	1.5
$\beta + \tau_2 \rightleftharpoons \tau_3 + \delta$	918	$U_7$	$\beta$	56.0	13.5	30.5
			$\tau_1$	70.0	14.0	16.0
			$\tau_3$	69.5	15.0	15.5
			$\delta$	59.5	9.5	31.0
$L + Y \rightleftharpoons \tau_1 + \text{Co}_2\text{Al}_9$	906	$U_8$	L	85.0	6.7	8.3
			Y	75.5	18.0	6.5
			$\tau_1$	73.5	16.0	10.5
			$\text{Co}_2\text{Al}_9$	82.0	13.0	5.0
$L + \delta + \tau_1 \rightleftharpoons \varepsilon$	900	$P_2$	L	84.0	1.0	15.0
			$\delta$	63.0	1.5	35.5
			$\tau_1$	70.0	6.5	23.5
			$\varepsilon$	75.0	2.4	22.6
$L + \tau_1 \rightleftharpoons \text{Co}_2\text{Al}_9 + \varepsilon$	888	$U_9$	L	85.0	2.5	12.5
			$\tau_1$	73.0	13.5	13.5
			$\text{Co}_2\text{Al}_9$	82.0	13.5	4.5
			$\varepsilon$	75.0	5.6	19.0



Reaction	$T$ [°C]	Type	Phase	Composition (at.%)		
				Al	Co	Ni
$Y + \tau_1 + \text{Co}_2\text{Al}_9 \rightleftharpoons \tau_2$	880	$P_3$	Y	75.5	18.0	6.5
			$\tau_1$	73.0	16.5	10.5
			$\text{Co}_2\text{Al}_9$	82.5	13.0	4.5
			$\tau_2$	75.0	16.5	8.5
$\tau_1 + \text{Co}_2\text{Al}_9 \rightleftharpoons \tau_2 + \varepsilon$	860	$U_{10}$	$\tau_1$	73.0	14.0	13.0
			$\text{Co}_2\text{Al}_9$	82.5	13.0	4.5
			$\tau_2$	75.0	16.0	9.0
			$\varepsilon$	75.0	10.0	15.0
$\beta + \tau_3 + \delta \rightleftharpoons \beta'$	850	$P_4$	$\beta$	56.0	13.5	30.5
			$\tau_3$	69.0	15.1	16.0
			$\delta$	60.0	9.0	31.0
			$\beta'$	57.0	13.0	30.0
$\beta + \tau_3 \rightleftharpoons \text{Co}_2\text{Al}_5 + \beta'$	750	$U_{11}$	$\beta$	56.5	22.0	21.5
			$\tau_3$	69.0	20.5	10.5
			$\text{Co}_2\text{Al}_5$	71.5	23.0	5.5
			$\beta'$	60.0	20.0	20.0
$L \rightleftharpoons \text{Co}_2\text{Al}_9 + (\text{Al}) + \varepsilon$	643	$E_1$	L	97.3	0.2	2.5
			$\text{Co}_2\text{Al}_9$	91.8	13.0	5.2
			(Al)	99.6	0.1	0.2
			$\varepsilon$	75.2	0.4	24.4

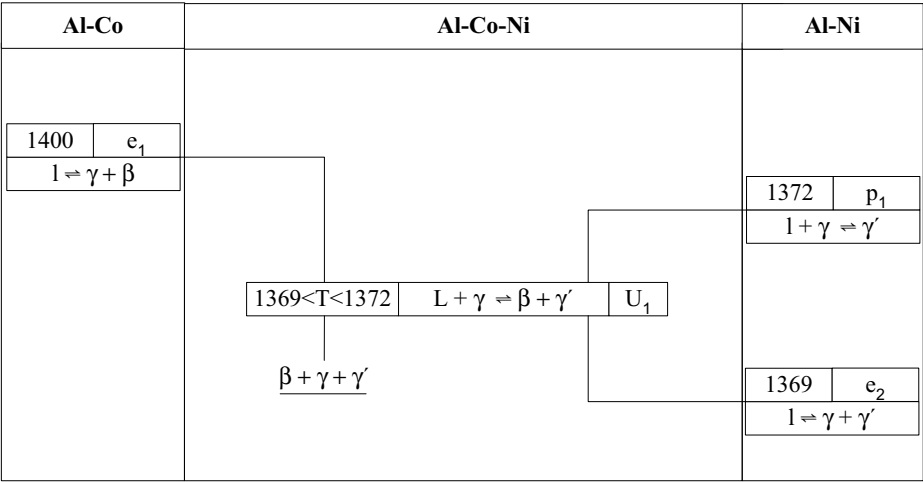
**Table 3:** Enthalpies of Formation  $\Delta H^f$  of the Ordered  $\beta$  phase with Compositions  $(\text{Co}_{1-x}\text{Ni}_x)_{0.50}\text{Al}_{0.50}$ ,  $(\text{Co}_{1-x}\text{Ni}_x)_{0.58}\text{Al}_{0.42}$  with  $0 \leq x \leq 1$  and  $\text{Co}_{0.15}\text{Ni}_{0.30}\text{Al}_{0.55}$  with B2 (*cP2*) Structure at 1073 K, Referred to Solid Ni ( $\text{Ni}_s$ ), Solid Co ( $\text{Co}_s$ ) and Liquid Al ( $\text{Al}_l$ ), [1998Gru1]

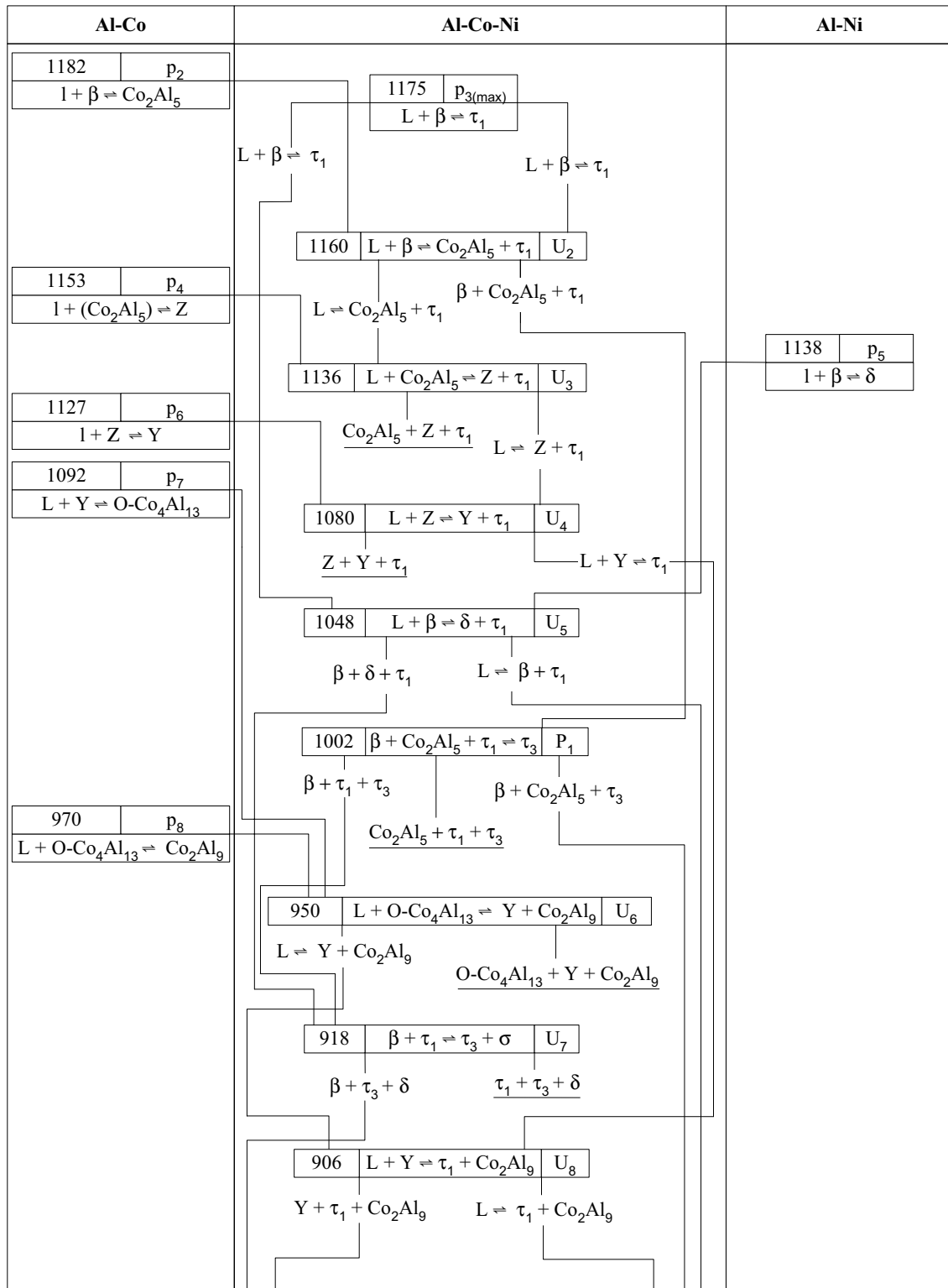
Composition of the $\beta$ phase (B2)	$\Delta H^f_{\text{B2}}$ [kJ·mol <sup>-1</sup> ]	Reaction of formation
$\text{Co}_{0.50}\text{Al}_{0.50}$	$-66.05 \pm 0.05$	$\text{Co}_s + \text{Al}_l \rightarrow \text{B2}$
$\text{Co}_{0.42}\text{Ni}_{0.08}\text{Al}_{0.50}$	$-66.31 \pm 0.10$	$\text{Co}_s + \text{Ni}_s + \text{Al}_l \rightarrow \text{B2}$
$\text{Co}_{0.38}\text{Ni}_{0.20}\text{Al}_{0.42}$	$-54.25 \pm 0.08$	$\text{Co}_s + \text{Ni}_s + \text{Al}_l \rightarrow \text{B2}$
$\text{Co}_{0.29}\text{Ni}_{0.29}\text{Al}_{0.42}$	$-55.10 \pm 0.15$	$\text{Co}_s + \text{Ni}_s + \text{Al}_l \rightarrow \text{B2}$
$\text{Co}_{0.25}\text{Ni}_{0.25}\text{Al}_{0.50}$	$-67.24 \pm 0.06$	$\text{Co}_s + \text{Ni}_s + \text{Al}_l \rightarrow \text{B2}$
$\text{Co}_{0.20}\text{Ni}_{0.38}\text{Al}_{0.42}$	$-57.39 \pm 0.14$	$\text{Co}_s + \text{Ni}_s + \text{Al}_l \rightarrow \text{B2}$
$\text{Co}_{0.17}\text{Ni}_{0.33}\text{Al}_{0.50}$	$-68.48 \pm 0.06$	$\text{Co}_s + \text{Ni}_s + \text{Al}_l \rightarrow \text{B2}$
$\text{Co}_{0.15}\text{Ni}_{0.30}\text{Al}_{0.55}$	$-66.73 \pm 0.07$	$\text{Co}_s + \text{Ni}_s + \text{Al}_l \rightarrow \text{B2}$
$\text{Co}_{0.13}\text{Ni}_{0.37}\text{Al}_{0.50}$	$-66.65 \pm 0.32$	$\text{Co}_s + \text{Ni}_s + \text{Al}_l \rightarrow \text{B2}$
$\text{Co}_{0.08}\text{Ni}_{0.42}\text{Al}_{0.50}$	$-70.04 \pm 0.12$	$\text{Co}_s + \text{Ni}_s + \text{Al}_l \rightarrow \text{B2}$
$\text{Ni}_{0.50}\text{Al}_{0.50}$	$-71.27 \pm 0.13$	$\text{Ni}_s + \text{Al}_l \rightarrow \text{B2}$

**Table 4:** Melting Enthalpies  $\Delta H_{\text{fus}}$ , Melting Temperatures  $T_{\text{fus}}$  and Melting Entropies  $\Delta S_{\text{fus}}$  of Quasiperiodic and Periodic Phases [1999Hol]

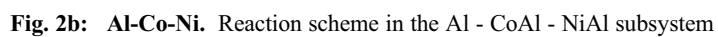
Alloy Composition	Heat Treatment	Phase	$\Delta H_{\text{fus}}$ [kJ·mol <sup>-1</sup> ]	$T_{\text{fus}}$ [K (°C)]	$\Delta S_{\text{fus}}$ [J·mol <sup>-1</sup> ·K <sup>-1</sup> ]
Co <sub>21.8</sub> Ni <sub>5.5</sub> Al <sub>72.7</sub>	1373 K (1100°C), 24 h	D	13.1 ± 0.4	1440 ± 5 (1167 ± 5)	9.1 ± 0.6
Co <sub>18</sub> Ni <sub>9.5</sub> Al <sub>72.5</sub>	1273 K (1000°C), 119 h	D	10.4 ± 0.3	1383 ± 5 (1110 ± 5)	7.5 ± 0.5
Co <sub>14.5</sub> Ni <sub>14.5</sub> Al <sub>71</sub>	1073 K (800°C), 75 h	D	10.3 ± 0.3	1400 ± 5 (1127 ± 5)	7.4 ± 0.5
Co <sub>18</sub> Ni <sub>7</sub> Al <sub>75</sub>	1148 K (875°C), 90 h	Y	14.2 ± 0.4	1368 ± 5 (1095 ± 5)	10.4 ± 0.7
Co <sub>21</sub> Ni <sub>5</sub> Al <sub>74</sub>	1173 K (900°C), 190 h	Z	14.4 ± 0.4	1405 ± 5 (1132 ± 5)	10.3 ± 0.8

**Fig. 1: Al-Co-Ni.**  
Reaction scheme in  
the partial Co - CoAl  
- NiAl - Ni system

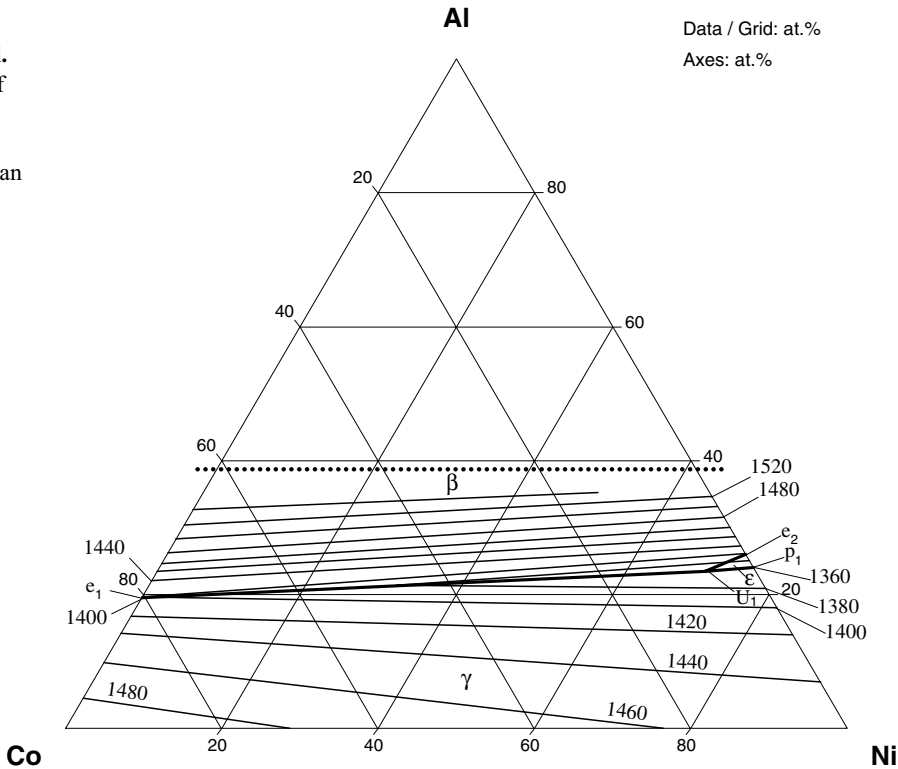




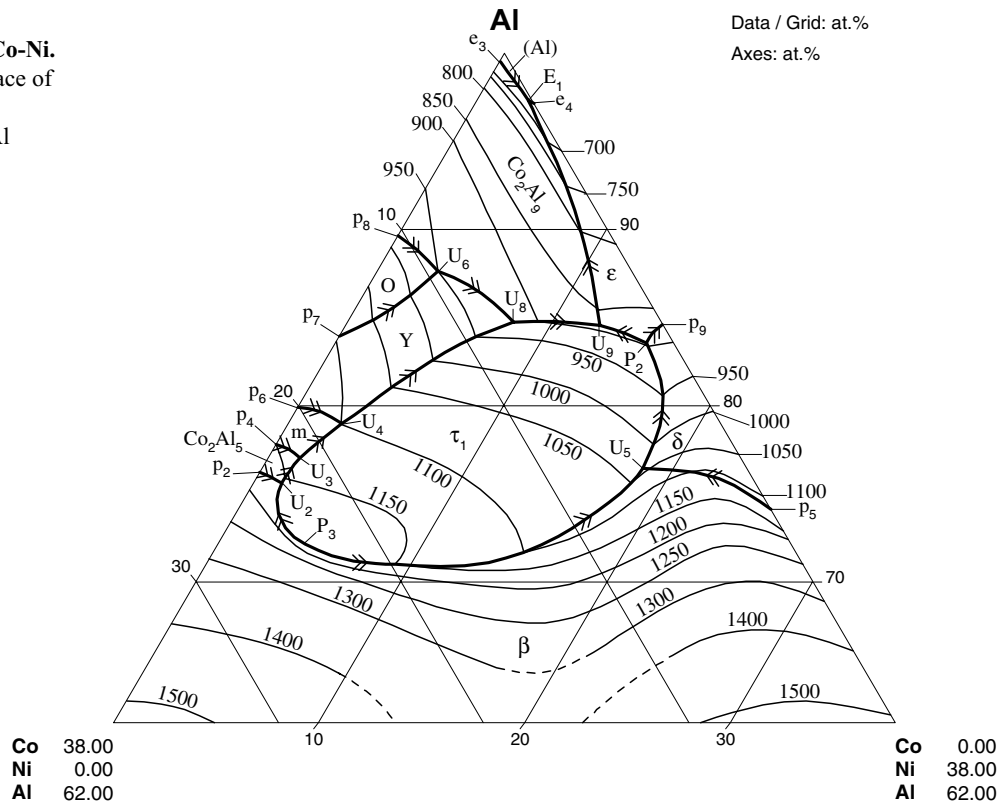
**Fig. 2a:** Al-Co-Ni. Reaction scheme in the Al - CoAl - NiAl subsystem



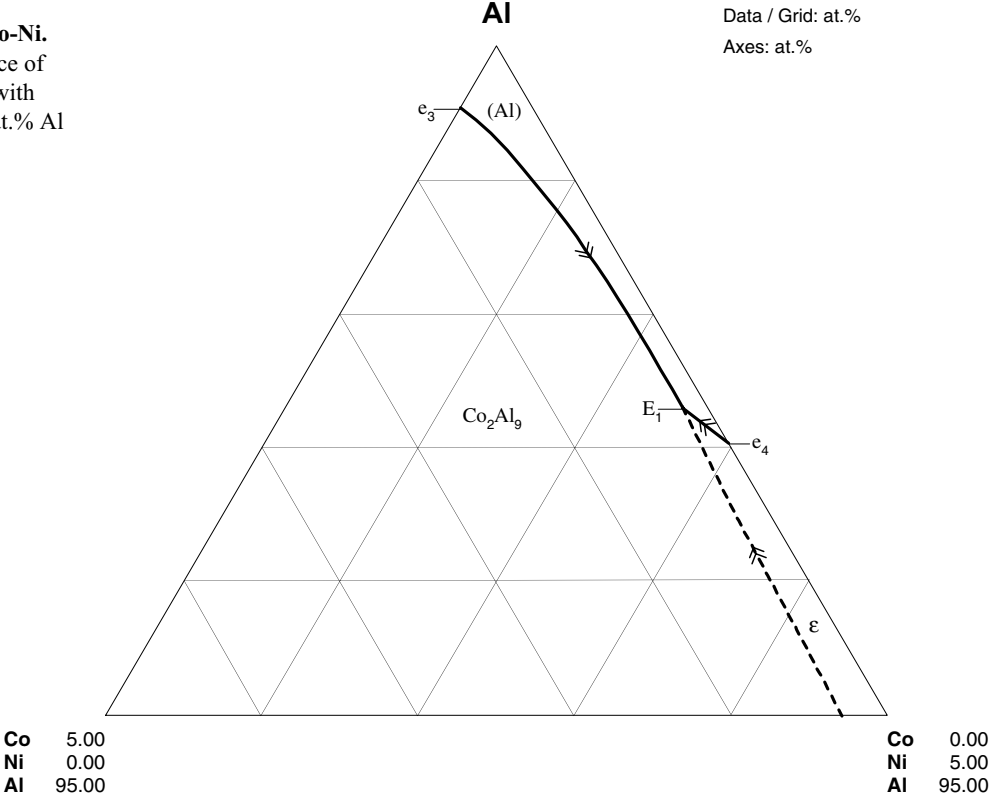
**Fig. 3: Al-Co-Ni.**  
Liquidus surface of  
the partial  
Co-CoAl-NiAl-Ni  
system with less than  
35 at.% Al



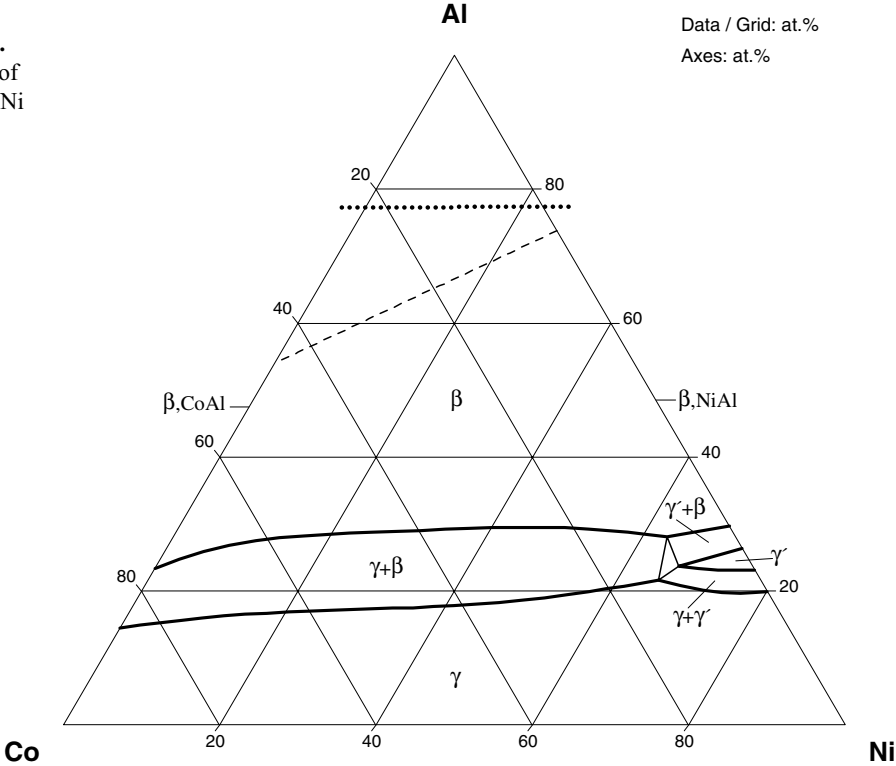
**Fig. 4: Al-Co-Ni.**  
Liquidus surface of  
the partial  
Co-CoAl-NiAl  
system



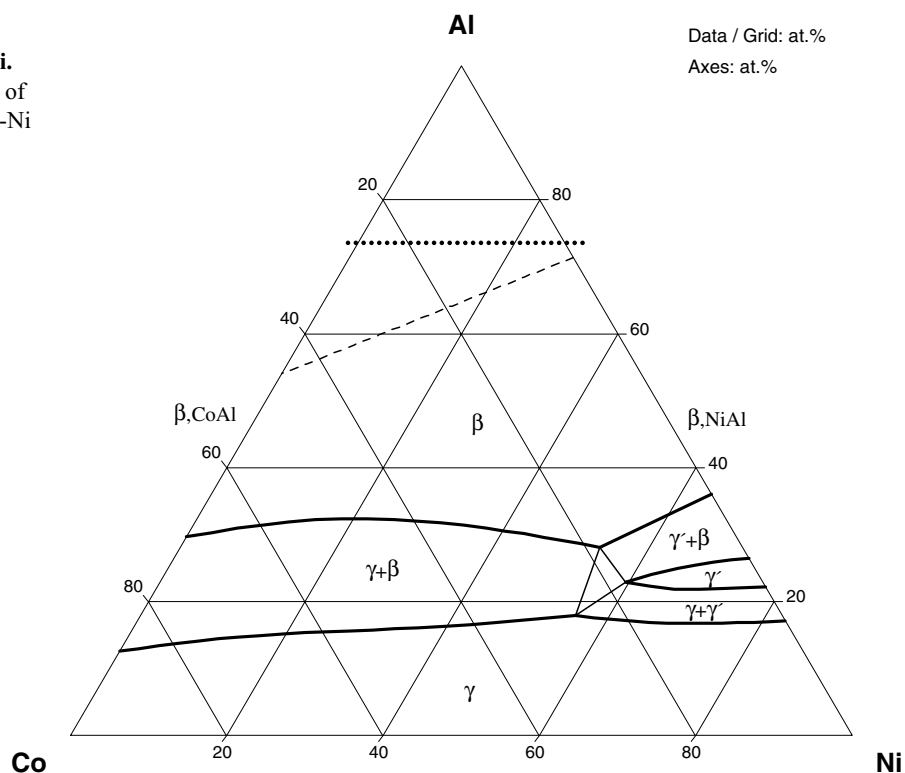
**Fig. 5: Al-Co-Ni.**  
Liquidus surface of  
the Al-corner with  
more than 95 at.% Al



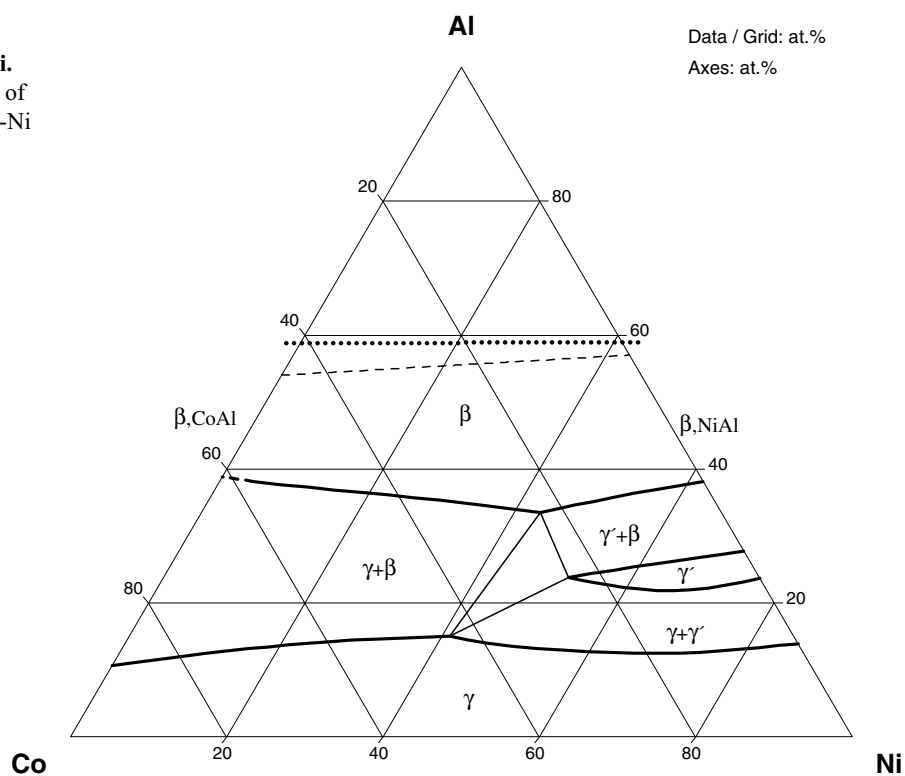
**Fig. 6: Al-Co-Ni.**  
Isothermal section of  
the Co-CoAl-NiAl-Ni  
partial system at  
1300°C



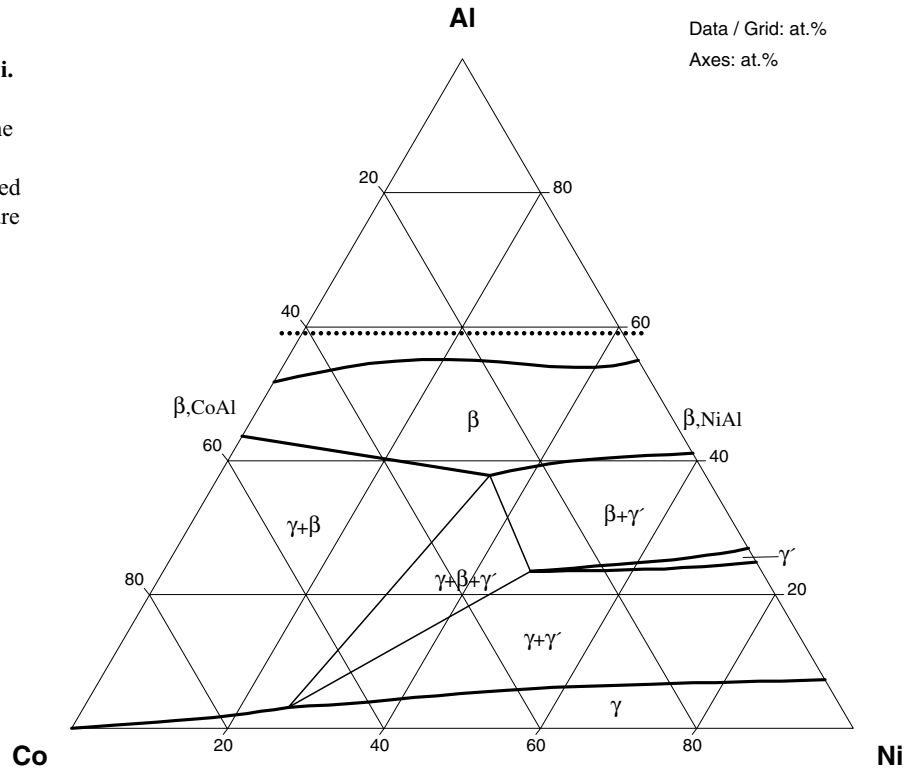
**Fig. 7: Al-Co-Ni.**  
Isothermal section of  
the Co-CoAl-NiAl-Ni  
partial system at  
1100°C



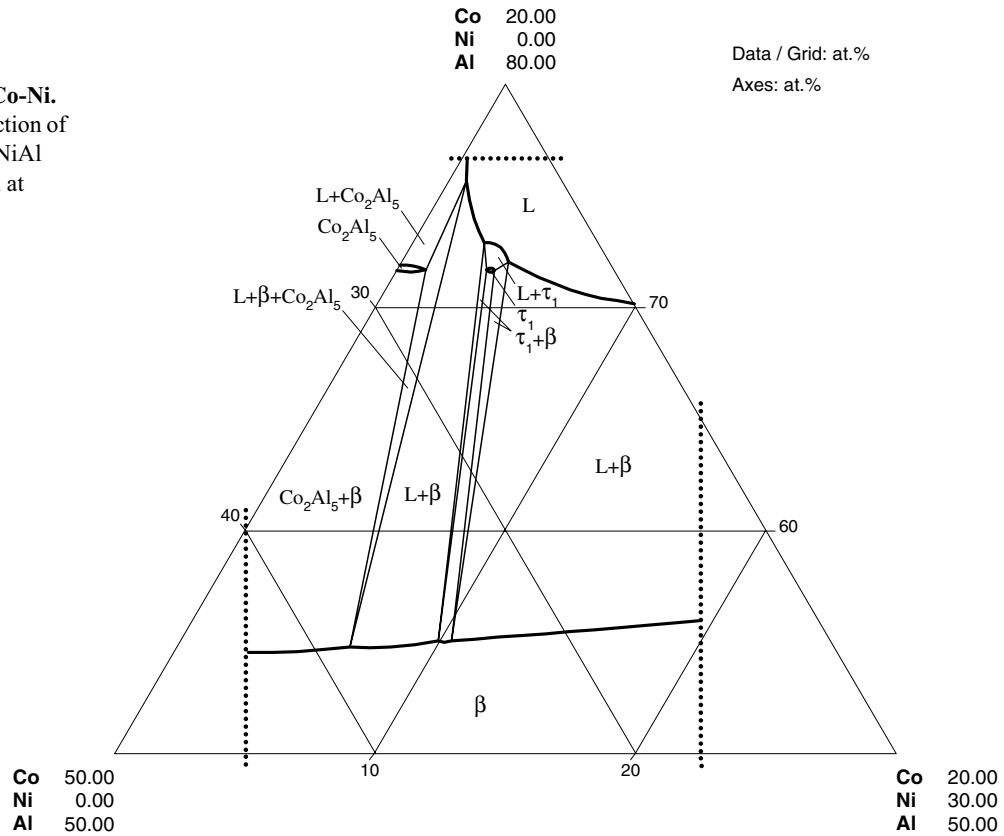
**Fig. 8: Al-Co-Ni.**  
Isothermal section of  
the Co-CoAl-NiAl-Ni  
partial system at  
900°C



**Fig. 9: Al-Co-Ni.**  
Diagram of phase compositions of the Co-CoAl-NiAl-Ni alloys slowly cooled to room temperature

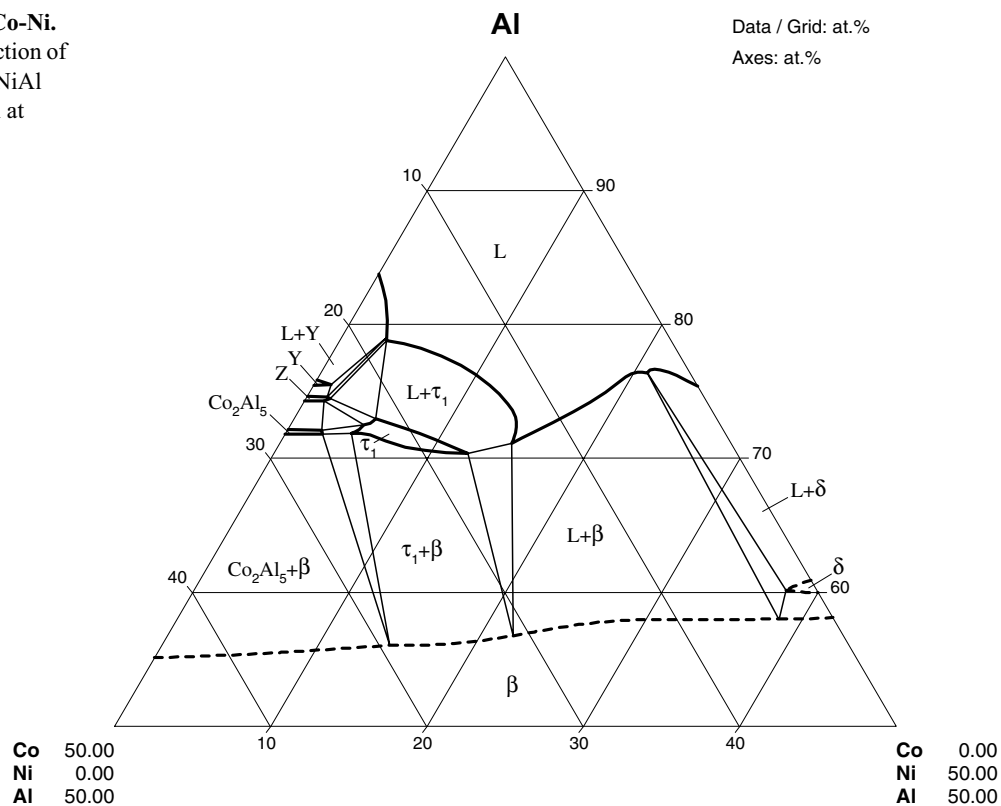


**Fig. 10: Al-Co-Ni.**  
Isothermal section of the Al-CoAl-NiAl partial system at 1170°C

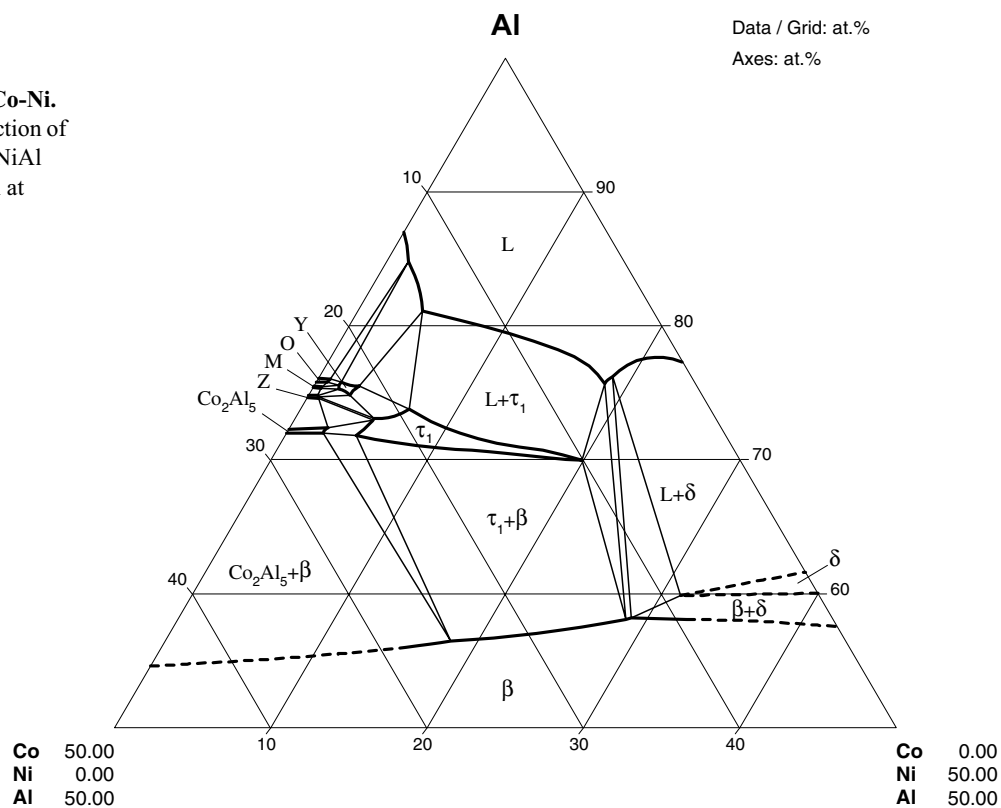




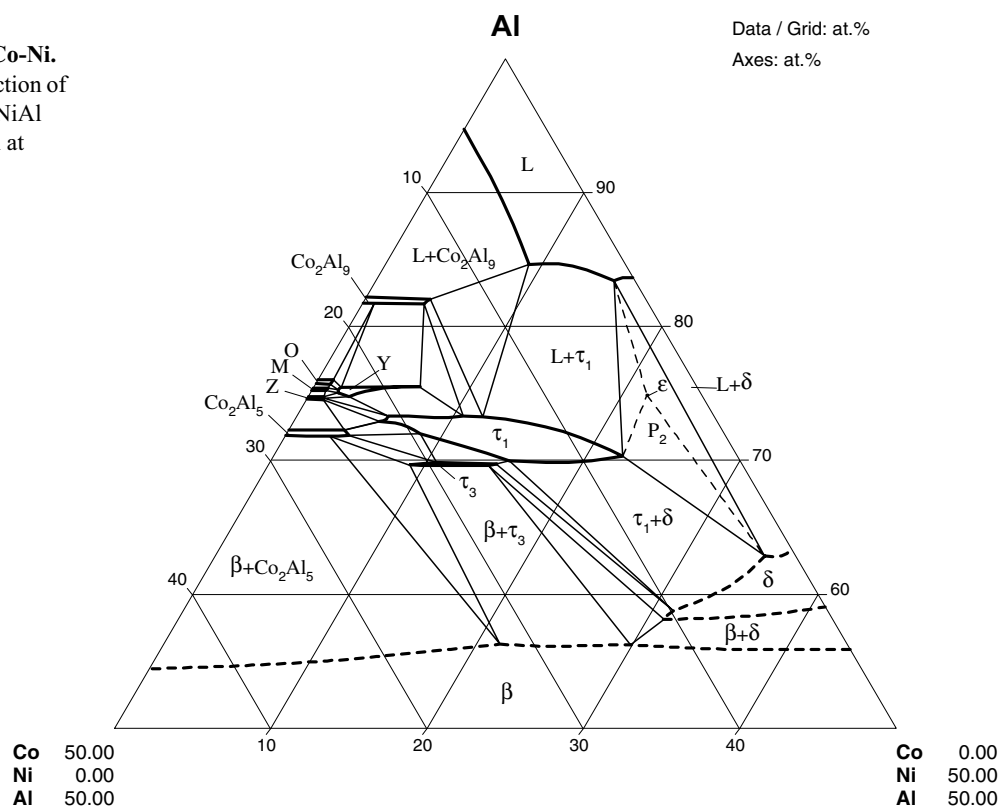
**Fig. 11: Al-Co-Ni.**  
Isothermal section of  
the Al-CoAl-NiAl  
partial system at  
1100°C



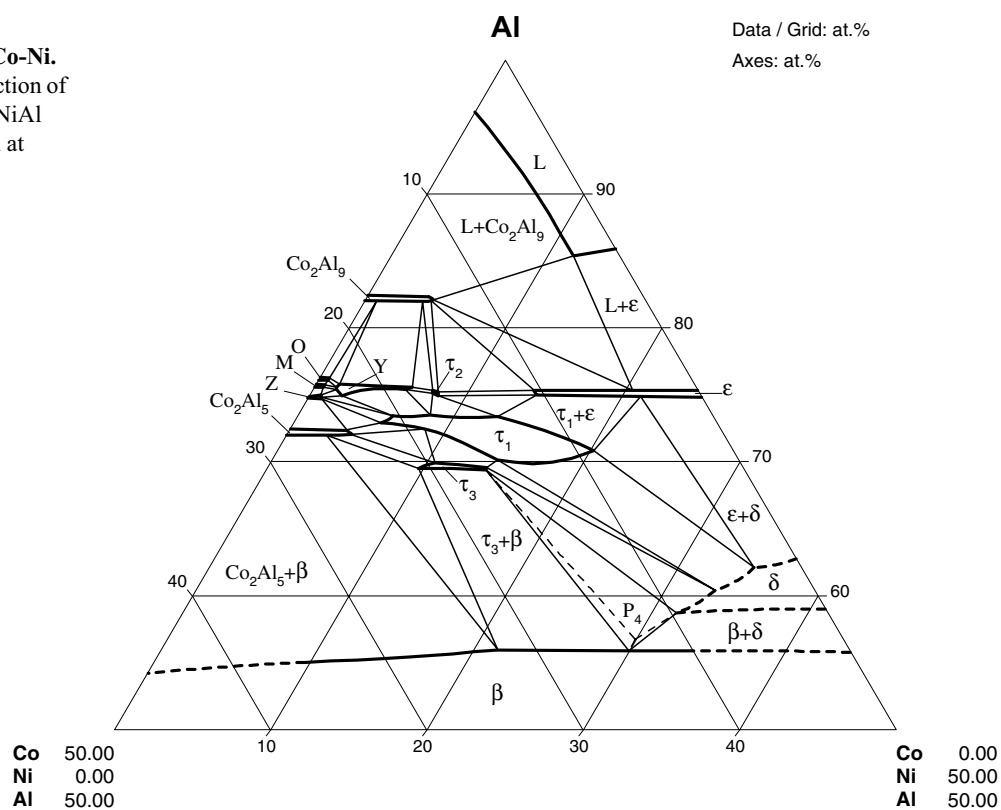
**Fig. 12: Al-Co-Ni.**  
Isothermal section of  
the Al-CoAl-NiAl  
partial system at  
1050°C



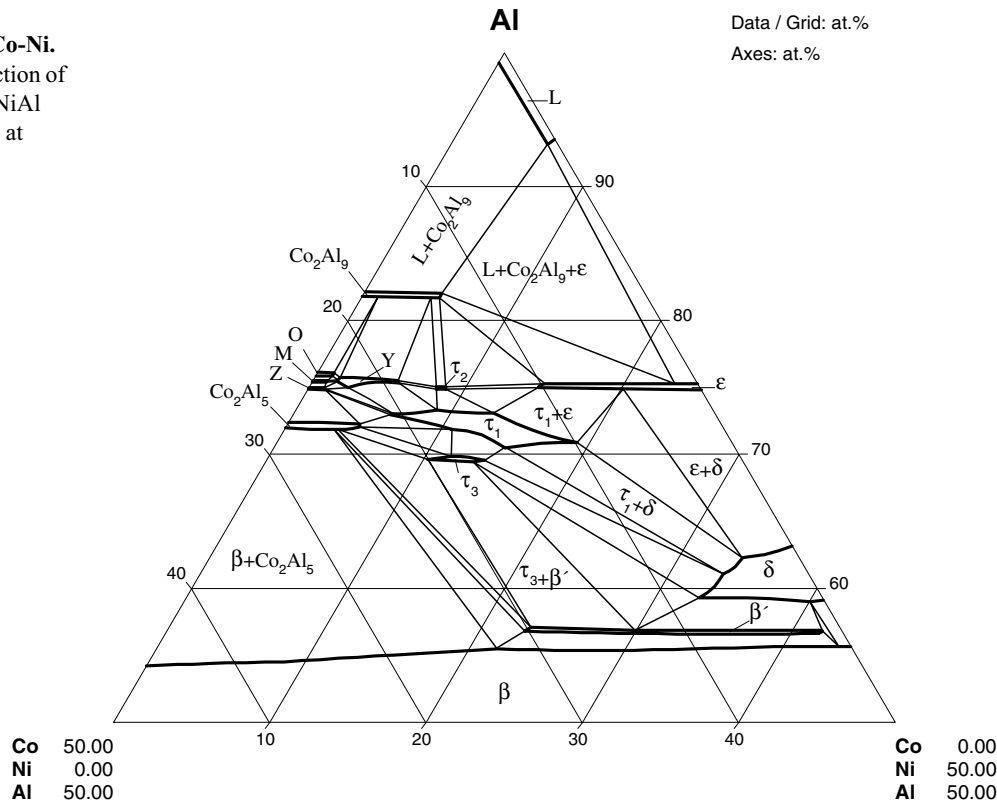
**Fig. 13: Al-Co-Ni.**  
Isothermal section of  
the Al-CoAl-NiAl  
partial system at  
900°C



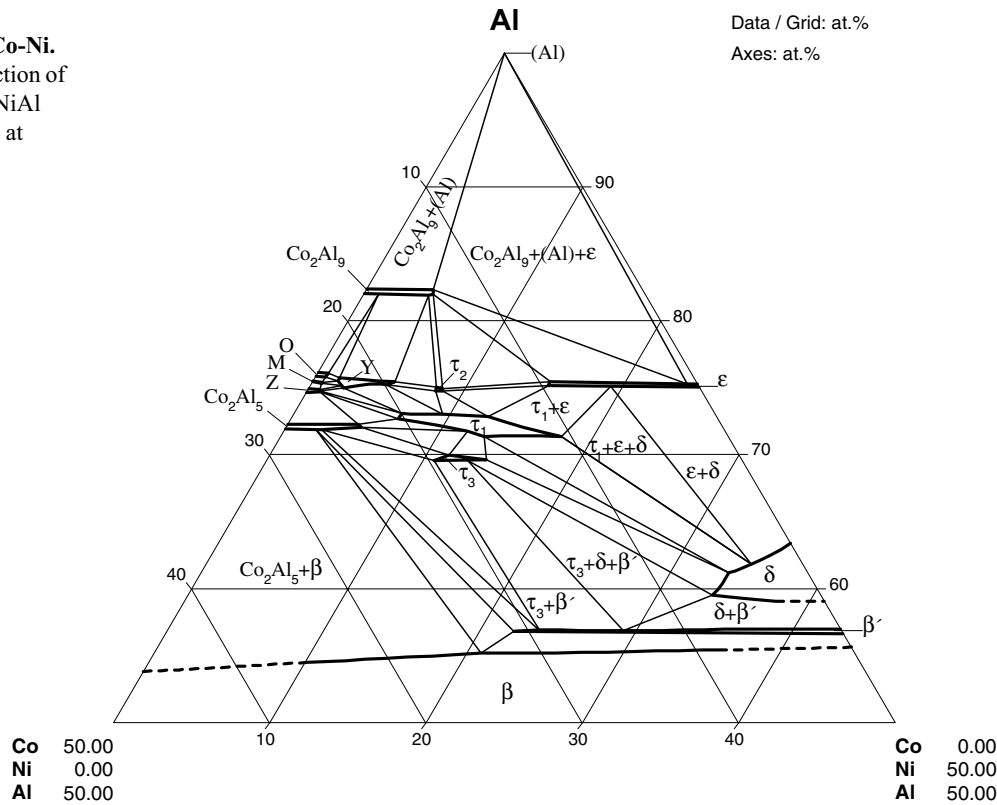
**Fig. 14: Al-Co-Ni.**  
Isothermal section of  
the Al-CoAl-NiAl  
partial system at  
850°C



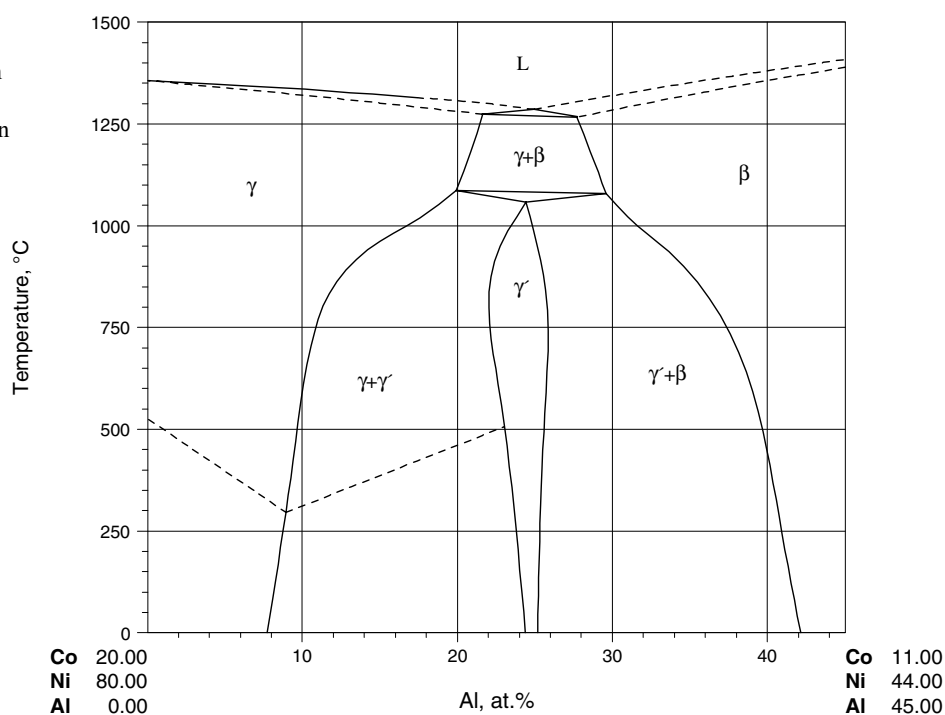
**Fig. 15: Al-Co-Ni.**  
Isothermal section of  
the Al-CoAl-NiAl  
partial system at  
730°C



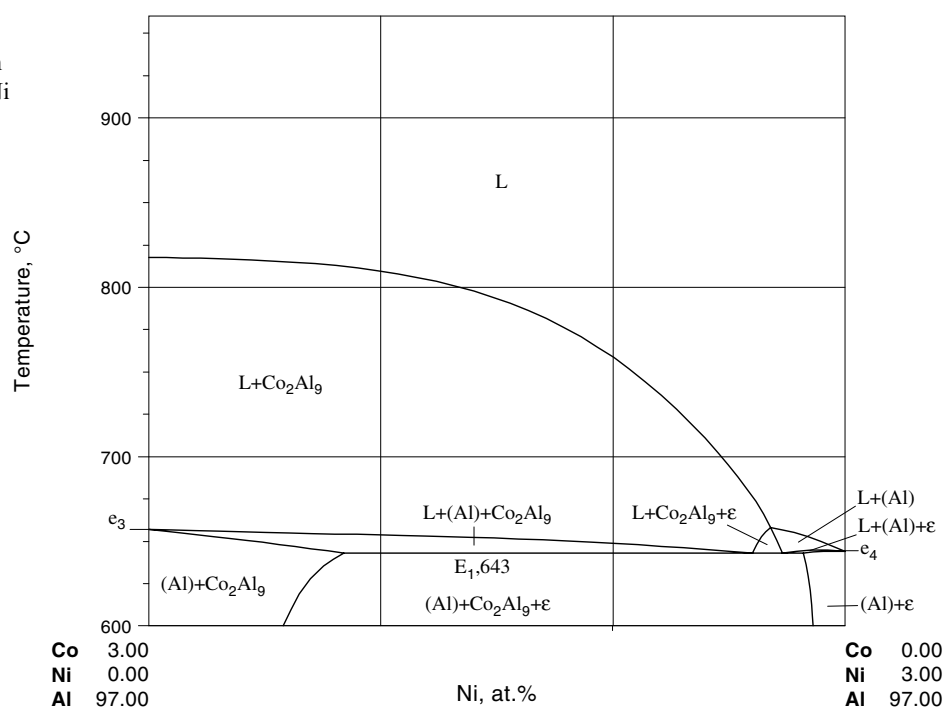
**Fig. 16: Al-Co-Ni.**  
Isothermal section of  
the Al-CoAl-NiAl  
partial system at  
600°C



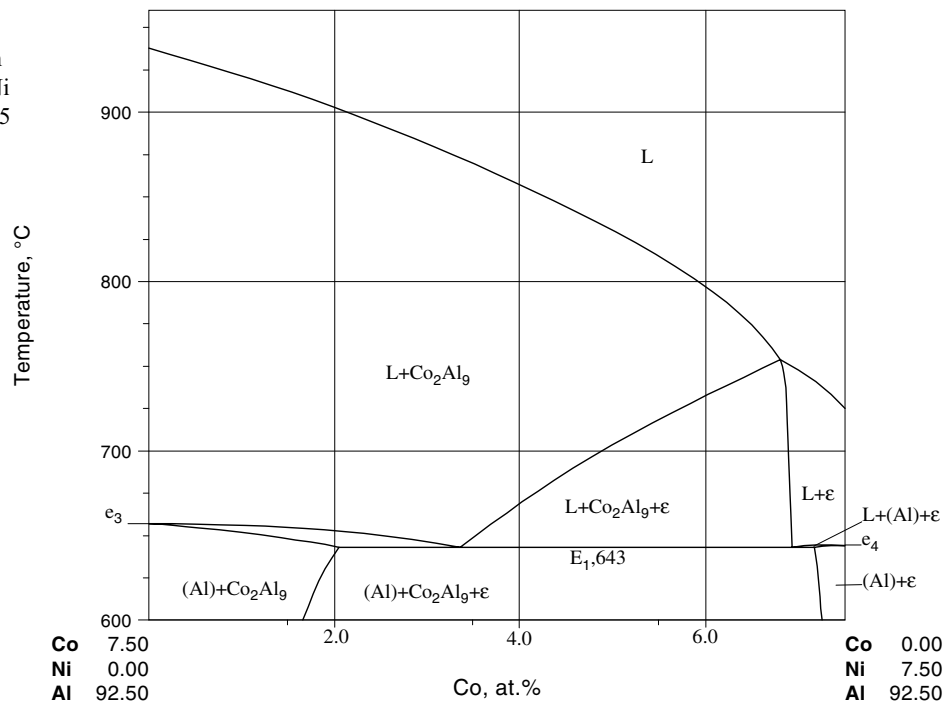
**Fig. 17: Al-Co-Ni.**  
Polythermal section  
within the Co:Ni =  
20:80 atomic ratio in  
Co-Ni edge of the  
ternary system



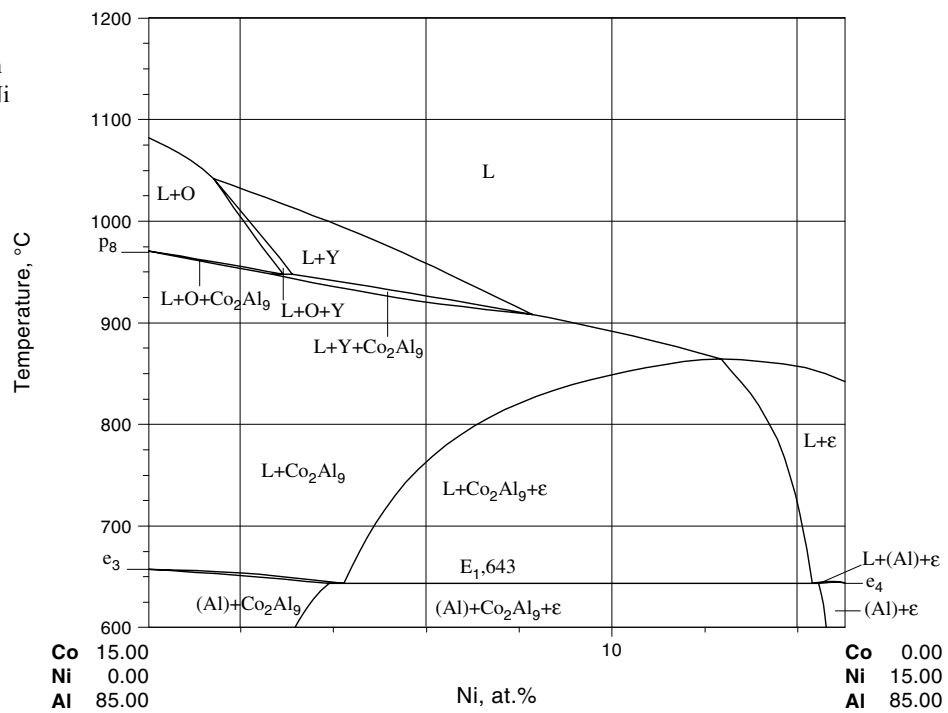
**Fig. 18a: Al-Co-Ni.**  
Polythermal section  
of the Al-AlCo-AlNi  
partial system at 97  
at.% Al



**Fig. 18b: Al-Co-Ni.**  
Polythermal section  
of the Al-AlCo-AlNi  
partial system at 92.5  
at.% Al



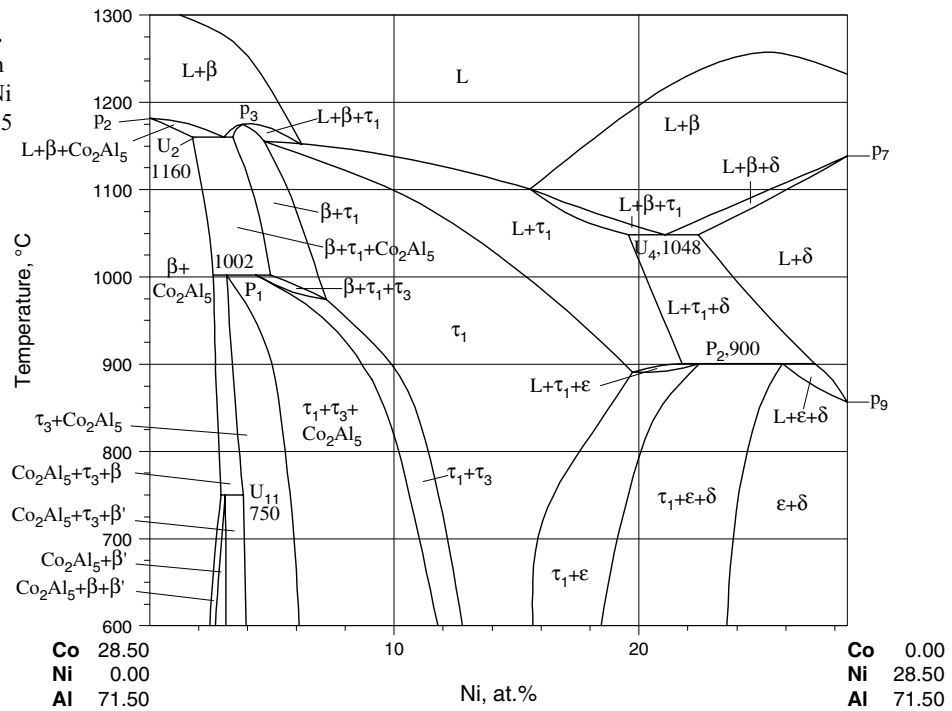
**Fig. 19a: Al-Co-Ni.**  
Polythermal section  
of the Al-AlCo-AlNi  
partial system at 85  
at.% Al



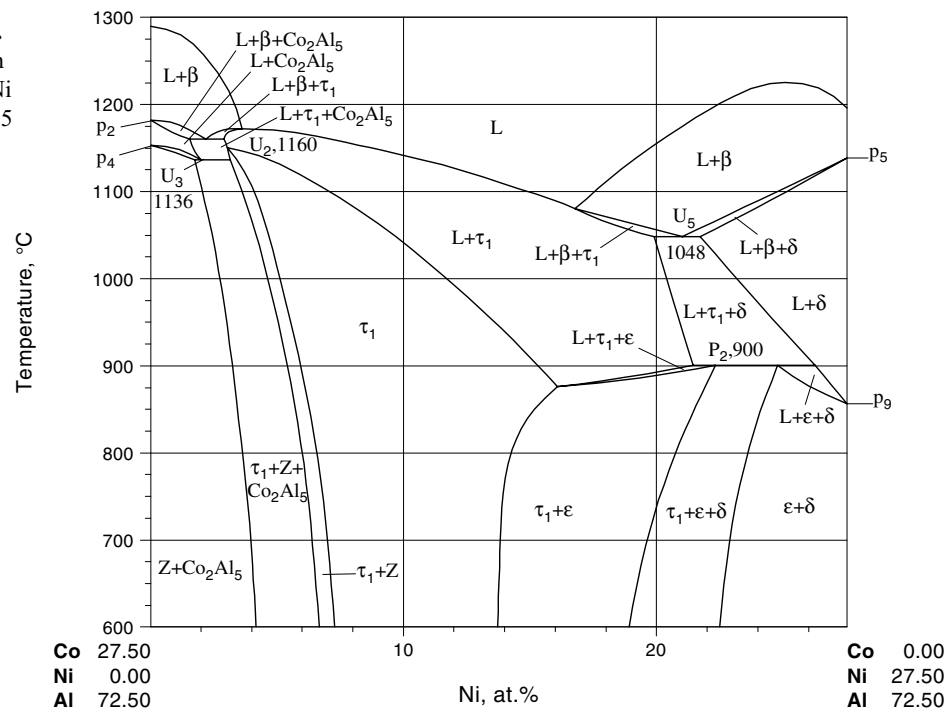
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**Fig. 21b: Al-Co-Ni.**  
Polythermal section  
of the Al-AlCo-AlNi  
partial system at 71.5  
at.% Al

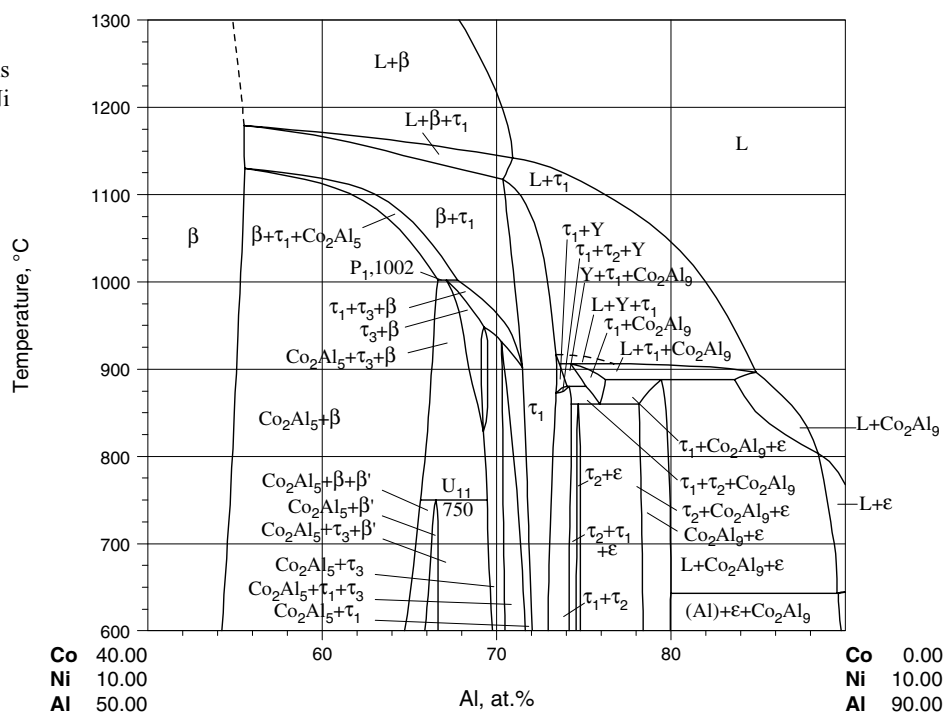


**Fig. 22: Al-Co-Ni.**  
Polythermal section  
of the Al-AlCo-AlNi  
partial system at 72.5  
at.% Al

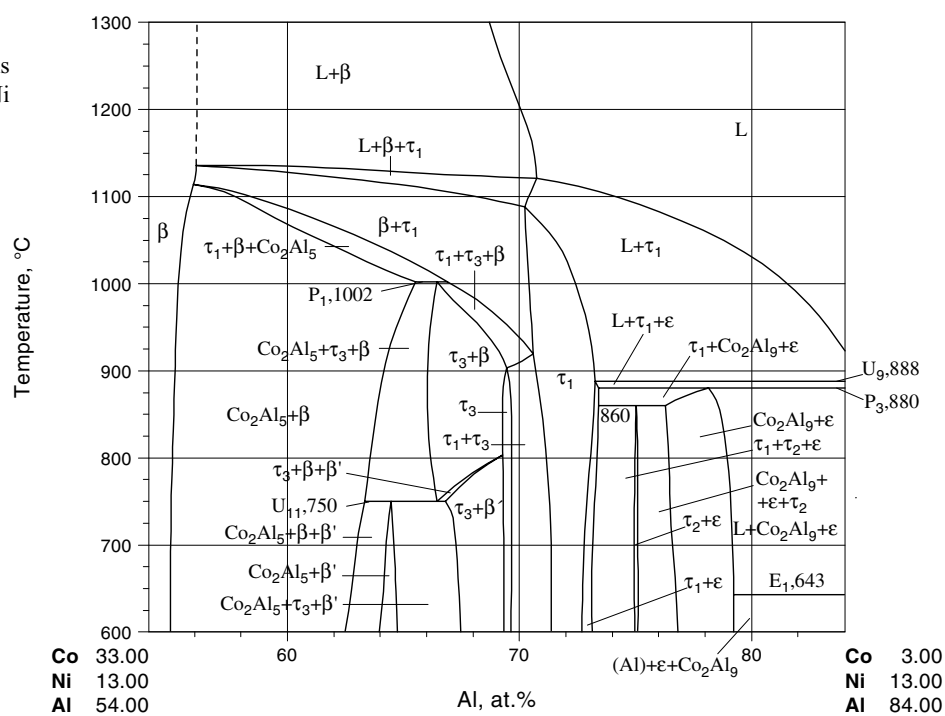




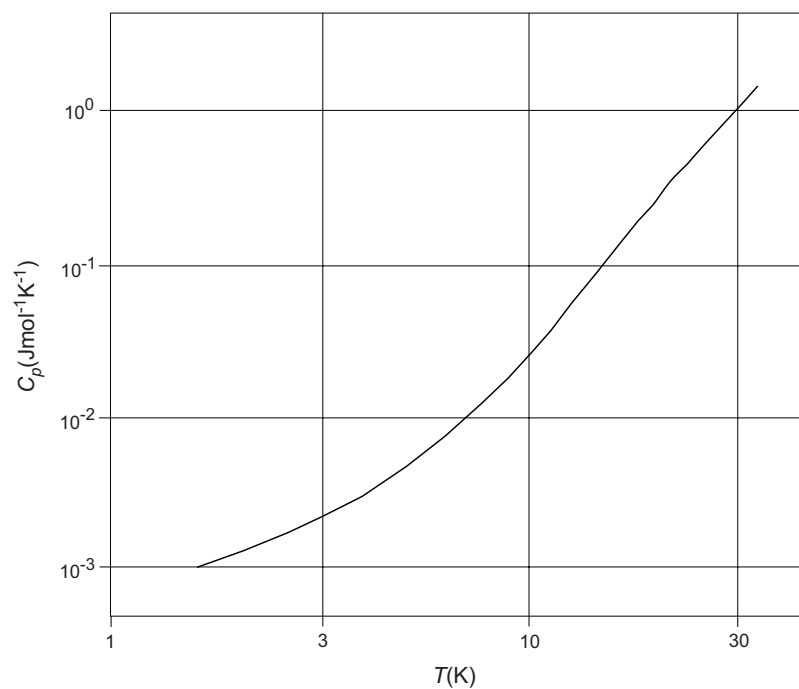
**Fig. 23a: Al-Co-Ni.**  
Polythermal sections  
of the Al-AlCo-AlNi  
partial system at 10  
at.% Ni



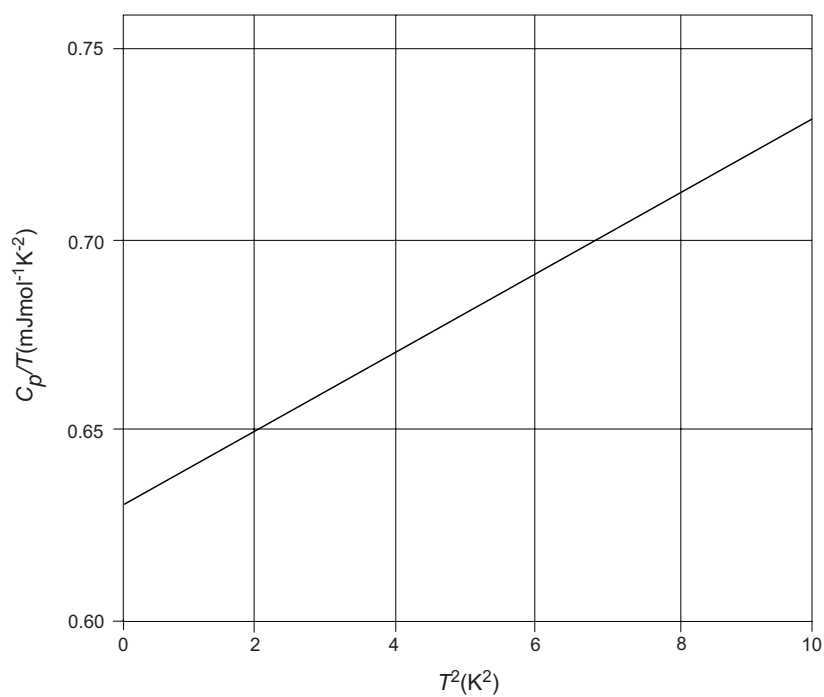
**Fig. 23b: Al-Co-Ni.**  
Polythermal sections  
of the Al-AlCo-AlNi  
partial system at 13  
at.% Ni



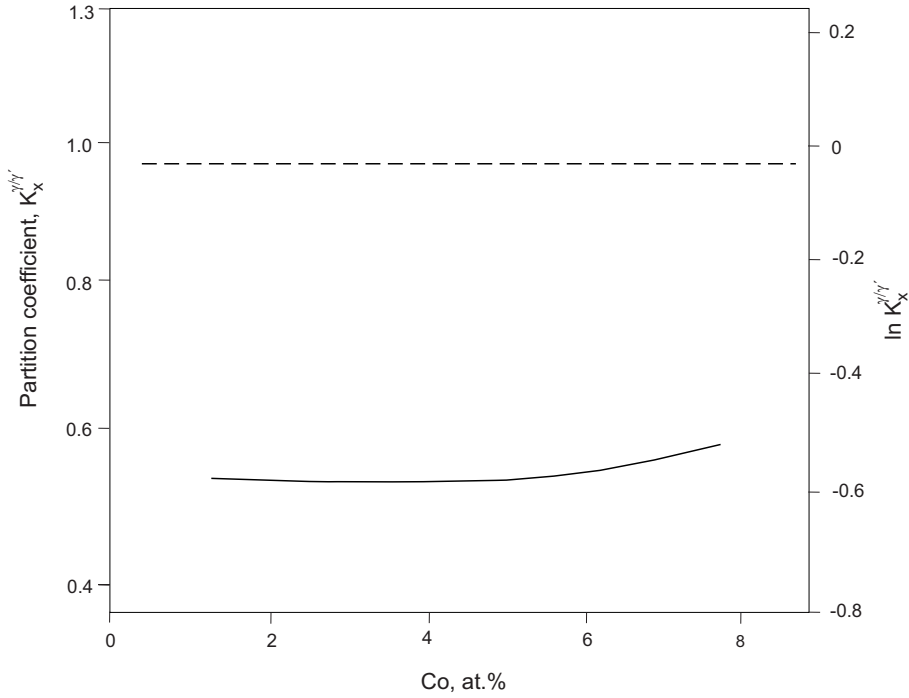
**Fig. 24a: Al-Co-Ni.**  
Specific heat of  
decagonal  
 $\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$   
quasicrystal vs  
temperature; between  
1.5 and 36 K [ $C_p$  vs  
 $T(\text{K})$ ]; after [1998Bia]



**Fig. 24b: Al-Co-Ni.**  
Specific heat of  
decagonal  
 $\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$   
quasicrystal vs  
temperature;  
between 1.5 and 3 K  
[ $C_p/T$  vs  $T^2$ ]; after  
[1998Bia]



**Fig. 25: Al-Co-Ni.**  
Partition coefficient  
between  $\gamma$  and  $\gamma$   
phases vs Co content  
at 1100°C after  
[1994Jia]



**Fig. 26: Al-Co-Ni.**  
Partition coefficient  
between  $\gamma$  and  $\gamma$   
phases vs Co content  
at 1100°C after  
[1994Jia]

