

## Aluminium – Boron – Nickel

*Peter Rogl*

### Literature Data

Transient liquid bonding (TLB) using B–Ni eutectic filler material proved to be an efficient process to produce interface-less joints in Ni-base superalloys. Control of process parameters avoiding the appearance of brittle boride phases, however, requires profound understanding of the diffusion process, phase boundaries and ultimately of phase equilibria in the ternary Al–B–Ni system.

Several research groups have dealt with the experimental constitution of the Al–B–Ni ternary system: (a) [1962Sta1, 1963Sta] proposed a tentative liquidus projection for Ni-rich alloys (50–100 at.% Ni) from metallographic and XRD inspection on about 40 ternary alloys prepared by high frequency induction melting in sintered alumina crucibles (air-cooled cast melts). An 800°C isothermal section was constructed [1962Sta1] based on alloys annealed in evacuated silica capsules for 300 h; (b) [1973Cha] prepared two isothermal sections at 800°C and 1000°C, based on XPD and microstructural analyses. The specimens (elemental powder compacts) were annealed in evacuated silica capsules at 1000, 800 and 600°C for not less than 150, 600 and 1000 h, respectively. Alloys containing more than 60 mass% Al were investigated at 600°C. Results of [1973Cha] confirmed the formation of the  $\tau_1$  phase with an extended homogeneity region, but showed the existence of further ternary compounds,  $\tau_2$  Ni<sub>5</sub>AlB<sub>4</sub> and  $\tau_3$  Ni<sub>8</sub>AlB<sub>11</sub>; (c) crystallographic studies were performed of the ternary boride,  $\tau_1$ , (Cr<sub>23</sub>C<sub>6</sub> type structure) with an extended homogeneity region by [1962Sta2, 1963Sta] and [1998Hil]; (d) a thermodynamic assessment of the Al–B–Ni system is due to [1999Cam] and in refined version from [2000Cam].

Phase relations in the Al–B–Ni system have been reviewed by [1989Sch, 1990Sch, 1999Cam].

### Binary Systems

The binary boundary systems Al–Ni and B–Ni are accepted from critical assessments of [2003Sal] and [Mas2], respectively. Although the system Al–B has been assessed and thermodynamically modelled by several authors, the system was adopted in the form described in Al–B–C [2003Gry].

### Solid Phases

Three ternary phases,  $\tau_1$  to  $\tau_3$ , were detected by [1973Cha] (Table 1), the latter (Ni<sub>8</sub>AlB<sub>11</sub>) with a polymorphic transition in the temperature range from 800 to 1000°C transforming from a monoclinic high-temperature structure to an unidentified structure at 800°C. The ternary phase,  $\tau_2$  Ni<sub>5</sub>AlB<sub>4</sub>, was only observed in the 800°C isothermal section [1973Cha]; its crystal structure is still unknown.

Whilst both research groups [1973Cha, 1962Sta1, 1962Sta2, 1963Sta] agree on the existence of the  $\tau_1$  phase with an extended region of homogeneity, discrepancy exists on the extent of the  $\tau_1$  phase at 800°C: [1962Sta1, 1962Sta2, 1963Sta] report on a narrow phase field extending from 21 to 34 at.% boron: Ni<sub>20</sub>Al<sub>3</sub>B<sub>6–12</sub> starting from the B-poor composition at 70Ni–8Al–22B (at.%) to the B-rich composition at 60Ni–10Al–30B (at.%). According to [1973Cha] the  $\tau_1$  phase region at 800°C is rather small extending at a constant Al-content of 10.3 at.% from 20 to 28 at.% B. The  $\tau_1$  phase field is more extensive at 1000°C ranging from 20 to 34 at.% B [1973Cha] in close resemblance to the data listed by [1962Sta1, 1962Sta2, 1963Sta] for 800°C. Only half the number of alloys were examined by [1973Cha] compared with [1962Sta1] but they were annealed for twice the time. Although it is difficult to judge, which version corresponds to true equilibrium, we may assume that Stadelmaier's results have suffered from lack of equilibrium and rather reveal the phase relations at about 1000°C.

[1962Sta2, 1963Sta] tried to explain the unusually large homogeneity region of  $\tau_1$  with strongly varying boron content on the basis of a partial replacement of single boron atoms by boron-pairs within the Archimedian Ni- prisms in the crystal structure of the Cr<sub>23</sub>C<sub>6</sub> type.

A detailed structural investigation of the homogeneity region of  $\tau_1$  employing X-ray single crystal diffractometry [1998Hil] suggests two substitution mechanisms: (i) Ni/Al replacement  $\text{Ni}_{20+x}\text{Al}_{3-x}\text{B}_6$  and (ii) substitution of Al-atoms by boron tetrahedra  $\text{Ni}_{20}\text{Al}_{3-2y}\text{B}_{6+8y}$ . Whilst the variation of composition from  $\text{Ni}_{20}\text{Al}_3\text{B}_6$  to  $\text{Ni}_{20}\text{Al}_{2.4}\text{B}_{8.4}$  seems to follow the experimental observations of [1962Sta1] and [1973Cha], the endpoints of the structural series  $\text{Ni}_{20}\text{Al}_{3-2y}\text{B}_{6+8y}$  for  $0.3 \leq y \leq 1$  are in conflict with the experimental phase region and certainly provoke further experimental studies.

The possibility of ternary phase formation by reaction of transition metal borides with Al in terms of the electron structure of the transition metals was discussed by [1981Ser].

### Invariant Equilibria

Figure 1 presents the reaction scheme for the Ni-rich part of the system. The maximum melting point of congruently-melting  $\tau_1$ , was said to be at a composition close to 60Ni-9Al-31B (at.%), however, no melting temperature was reported [1962Sta1]. Four ternary invariant reactions were proposed by [1962Sta1], although no temperatures were given and composition of the phases involved can only be guessed from a graph presented; see Table 2. Furthermore the B–Ni binary phase diagram adopted by [1962Sta1] has been revised since, requiring amendments to the reactions proposed by [1962Sta1]: the ternary eutectic reaction  $L \rightleftharpoons (\text{Ni}) + \tau_1 + \text{Ni}_3\text{B}$ , originally had  $\text{Ni}_2\text{B}$  as a product phase, but the transition reaction  $U_1, L + \text{NiAl} \rightleftharpoons \text{Ni}_3\text{Al} + \tau_1$  and the ternary eutectic reaction  $E_1, L \rightleftharpoons (\text{Ni}) + \text{Ni}_3\text{Al} + \tau_1$ , are unchanged. The primary solidification region for “ $\text{Ni}_3\text{B}_2$ ” [1962Sta1] needs to be replaced by the phases o- $\text{Ni}_4\text{B}_3$  and m- $\text{Ni}_4\text{B}_3$ . According to [1962Sta1] there are maximum points on three of the monovariant curves. These correspond to the pseudobinary equilibria  $L \rightleftharpoons (\text{Ni}) + \tau_1$ ,  $L \rightleftharpoons \text{NiAl} + \tau_1$  and  $L \rightleftharpoons \text{Ni}_3\text{B} + \tau_1$ .

The fourth reaction,  $L \rightleftharpoons \tau_1 + \text{NiAl} + \text{NiB}$ , as stated by [1962Sta1], is rather unlikely, as this region of the ternary phase diagram is relatively complex due to binary reactions, which will extend into the ternary in a manner currently unknown.

The thermodynamic calculation [1999Cam] lists the same four ternary invariant reactions as observed by [1962Sta1]. Calculated reaction temperatures and compositions of the liquid phases involved are given dependent on two different assessments for the Al–Ni binary, [1997Ans] and [1998Hua]. There are, however, a series of major discrepancies, as seen from the comparison in Table 2.

A detailed study by DTA and Knudsen-effusion mass spectroscopy [1990Dha] comparing four binary alloys,  $\text{Ni}_{1-x}\text{Al}_x$ ,  $x = 0.20, 0.23, 0.24$  and  $0.26$  with those containing  $0.5$  at.% B, showed that minor additions of boron altered considerably the phase boundaries.

### Liquidus Surface

A liquidus surface for the region with more than 50 at.% Ni was constructed by [1962Sta1]. As mentioned under “Invariant Equilibria”, it needs revision to comply with the accepted binary B–Ni system. The region with less than 30 at.% B is shown in Fig. 2. Due to casting alloys in air (eventual burn up of boron), Stadelmaier's reaction isotherms,  $E_1$ ,  $E_2$  and  $U_1$  may have shifted to lower boron contents than shown [1962Sta1]. This would be in better agreement to a non-depleted eutectic  $E_1$ .

### Isothermal Sections

A partial isothermal section at  $1000^\circ\text{C}$  (see Fig. 3) was determined by [1973Cha] for the region Ni–NiAl–B. Phase equilibria at  $800^\circ\text{C}$  are presented in Fig. 4 and are essentially based on the investigation by [1973Cha]: alloys containing more than 60 at.% Al were annealed at  $600^\circ\text{C}$ . However, no complete  $600^\circ\text{C}$  isothermal section was reported by [1973Cha]. For an extensive discussion of the homogeneity region of the  $\tau_1$  phase, see section “Solid Phases”. Both isothermal sections, Fig. 3 and Fig. 4, have been amended to comply with the accepted binary boundary systems. Changes in particular concern the phase  $\text{AlB}_{12}$  as well as the solubility of Al and Ni in ( $\beta\text{B}$ ).

## Thermodynamics

A thermodynamic modelling of the system Al-B-Ni was performed by [1999Cam] using the CALPHAD approach with Redlich-Kister polynomial description of the Gibbs energy functions [1985Sun]. The binary systems Al-B and B-Ni were included in the modelling. In contrast to earlier treatment, boron was taken as an interstitial element in the solid metal solutions and in  $\text{Ni}_3\text{Al}$  [1999Cam]. Although most of the experimental phase relations are revealed by the thermodynamic calculation, there are three major points of disagreement:

- (i) a rather high thermal stability of  $\text{AlB}_{12}$  favours equilibria with  $\text{AlB}_{12}$  over those with  $(\beta\text{B})$  i.e. at  $800^\circ\text{C}$  rather  $\text{AlB}_{12}+\text{NiB}$ ,  $\text{AlB}_{12}+\text{Ni}_8\text{AlB}_{11}$ ,  $\text{AlB}_{12}+\text{Ni}_5\text{AlB}_4$ , than  $(\beta\text{B})+\text{Ni}_8\text{AlB}_{11}$ ,  $(\beta\text{B})+\text{Ni}_5\text{AlB}_4$ ;
- (ii) a higher stability is calculated at  $1000^\circ\text{C}$  for the two-phase equilibrium  $m\text{-Ni}_4\text{B}_3+\text{Ni}_8\text{AlB}_{11}$  than the experimentally observed  $\text{NiB}+\tau_1$ ;
- (iii) the calculated homogeneity region of  $\tau_1$  is still significantly smaller than experimentally observed.

With respect to transient liquid bonding, particularly the location of the three-phase field  $\tau_1+(\text{Ni})+\text{liquid}$  at  $1200^\circ\text{C}$  and  $1300^\circ\text{C}$  was discussed with respect to the variation obtained in the calculation, when two different assessments were used for the Al-Ni binary, namely [1997Ans] and [1998Hua].

Based on the thermodynamic assessment [1999Cam], TLP-simulations and experiments were performed by [2000Cam] monitoring the diffusion path for the TLP bonds in a Ni-10.3Al (at.%) alloy + Ni-10B (at.%) filler material at  $1315^\circ\text{C}$  after isothermal holds of 1, 900, 1800 and 3600 sec. Composition-dependent diffusion mobilities were assessed for the ternary system. Adjusting the free energy of the  $\tau_1$  phase to yield its experimentally observed mole fraction, the simulations predicted the observed precipitation and later dissolution of the  $\tau_1$  phase during the bonding process [2000Cam]. The corresponding calculated tie-triangle at  $1315^\circ\text{C}$  was given as:  $\text{L}(87\text{Ni}3\text{Al}10\text{B})+\tau_1(69\text{Ni}310\text{Al}21\text{B})+(\text{Ni})$  (92.3Ni6.8Al0.5B) (read from diagram in at.%).

## Notes on Materials Properties and Applications

Low density, high oxidation resistance and unusual yield strength dependence on temperature have raised considerable interest in boron-doped polycrystalline intermetallic alloys,  $\text{NiAl}$  and  $\text{Ni}_3\text{Al}$ , as high temperature structural materials. The acute increase in ductility when a small amount of boron (less than 1 at.%) is added to  $\text{Ni}_3\text{Al}$  has evoked a series of investigations, which are briefly summarized in the following. The microstructure of boron-doped N-atomized  $\text{Ni}_3\text{Al}$  powders  $(\text{Ni}_{0.76}\text{Al}_{0.24})_{99.75}\text{B}_{0.25}$  and  $(\text{Ni}_{0.76}\text{Al}_{0.25})_{99}\text{B}_1$ , has been characterized by LOM and REM revealing remarkable variation in solidification morphology and phase reaction as a function of powder size [1989Hua]: the degree of boron segregation appeared to be significantly reduced, as the formation of  $\text{M}_{23}\text{B}_6$ -boride was suppressed in powders below  $30\text{ }\mu\text{m}$  diameter.

Ultimate and yield strength at 20 and  $800^\circ\text{C}$  of monocrystalline  $\text{Ni}_3\text{Al}$  increase with the B-content to reach a maximum for 0.52 and 1.37 at.% B, dropping slowly for higher B-contents up to 2.22 at.% [1991Guo]. When the B-content exceeds 1.37 at.% B, a eutectic structure  $\text{Ni}_3\text{Al}+\text{Ni}_{20}\text{Al}_3\text{B}_6$  was formed [1991Guo]. Arc melting behavior of continuously cast thin sheet and cast ingots of  $\text{Ni}_3\text{Al}$  containing B and Zr was studied by [1991Li]. The evolution of recrystallization texture in cold rolled  $\text{Ni}_{76}\text{Al}_{24}(\text{B})$  on annealing has been investigated by [2000Cho] dividing the annealing process into three stages: recovery, reordering and recrystallization.

Monitoring the distribution of boron in a rapidly solidified alloy,  $(\text{Ni}_{76}\text{B}_{24})_{99.76}\text{B}_{0.24}$ , via atom probe field-ion microscopy, [1987Hor] found B to segregate to both anti phase boundaries and grain boundaries. A 0.4 to 1.2 nm thick boron-enriched phase was observed on most of the grain boundaries in a nonuniform distribution. Microstructure and mechanical properties of rapidly solidified Ni-Al ribbons (68-90 at.% Ni) with 0, 200, 2000 and 4000 mass ppm B showed absence of antiphase domain boundaries for hypo-eutectic compositions but a bimodal distribution of APD: for hyper-eutectic compositions [1996Lim]: explanation was based on the metastable Ni-Al phase diagram. Single crystals of  $\text{Ni}_3\text{Al}$ , doped with 0 to 1 at.% B, were examined by TEM after slight compressive deformation. APB and SISF (superlattice intrinsic stacking fault) energies were calculated [1991Yan].

Intergranular segregation of B in Ni<sub>3</sub>Al was investigated by [1992Cho] in terms of equilibrium segregation and segregation kinetics on high purity Ni<sub>76</sub>Al<sub>24</sub> alloys containing 0.048, 0.144, 0.240 and 0.480 at.% B, aged from 600 to 1050°C to attain equilibrium. The energy of binding of a B-atom to the grain boundary was calculated to be in the range of 0.15-0.45 eV per atom increasing with increasing temperature and decreasing bulk B-content [1992Cho]. The diffusion coefficient of B in Ni<sub>3</sub>Al at 500°C was given as  $5 \cdot 10^{-21} \text{ m}^2 \cdot \text{s}^{-1}$ , at 700°C between  $10^{-16}$  and  $10^{-17} \text{ m}^2 \cdot \text{s}^{-1}$ . The activation energy for diffusion of B in Ni<sub>3</sub>Al was reported to be between 200 and 300 kJ·mol<sup>-1</sup>.

Atomistic simulations (EAM= embedded atom method [2001Zhe, 2002Zhe], and LMTO= Linearized Muffin Tin Orbital method [1990Che] have been employed to study the bulk effects of B on the Ni<sub>3</sub>Al -xB grain boundary [2001Zhe, 2002Zhe] proposing that B atoms induce Ni for Al substitution and as a consequence B for Ni substitution. It was found that when x increases from 0.1 to 1.0 the probability for B to occupy interstitial sites decreases from 97.3 to 38.8 % whilst substitutional occupancy increases from 2.7 to 61.2 % [2001Zhe, 2002Zhe].

Defect strengthening and solution hardening by the addition of boron to NiAl alloys has been studied by [1992Jay, 1993Wu, 1993Tan]. The addition of 0.05 mass% B was found to increase the lattice parameter and the hardness of Ni-rich NiAl, whereas there was no effect for Al-rich NiAl.

The diffusive behavior of B-atoms in Ni<sub>3</sub>Al (0.98 at.% B) alloys was investigated by positron annihilation: to achieve moderate segregation of B-atoms to grain boundaries without boride formation, the alloy was recommended to be cooled in air after anneal at high temperature [1995Li].

Ni<sub>20</sub>Al<sub>3</sub>B<sub>6</sub> was said to exhibit temperature independent susceptibility down to liquid nitrogen temperatures [1967Hir]

By reacting compacted powders of 1Ni<sub>2</sub>B+5Al at 675°C under argon and subsequently dissolving the Al with 6N KOH, [1966Jah] was able to produce a porous active B-Ni catalyst.

## References

- [1962Sta1] Stadelmaier, H.H., Fraker, A.C., "The Ni Corner of the Ni-Al-B Ternary System" (in German), *Metall*, **16**, 212-214 (1962) (Equi. Diagram, Crys. Structure, Experimental, 10)
- [1962Sta2] Stadelmaier, H.H., Yun, T.S., "Ternary Borides with the Cr<sub>23</sub>C<sub>6</sub>-Structure" (in German), *Z. Metallkd.*, **53**, 754-756 (1962) (Crys. Structure, Experimental, 13)
- [1963Sta] Stadelmaier, H.H., Draughn, R.A., Hofer, G., "The Structure of Ternary Borides of the Cr<sub>23</sub>C<sub>6</sub> Type" (in German), *Z. Metallkd.*, **54**, 640-644 (1963) (Crys. Structure, Experimental, 10)
- [1966Jah] Jahnke, H., "Investigations on Nickel Borides from Ternary Nickel-Boron-Aluminium" (in German), *Bosch Technische Berichte*, **1**, 242-245 (1966) (Experimental, 0)
- [1967Hir] Hirota, H., "Magnetic Properties of Borides with a Cr<sub>23</sub>C<sub>6</sub>-Type Structure", *J. Phys. Soc. Jpn.*, **23**(5), 512-516 (1967) (Experimental, Magn. Prop., 7)
- [1973Cha] Chaban, N.F., Kuz'ma, Yu.B., "Isothermal Cross Sections of the Systems (Co,Ni)-(Al, Si)-B", *Inorg. Mater.*, **9**, 1886-1889 (1973), translated from *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **9**, 2136-2140 (1973) (Experimental, Equi. Diagram, Crys. Structure, #, 18)
- [1981Ser] Serebryakova, T.I., "Reactions of Transition Metal Diborides with Aluminium", *Sov. Powder Metall. Met. Ceram. (Engl. Trans.)*, **20**, 705-708 (1981), translated from *Poroshk. Metall.*, (10), 45-49 (1981) (Crys. Structure, 9)
- [1985Sun] Sundmann, B., Jansson, B., Andersson, J.O., "The Thermocalculated Databank System", *Calphad*, **9**, 153-159 (1985) (Thermodyn., Calculation)
- [1986Hua] Huang, S.C., Briant, C.L., Chang, K.-M., Taub, A.I., Hall, E.L., "Carbon Effects in Rapidly Solidified Ni<sub>3</sub>Al", *J. Mater. Res.*, **1**(1), 60-67 (1986) (Experimental, Mechan. Prop., 27)
- [1987Hor] Horton, J.A., Miller, M.K., "Atom Probe Analysis of Grain Boundaries in Rapidly Solidified Ni<sub>3</sub>Al", *Acta Metall.*, **35**, 133-141 (1987) (Equi. Diagram, Experimental, 22)
- [1987Kha] Khadkikar, P.S., Vedula, K., "An Investigation of the Ni<sub>5</sub>Al<sub>3</sub> Phase", *J. Mater. Res.*, **2**(2), 163-167 (1987) (Crys. Structure, Experimental, 7)

- [1988Li] Li, X.Z., Kuo, K.H., "Decagonal Quasicrystals with Different Periodicities along the Tenfold Axis in Rapidly Solidified Al-Ni Alloys", *Phil. Mag. Let.*, **58**(3), 167-171 (1988) (Experimental, Crys. Structure, 14)
- [1989Ell] Ellner, M., Kek, S., Predel, B., " $\text{Ni}_3\text{Al}_4$  - A Phase with Ordered Vacancies Isotypic to  $\text{Ni}_3\text{Ga}_4$ ", *J. Less-Common Met.*, **154**(1), 207-215 (1989) (Experimental, Crys. Structure, 26)
- [1989Hua] Huang, S.C., Ritter, A.M., "Microstructure of Atomized  $\text{Ni}_3\text{Al}$ -B Powder", *J. Mater. Res.*, **4**, 288-293 (1989) (Equi. Diagram, Experimental, 17)
- [1989Sch] Schmid, E.E., "The Al-B-Ni (Aluminum-Boron-Nickel) System", *Bull. Alloy Phase Diagrams*, **10**(5), 537-539 (1989) (Assessment, Crys. Structure, Equi. Diagram, 3)
- [1990Sch] Schmid, E.E., "Al-B-Ni (Aluminum-Boron-Nickel)", MSIT Ternary Evaluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), MSI, Materials Science International Services GmbH, Stuttgart; Document ID: 10.14586.1.20, (1990) (Crys. Structure, Equi. Diagram, Assessment, 5)
- [1990Che] Chen, S.P., Voter, A.F., Albers, R.C., Boring, A.M., Hay, P.J., "Investigation of the Effects of Boron on  $\text{Ni}_3\text{Al}$  Grain Boundaries by Atomistic Simulations", *J. Mater. Res.*, **5**(5), 955-970 (1990) (Calculation, Crys. Structure, Experimental, Mechan. Prop., 62)
- [1990Dha] Dharwadkar, S. R., Hilpert, K., Kobertz, D., Venugopal, V., Nickel, H., "Differential Thermal Analysis and Knudsen Effusion Mass Spectrometry in the Determination of Phase Equilibrium Diagrams in Nickel-Based Superalloys", *High Temp. Sci.*, **28**, 203-215 (1990) (Equi. Diagram, Experimental, Phys. Prop., Thermodyn., 19)
- [1991Guo] Guo, J., Sun, Ch., Li, H., Zhang, Zh., Tang, Y., Hu, Zh., "Effect of Boron Content on Mechanical Properties of Monocrystalline  $\text{Ni}_3\text{Al}$ ", *Mater. Res. Soc. Symp. Proc.: High-Temp. Ordered Intermetallic Alloys IV*, **213**, 655-659 (1991) (Experimental, Crys. Structure, Mechan. Prop., Phys. Prop., 6)
- [1991Kim] Kim, Y.D., Wayman, C.M., "Transformation and Deformation Behavior of Thermoelastic Martensite Ni-Al Alloys Produced by Powder Metallurgy Method" (in Korean), *J. Korean Inst. Met. Mater.*, **29**(9), 960-966 (1991) (Mechan. Prop., Experimental, 15)
- [1991Li] Li, H., Chaki, T.K., "Cracking in the Weld Heat-Affected Zone of Continuously Cast Sheet and Ingot of  $\text{Ni}_3\text{Al}$ ", *Mater. Res. Soc. Symp. Proc.: High-Temp. Ordered Intermetallic Alloys IV*, **213**, 919-924 (1991) (Experimental, 16)
- [1991Yan] Yan, W., Jones, I.P., Smallman, R.E., "The Effect of Boron on Dislocations in  $\text{Ni}_3\text{Al}$ ", *Phys. Status Solidi A*, **125A**, 469-479 (1991) (Experimental, 17)
- [1992Cho] Choudhury, A., White, C. L., Brooks, C. R., "The Intergranular Segregation of Boron in  $\text{Ni}_3\text{Al}$ : Equilibrium Segregation and Segregation Kinetics", *Acta Metall. Mat.*, **40**(1), 57-68 (1992) (Equi. Diagram, Experimental, Kinetics, Theory, Thermodyn., 41)
- [1992Jay] Jayaram, R., Miller, M.K., "An APFIM Analysis of Grain Boundaries and Precipitation in Boron Doped NiAl", *Surf. Sci.*, **266**, 310-315 (1992) (Experimental, Mech. Prop., 15)
- [1992Mur] Murakami, Y., Otsuka, K., Hanada, S., Watanabe, S., "Crystallography of Stress-Induced B2 $\rightarrow$ 7R Martensitic Transformation in a Ni-37.0 at.% Al Alloy", *Mater. Trans., JIM*, **33**(3), 282-288 (1992) (Crys. Structure, Experimental, 25)
- [1992Var] Vardiman, R.G., "Microstructures in Aluminium, Ion Implanted with Boron and Heat Treated", *Acta Metall. Mater.*, **40**, 1029-1035 (1992) (Crys. Structure, Experimental, 7)
- [1993Kha] Khadkikar, P.S., Locci, I.E., Vedula, K., Michal, G.M., "Transformation to  $\text{Ni}_5\text{Al}_3$  in a 63.0 at.% Ni-Al Alloy", *Metall. Trans. A*, **24A**, 83-94 (1993) (Equi. Diagram, Crys. Structure, Experimental, 28)
- [1993Tan] Tan, Y., Shinoda, T., Mishima, Y., Suzuki, T., "Defect Hardening by the Deviation from Stoichiometry in NiAl", *J. Jpn. Inst. Metals*, **57**(2), 220-227 (1993) (Experimental, Crys. Structure, Mech. Prop., Equi. Diagram, 65)
- [1993Wer] Werheit, H., Kuhlmann, U., Laux, M., Lundström, T., "Structural and Electronic Properties of Carbon-Doped  $\beta$ -Rhombohedral Boron", *Phys. Status Solidi*, **B179**, 489-511 (1993) (Crys. Structure, Phys. Prop., Experimental, 51)

- [1993Wu] Wu, T.C., Sass, S.L., "The Influence of Boron Additions on Microstructure of Stoichiometric NiAl", *Scr. Metall. Mater.*, **28**(10), 1287-1292 (1993) (Experimental, Crys. Structure, 10)
- [1994Dus] Duschaneck, H., Rogl, P., "The System Al-B", *J. Phase Equilib.*, **15**(5), 543-552 (1994) (Crys. Structure, Equi. Diagram, Experimental, #, 78) see also *ibid.*, **16**(1), 6 (1995)
- [1994Mur] Murthy, A.S., Goo, E., "Triclinic Ni<sub>2</sub>Al Phase in 63.1 Atomic Percent NiAl", *Met. Mater. Trans., A*, **25A**(1), 57-61 (1994) (Crys. Structure, Experimental, 10)
- [1995Li] Li, G., Deng, W., Xiong, L. Guo, J. Wang, Z., "Diffusive Behaviour of Boron in Ni<sub>3</sub>Al (0.98at.%B) Investigated by Positron Annihilation Technique" (in Chinese), *Nucl. Techn.*, **18**, 148-150 (1995) (Experimental)
- [1996Lim] Lima, M.S.F., Ferreira, P.I., "Microstructure and Mechanical Properties of Ni-Al and Ni-Al-B Alloys Produced by Rapid Solidification Technique", *Intermetallics*, **4**, 85-90 (1996) (Experimental, Mechan. Prop., Crys. Structure, 19)
- [1996Pau] Paufler, P., Faber, J., Zahn, G., "X-Ray Single Crystal Diffraction Investigation on Ni<sub>1+x</sub>Al<sub>1-x</sub>", *Acta Crystallogr. A*, **A52**, C-319 (1996) (Crys. Structure, Experimental, 3)
- [1996Vik] Viklund, P., Häußermann, U., Lidin, S., "NiAl<sub>3</sub>: A Structure Type of its Own?", *Acta Crystallogr. A*, **A52**, C-321 (1996) (Crys. Structure, Experimental)
- [1997Ans] Ansara, I., Dupin, N., Lukas, H.L., Sundman, B., "Thermodynamic Assessment of the Ni-Al System", *J. Alloys Compd.*, **247**, 20-30 (1998) (Thermodyn., Equi. Diagram, 70)
- [1997Bat] Battezzati, L., Antonione, C., Baricco, M., "Undercooling of Ni-B and Fe-B Alloys and Their Metastable Phase Diagrams", *J. Alloys Compd.*, **247**(1-2), 164-171 (1997) (Experimental, Equi. Diagram, 22)
- [1997Bou] Bouche, K., Barbier, F., Coulet, A., "Phase Formation During Dissolution of Nickel in Liquid Aluminium", *Z. Metallkd.*, **88**(6), 446-451 (1997) (Thermodyn., Experimental, 15)
- [1997Poh] Pohla, C., Ryder, P.L., "Crystalline and Quasicrystalline Phases in Rapidly Solidified Al-Ni Alloys", *Acta Mater.*, **45**, 2155-2166 (1997) (Experimental, Crys. Structure, 48)
- [1997Pot] Potapov, P.L., Song, S.Y., Udovenko, V.A., Prokoshkin, S.D., "X-Ray Study of Phase Transformations in Martensitic Ni-Al Alloys", *Metall. Mater. Trans. A*, **28A**, 1133-1142 (1997) (Crys. Structure, Experimental, 40)
- [1998Hil] Hillebrecht, H., Ade, M., "Al-Atoms Versus B<sub>4</sub>-Tetrahedra - A Surprising Mode of Substitution in Tau-Borides Ni<sub>20</sub>Al<sub>3</sub>B<sub>6</sub> and Ni<sub>20</sub>AlB<sub>14</sub>" (in German), *Angew. Chem.*, **110**(7), 981-983 (1998) (Crys. Structure, Experimental, 21)
- [1998Hua] Huang, W., Chang, Y. A., "A Thermodynamic Analysis of the Ni-Al System", *Intermetallics*, **6**, 487-498 (1998) (Thermodyn., Equi. Diagram, 56)
- [1998Rav] Ravelo, R., Aguilar, J., Baskes, M., Angelo, J.E., Fultz, B., Holian, B.L., "Free Energy and Vibrational Entropy Difference between Ordered and Disordered Ni<sub>3</sub>Al", *Phys. Rev. B*, **57**(2), 862-869 (1998) (Thermodyn., Theory, Calculation, 43)
- [1998Sim] Simonyan, A.V., Ponomarev, V.I., Khomenko, N.Yu., Vishnyakova, G.A., Gorshkov, V.A., Yuhvid, V.I., "Combustion Synthesis of Nickel Aluminides", *Inorg. Mater.*, **34**(6), 558-561 (1998), translated from *Neorgan. Mater.*, **34**(6), 684-687 (1998) (Crys. Structure, Experimental, 12)
- [1999Bur] Burkhardt, U., Grin, Y., "Refinement of the Aluminium Diboride Crystal Structure", *Abstract 13<sup>th</sup> International Symposium on Boron, Borides and Related Compounds*, Dinard, France, P13, (1999) (Crys. Structure, 3)
- [1999Cam] Campbell, C.E., Kattner, U.R., "A Thermodynamic Assessment of the Ni-Al-B System", *J. Phase Equilib.*, **20**(5), 485-496 (1999) (Assessment, Equi. Diagram, 50)
- [2000Hig] Higashi, I., "Crystal Chemistry of  $\alpha$ -AlB<sub>12</sub> and  $\gamma$ -AlB<sub>12</sub>", *J. Solid State Chem.*, **154**, 168-176 (2000) (Crys. Structure, Experimental, 18)
- [2000Cam] Campbell, C.E., Boettinger, W.J., "Transient Liquid-Phase Bonding in the Ni-Al-B System", *Metall. Trans. A*, **31A**, 2835-2847 (2000) (Equi. Diagram, Experimental, 37)

- [2000Cho] Chowdhury, S.G., Ray, R.K., Jena, A.K., "Texture Evolution During Recrystallization in a Boron-doped Ni76Al24 Alloy", *Mater. Sci. Eng. A*, **A277**, 1-10 (2000) (Crys. Structure, Experimental, Mechan. Prop.)
- [2000Hal] Hall, A., Economy, J., "The  $\text{Al}_{(L)} + \text{AlB}_{12} \rightleftharpoons \text{AlB}_2$  Peritectic Transformation and Its Role in the Formation of High Aspect Ratio  $\text{AlB}_2$  Flakes", *J. Phase Equilib.*, **21**(1), 63-69 (2000) (Equi. Diagram, Experimental, 21)
- [2001Zhe] Zheng, L.-P., Li, D.-X., Qiu, S., Zhou, W.-J., Jiang, B.-Y., "Dependence of Ni, Al and B Bondary Concentrations on the B Bulk Concentration for the  $\text{Ni}_3\text{Al}-x$  at.% B Grain Boundary", *Nucl. Instrum. Methods Phys. Res./B*, **184**, 354-360 (2001) (Experimental, Phys. Prop., 20)
- [2002Zhe1] Zheltov, P., Grytsiv, A., Rogl, P., Velikanova, T.Ya., Research at Univ. Vienna, (2002) (Equi. Diagram, Crys. Structure)
- [2002Zhe] Zheng, L.-P., Li, D.-X., Zhu, Z.-Y., Jiang, W.-Z., Jiang, B.-Y., Liu, X.-H., "Monte Carlo Simulation Study of the Bulk Effects of Boron on the  $\text{Ni}_3\text{Al}-x$  at.% B Grain Boundary", *Mater. Lett.*, **56**, 65-70 (2002) (Equi. Diagram, Experimental, Phys. Prop., 13)
- [2003Gry] Grytsiv, A., Rogl, P., "Aluminium-Boron-Carbon", MSIT Ternary Evaluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), MSI, Materials Science International Services GmbH, Stuttgart, to be published, (2003) (Equi. Diagram, Crys. Structure, Review, 116)
- [2003Sal] Saltykov, P., Cornish, L., Cacciamani, G., "Al-Ni (Aluminium-Nickel)", MSIT Binary Evaluation Program, in *MSIT Workplace*, Effenberg, G. (Ed.), MSI, Materials Science International Services GmbH, Stuttgart; to be published, (2003) (Equi. Diagram, Review, 164)

**Table 1:** Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
( $\beta\text{Al}$ )	$hP2$ $P6_3/mmc$ Mg	$a = 269.3$ $c = 439.8$	at 25°C, 20.5 GPa [Mas2]
( $\alpha\text{Al}$ ) < 660.452	$cF4$ $Fm\bar{3}m$ Cu	$a = 404.96$	at 25°C [Mas2] dissolves 0.01 at.% Ni at 639.9°C [Mas2]
(Ni) < 1455	$cF4$ $Fm\bar{3}m$ Cu	$a = 352.40$	at 25°C [Mas2] dissolves 20.2 at.% Al at 1385°C [Mas2] dissolves 0.3 at.% B at 1093°C [Mas2]
( $\beta\text{B}$ ) < 2092	$hR333$ $R\bar{3}m$ $\beta\text{B}$	$a = 1093.30$ $c = 2382.52$ $a = 1096.5$ $c = 2386.8$ $a = 1096.15$ $c = 2385.44$ $a = 1095.84$ $c = 2385.46$	[Mas2, 1993Wer] dissolves up to ca 2 at.% Ni at 1035°C at $\text{AlB}_{31}$ [V-C2] for $\text{NiB}_{48.5}$ [V-C2] for $\text{NiB}_{\sim 20}$ [V-C2]
$\text{Al}_2\text{B}_3$ $\leq 525$	$hR^*$ $\text{Al}_2\text{B}_3$ (?)	$a = 1840$ $c = 896$	at 60 at.% B [1992Var] Metastable?

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
AlB <sub>2</sub> ≤ 956±5	<i>hP3</i> <i>P6/mmm</i> AlB <sub>2</sub>	$a = 300.6$ $b = 325.2$ $a = 300.67 \pm 0.01$ $b = 325.36 \pm 0.02$ $a = 300.43 \pm 0.03$ $b = 325.19 \pm 0.06$	temperature from [2000Hal] [1994Dus] [2002Zhe1] [1999Bur] for Al <sub>0.9</sub> B <sub>2</sub>
αAlB <sub>12</sub> ≤ 2050	<i>tP216</i> <i>P4<sub>1</sub>2<sub>1</sub>2</i> αAlB <sub>12</sub>	$a = 1015.8$ $c = 1427.0$ $a = 1014.93 \pm 0.07$ $c = 1425.0 \pm 0.5$	[1994Dus] $\rho_{\text{exp.}} = 2.65 \text{ Mgm}^{-3}$ [2002Zhe1]
γAlB <sub>12</sub>	<i>oP384</i> <i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i> γAlB <sub>12</sub>	$a = 1014.4$ $b = 1657.3$ $c = 1751.0$	[1994Dus, 2000Hig] metastable phase or ternary product stabilized by small amounts of impurity metals present in Al flux grown material; $\rho_{\text{exp.}} = 2.56 \text{ Mgm}^{-3}$
NiAl <sub>3</sub> < 856	<i>oP16</i> <i>Pnma</i> NiAl <sub>3</sub>	$a = 661.3 \pm 0.1$ $b = 736.7 \pm 0.1$ $c = 481.1 \pm 0.1$ $a = 659.8$ $b = 735.1$ $c = 480.2$	[1996Vik] [Mas2] [1997Bou, V-C2]
Ni <sub>2</sub> Al <sub>3</sub> < 1138	<i>hP5</i> <i>P<math>\bar{3}m1</math></i> Ni <sub>2</sub> Al <sub>3</sub>	$a = 402.8$ $b = 489.1$	36.8 to 40.5 at.% Ni [Mas2] [1997Bou, V-C2]
Ni <sub>3</sub> Al <sub>4</sub> < 702	<i>cI112</i> <i>Ia<math>\bar{3}d</math></i> Ni <sub>3</sub> Ga <sub>4</sub>	$a = 1140.8 \pm 0.1$	[1989Ell, V-C2]
NiAl < 1651	<i>cP2</i> <i>Pm<math>\bar{3}m</math></i> CsCl	$a = 286.0$ $a = 287$ $a = 288.72 \pm 0.02$ $a = 287.98 \pm 0.02$	42 to 69.2 at.% Ni [Mas2] [1987Kha] at 63 at.% Ni [1993Kha] at 50 at.% Ni [1996Pau] at 54 at.% Ni [1996Pau]
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]
Ni <sub>3</sub> Al < 1372	<i>cP4</i> <i>Pm<math>\bar{3}m</math></i> AuCu <sub>3</sub>	$a = 356.77$ $a = 358.9$ $a = 356.32$ $a = 357.92$ $a = 357.3$	73 to 76 at.% Ni [Mas2] [1986Hua] at 63 at.% Ni [1993Kha] disordered [1998Rav] ordered [1998Rav] for Ni <sub>75</sub> Al <sub>24</sub> B [V-C2]



Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
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>	$a = 868.5 \pm 0.6$ $b = 623.2 \pm 0.4$ $c = 618.5 \pm 0.4$ $\beta = 96.50 \pm 0.05^\circ$	Metastable [1988Li, 1997Poh]
Ni <sub>x</sub> Al <sub>1-x</sub>	<i>tP4</i> <i>P4/mmm</i> AuCu	$a = 383.0$ $c = 320.5$ $a = 379.5$ $c = 325.6$ $a = 379.5$ $c = 325.6$ $a = 375.1$ $c = 330.7$ $a = 379.9$ to $380.4$ $c = 322.6$ to $323.3$ $a = 371.7$ to $376.8$ $c = 335.3$ to $339.9$ $a = 378.00$ $c = 328.00$	Martensite, metastable $0.60 < x < 0.68$ [1993Kha] at 62.5 at.% Ni [1991Kim] at 63.5 at.% Ni [1991Kim] at 66.0 at.% Ni [1991Kim] at 64 at.% Ni [1997Pot] at 65 at.% Ni [1997Pot] [1998Sim]
	<i>m**</i>	$a = 418$ $b = 271$ $c = 1448$ $\alpha = 90^\circ$ $\beta = 93.4^\circ$ $\gamma = 90^\circ$	[1992Mur]
Ni <sub>2</sub> Al	<i>hP3</i> <i>P<math>\bar{3}m1</math></i> CdI <sub>2</sub>	$a = 407$ $c = 499$	Metastable [1993Kha]
	<i>aP126</i> <i>P<math>\bar{1}</math></i>	$a = 1252$ $b = 802$ $c = 1526$ $\alpha = 90^\circ$ $\beta = 109.7^\circ$ $\gamma = 90^\circ$	[1994Mur]
D <sub>1</sub>	decagonal		Metastable [1988Li]
D <sub>4</sub>	decagonal		Metastable [1988Li]
Ni <sub>3</sub> B < 1156	<i>oP16</i> <i>Pnma</i> Fe <sub>3</sub> C	$a = 521.99$ $b = 661.46$ $c = 436.30$ $a = 530.62$ $b = 667.50$ $c = 444.14$	at 25°C [V-C2, Mas2] at 1100°C [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Ni <sub>2</sub> B < 1125	<i>tI</i> 12 <i>I4/mcm</i> CuAl <sub>2</sub>	<i>a</i> = 499.1 <i>c</i> = 424.7	[V-C2, Mas2]
<i>o</i> -Ni <sub>4</sub> B <sub>3</sub> < 1025	<i>oP</i> 28 <i>Pnma</i> <i>o</i> -Ni <sub>4</sub> B <sub>3</sub>	<i>a</i> = 1195.40 <i>b</i> = 298.15 <i>c</i> = 656.84	at 41.4 at.% B [V-C2, Mas2]
<i>m</i> -Ni <sub>4</sub> B <sub>3</sub> < 1031	<i>mC</i> 28 <i>C2/c</i> <i>m</i> -Ni <sub>4</sub> B <sub>3</sub>	<i>a</i> = 642.82 <i>b</i> = 487.95 <i>c</i> = 781.90 $\beta$ = 103.47°	at 43.9 at.% B [V-C2, Mas2]
NiB < 1035	<i>oC</i> 8 <i>Cmcm</i> CrB	<i>a</i> = 292.9 <i>b</i> = 739.2 <i>c</i> = 296.1	[V-C2, Mas2]
* $\tau_1$ , Ni <sub>20</sub> Al <sub>3</sub> B <sub>6+x</sub>	<i>cF</i> 116 <i>Fm</i> $\bar{3}m$ Cr <sub>23</sub> C <sub>6</sub>	<i>a</i> = 1048.5 <i>a</i> = 1048 <i>a</i> = 1062 <i>a</i> = 1049.5 <i>a</i> = 1055.2 <i>a</i> = 1048.5 9 <i>a</i> = 1051.10 <i>a</i> = 1051.93 <i>a</i> = 1056.89 <i>a</i> = 1058.95 <i>a</i> = 1059.22 <i>a</i> = 1061.67	Ni <sub>7.1</sub> Al <sub>0.8</sub> B <sub>2.1</sub> [V-C2] Ni <sub>20</sub> Al <sub>3</sub> B <sub>6</sub> [1973Cha]; 1000°C Ni <sub>20</sub> Al <sub>3</sub> B <sub>12</sub> [1973Cha]; 1000°C alloy 65Ni10Al25B [1962Sta2]; 800°C <sup>#</sup> alloy 60Ni10Al30B [1962Sta2]; 800°C <sup>#</sup> Ni <sub>20.5</sub> Al <sub>2.5</sub> B <sub>6</sub> [1998Hil] Ni <sub>20</sub> Al <sub>3</sub> B <sub>6</sub> [1998Hil] Ni <sub>20</sub> Al <sub>2.7</sub> B <sub>7</sub> [1998Hil] Ni <sub>20</sub> Al <sub>2.4</sub> B <sub>8.4</sub> [1998Hil] Ni <sub>20</sub> Al <sub>1.1</sub> B <sub>13.5</sub> [1998Hil] Ni <sub>20</sub> Al <sub>1.2</sub> B <sub>13.2</sub> [1998Hil] Ni <sub>20</sub> AlB <sub>14</sub> [1998Hil]
Ni <sub>23</sub> B <sub>6</sub>	-	-	metastable, [1997Bat]
* $\tau_2$ , Ni <sub>5</sub> AlB <sub>4</sub> ≤ 800	-	-	[1973Cha]
* $\tau_3$ , Ni <sub>8</sub> AlB <sub>11</sub> (h) > 800	monoclinic	<i>a</i> = 3580 <i>b</i> = 1093 <i>c</i> = 1630 $\beta$ = 112°	[1973Cha], from single crystal rotation photographs
* $\tau_3$ , Ni <sub>8</sub> AlB <sub>11</sub> (r) ≤ 800	-	-	[1973Cha]

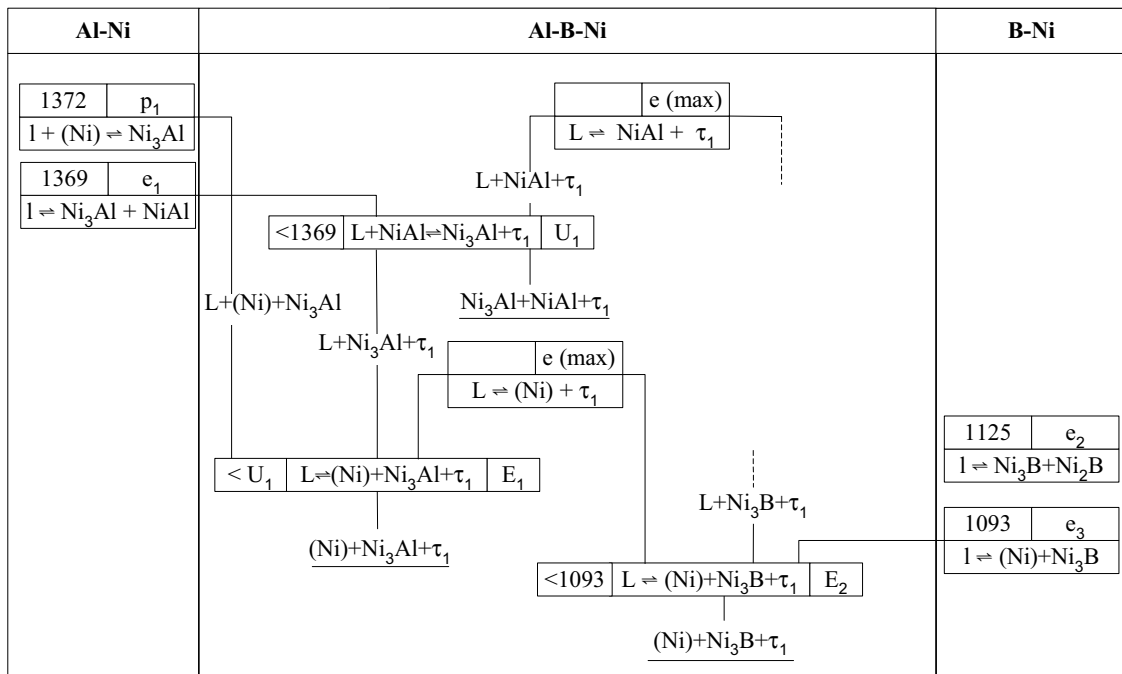
# for a discussion of phase region and equilibrium conditions, see section “Solid Phases”.

**Table 2:** Invariant Equilibria (data are only available for the liquid phase)

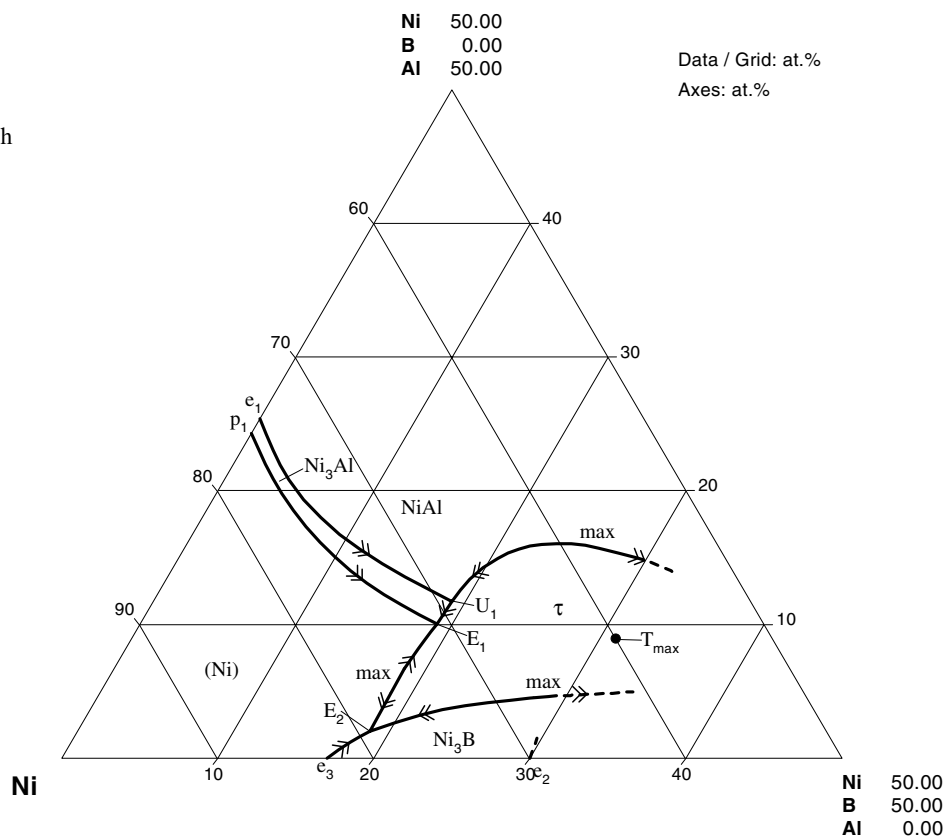
Reaction	$T [^{\circ}\text{C}]$ Experimental, [1962Sta1]	$T [^{\circ}\text{C}]$ Calculated,* [1999Cam]	Type	Phase	Composition (at.%) Experimental <sup>#</sup>			Composition (at.%) Calculated [1999Cam]		
					Ni	Al	B	Ni	Al	B
$\text{L} \rightleftharpoons \text{NiAl} + \tau_1$	-	-	e, max	L	-	-	-	-	-	-
$\text{L} + \text{NiAl} \rightleftharpoons \text{Ni}_3\text{Al} + \tau_1$	<1369	1348	$\text{U}_1$	L	~69	~13	~18	73.8	24.1	2.1
$\text{L} \rightleftharpoons (\text{Ni}) + \tau_1$	-	-	e, max	L	~75	~7	~18	-	-	-
$\text{L} \rightleftharpoons (\text{Ni}) + \text{Ni}_3\text{Al} + \tau_1$	< $\text{U}_1$	1349	$\text{E}_1$	L	~69	~10	~18	75.4	22.5	2.1
$\text{L} \rightleftharpoons (\text{Ni}) + \text{Ni}_3\text{B} + \tau_1$	<1093	1090	$\text{E}_2$	L	~79	~3	~18	83.8	0.03	16.2
$\text{L} \rightleftharpoons \text{NiAl} + \text{NiB} + \tau_1$	-	692	$\text{E}_3$	L	~52	~10	~38	34.2	17.9	47.9

\* calculated data refer to the Al-Ni binary modeled by [1998Hua]; data changed slightly if the model of [1997Ans] was used; for details see original work by [1999Cam].

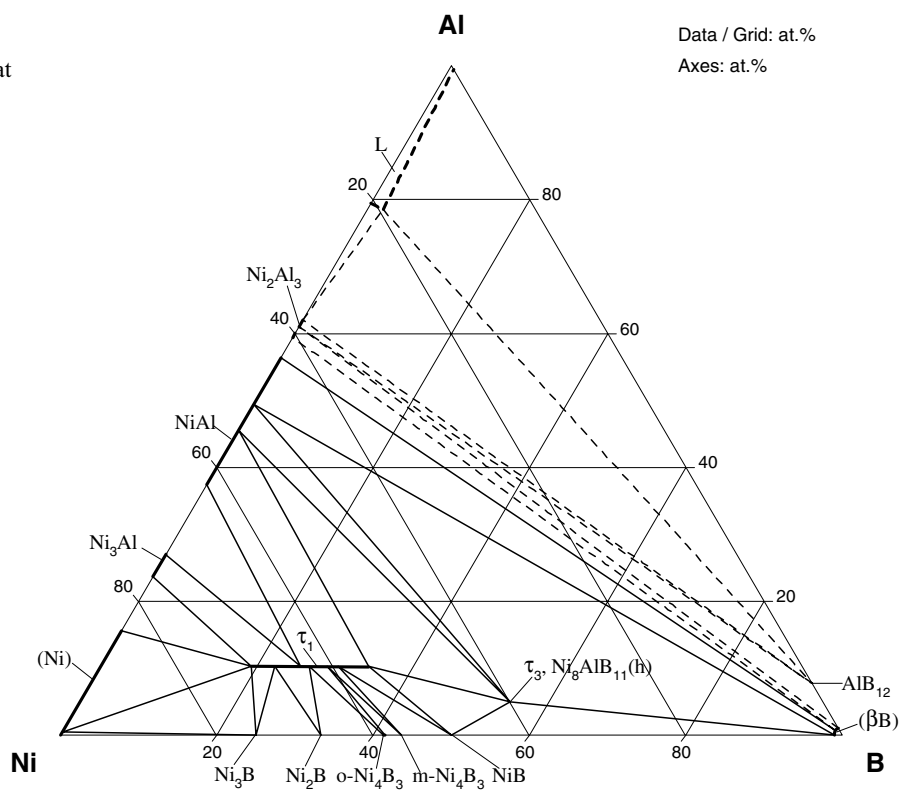
<sup>#</sup> values read from small diagram [1962Sta1].

**Fig. 1:** Al-B-Ni. Partial reaction scheme

**Fig. 2: Al-B-Ni**  
Partial liquidus  
surface in the Ni-rich  
region after  
[1962Sta1]



**Fig. 3: Al-B-Ni.**  
Isothermal section at  
1000°C



**Fig. 4: Al-B-Ni.**  
Isothermal section at  
800°C

