Aluminium – Boron – Nitrogen

Vasyl' Tomashik

Literature Data

A critical assessment of the Al-B-N ternary system has been published by [1990Jeh], which included the literature data up to 1986. Literature data up to 1991 have been critically reviewed by [1992Rog] and later by [1998Rem]. Subsequently this system was investigated experimentally by several techniques and for different temperature and composition ranges and calculated thermodynamically. The present assessment takes into account all available data.

Information on Al-B-N phase relations appeared for the first time in the work of [1965Pri], where the prospects were discussed to develop from this system alloys with special physical properties. Today general agreement exists that there are no ternary compounds in this system. Various methods were used to prepare the specimens. [1966Pri, 1968Pri, 1972Mog, 1979Sir, 1980Ole, 1982And2] used pressure sintering of polycrystalline samples Al+BN or AlN+B at various temperatures and found that the density of the Al+BN samples decreases after sintering whilst the sintering of AlN+B samples leads to increasing density [1966Pri, 1968Pri]. BN interacts with Al in the process of hot pressing and forms AlN [1972Mog]. The sintering of polycrystalline BN-Al specimens (1500-3000°C and 5-9.5 GPa) yielded cubic BN containing 2-3 mass% dissolved Al; higher Al contents resulted in the formation of *h*-BN, AlB_{12} and AlN [1979Sir]. According to the data of [1999Bez] the interaction of Al melt and *c*-BN at 8GPa begins at 1270°C with the formation of AlN, AlB_2 and AlB_{12}. It was determined that the lattice constant of *c*-BN increases at the reaction sintering of *c*-BN and Al [2000Bez].

AlN was found to act as a catalyst for the synthesis of cubic BN from hexagonal BN under the inert or reducing atmosphere in lowering the temperature and pressure conditions [1977But, 1979Maz, 1980Ole, 1981Hir]. At 1600°C and 6.5 GPa the well-crystallized hexagonal BN could be completely be converted into *c*-BN by adding 20 mole% AlN and 20 mass% of toluene [1981Hir]. Reducing atmosphere in the high-pressure cell should enhance the catalytic effect of AlN.

[1972Lyu, 1973Lyu] alternatively prepared Al+B+N alloys by nitrating complex Al and B salts or mixtures of metal and complex salts in NH_3 atmosphere.

The experimental results allow to conclude that the mutual solid solubility of AlN and BN in the quasibinary system AlN-BN is small [1965Pri, 1972Lyu, 1973Lyu, 1979Sir, 1982And1, 1982And2, 1989Pol]. The lattice parameter of BN increased from 361 to 364.4 pm on saturation with Al [1977But]. According to calculations of the lattice parameters, using a model with the eight-atom clusters, the average value of lattice constant varies linearly with t composition for the $Al_xB_{1-x}N$ solid solution at 830°C and the calculated value of the fluctuation *a* at $x = 0.5$ is equal to 37 pm [2002Tel].

In the reaction of BN crucibles with liquid Al, AlB_2 and AlB_{12} boride inclusions are formed [1967Lue]. In Al containing BN films prepared by dual-ion beam sputtering, the amount of cubic phase decreased monotonically with increasing Al concentration. The recorded structure of such films changed to that of hexagonal BN when the content of Al exceeded 3.2 at.% [2002Kur].

Binary Systems

For the best match of ternary and binary data the binary descriptions of the MSIT Binary Evaluation Program are accepted here: Al-B [2003Ted], Al-N [2003Fer] and B-N [2003Rec].

Solid Phases

No ternary compound exists in the Al-B-N system. All unary and binary phases are listed in Table 1.

Pseudobinary Systems

A hypothetical phase diagram of the AlN-BN pseudobinary system was constructed in the investigation at 8-9 GPa and 2000-2500°C [1980Bar]. Homogeneous solid solutions were obtained at the simultaneous nitration in the NH_3 flow of BN and Al powder. Later [1983But] found that the *c*-BN solid solutions contains up to 25 mole% AlN (Table 1). It is worth noting that the phase diagram presented there is in disagreement with the Phase Rule and the large solubility ranges disagree with the information given by [1989Pol], who reports that the solubility of BN in AlN is small and that the lattice parameter of AlN after annealing of the mixtures AlN+BN at 7 GPa and 1500°C does not change. Quantum-chemical calculations indicate that the phase based on BN has the highest stability in the system [1982And1, 1982And2].
Thermodynamic calculations based on a regular solution model have predicted an unstable region of mixing to occur in the AlN-BN system [2001Tak]. The interaction parameter (138.5 $kJ \cdot mol^{-1}$) that was used in the calculations has been analytically obtained by the valence force field model, modified for wurtzite structures. According to the interaction parameter the value of the critical temperature is found to be 8060°C. The phase diagram of the AlN-BN system including the spinodal and binodal curves was also calculated using the generalized quasichemical approximation and *ab-initio* total energy method [2002Tel]. From these calculations the critical temperature appears to be very high, approximately 9230°C, which results in a very large miscibility gap. The phase diagram as far as obtained experimentally, verifies that there is spinodal decomposition for the $Al_xB_{1-x}N$ alloys in the interval $0.051 < x < 0.963$.

Invariant Equilibria

The reaction scheme given in Fig. 1 incorporates the “Thermo-Calc” calculations by [1993Wen] and the binary data given by [2003Ted, 2003Fer, 2003Rec].

Isothermal Sections

At room temperature the Al-B-N system is divided into five triangles (Al-AlB_2-AlN, AlN-AlB_2-AlB_{12}, AlN-AlB_{12}-BN, AlB_{12}-B-BN and AlN-BN-N) without solid solubility of the third component in all binary compounds [1979Sir, 1990Jeh]. According to the data of [2002Riz] the Al-B-N ternary system at 1500°C can be divides into four triangles (Al-AlB_{12}-AlN, AlB_{12}-AlN-BN, AlB_{12}-B-BN and AlN-BN-N). Isothermal sections at 2500°C and 100 kPa or 2500°C and 8 GPa presented by [1982And2] reveal a rather unusual extension of the AlN and BN solid solutions based on. Phase equilibria in the Al-B-N system at 900°C under 100 kPa argon (in the absence of external nitrogen) have been established from X-ray powder diffraction analysis [1991Rem, 1992Rog] and are given in Fig. 2. This isothermal section was reproduced in the review [1994Mch]. Lattice parameters suggest a mutual solubility of AlN and BN of less than ~4 mole% with no significant changes in solubility between 900 and 1600°C and nitrogen practically does not dissolve in the binary aluminium borides. Some isothermal sections have been calculated using the program Thermo-Calc (Figs. 3-9) [1993Wen].

Notes on Materials Properties and Applications

The addition of 10 vol.% Al allows to improve the sintering ability of BN-TiB_2 material for the manufacture of evaporation boats [1972Mog].
The compressive stress of 5.6 GPa and the hardness value of 60 GPa of the BN films were reduced to 2 and 13 GPa respectively after adding 3.2 at.% Al [2002Kur]. Compared with pure cubic BN film the oxidation resistance of the BN films improves drastically with Al additions of less then 2.3 at.%. The addition of Al is a very effective technique for preventing delaminating and for controlling internal stress, as well as improving the oxidation resistance.
A linear behavior of the bulk modulus with composition was obtained for $Al_xB_{1-x}N$ ternary alloys (from 209 GPa for AlN to 386 GPa for BN) [2002Tel].

Miscellaneous

The wetting angle of Al on *h*-BN, as measured by the sessile drop method at 1000°C, was given as Θ=157° [1966Yas]. For *c*-BN the wetting angle increases with increasing pressure: 40° at 2.5 GPa and 1450°C; 85° respectively 60° at 8.0 GPa and 1700°C, respectively 2000°C [1999Bez].

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αAl) < 660.452	*cF*4 $Fm\bar{3}m$ Cu	a = 404.96	at 25°C [Mas2]
(βB) < 2092	*hR*333 $R\bar{3}m$ βB	a = 1093.30 c = 2382.52 a = 1092.2 c = 2381.1 a = 1096.5 c = 2386.8 a = 1097.4 c = 2387.7	[Mas2, 1993Wer] at 1.1 at.% C [1993Wer] linear da/dx, dc/dx at AlB_{31} [V-C2] from samplr $Al_4B_{95}C_1$, quenched from 1400°C, contains $Al_3B_{48}C_2$ and αAlB_{12} [1993Bau]
(αN) < -237.54	*cP*8 *Pa3* αN	a = 566.1	[Mas2]
αAlB_{12} < 2050	*tP*216 $P4_12_12$ αAlB_{12}	a = 1015.7 ± 0.5 c = 1475 ± 11	[2003Ted]
γAlB_{12} < 1450	*oP*384 $P2_12_12_1$ γAlB_{12}	a = 1014.0 b = 1657.3 c = 1751.0	[2003Ted]
AlB_2 ≤ 956±5	*hP*3 *P6/mmm* AlB_2	a = 300.58 ± 0.05 c = 325.33 ± 0.08	[2003Ted]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Al_2B_3 < 525	*hR** Al_2B_3	*a* = 1840 *c* = 896	[2003Ted] metastable
AlN < 2434.7	*hP*4 ZnS	*a* = 311.14 *c* = 497.92	at 25°C [2003Fer]
h-BN < 2397	*hP*4 $P6_3mc$ BN	*a* = 250.4 *c* = 666.1	[2003Rec]
c-BN	*cF*8 $F\bar{4}3m$ ZnS	*a* = 361.53 ± 0.04	[2003Rec]
w-BN	*hP*4 $P6_3/mmc$ ZnS	*a* = 255.0 ± 0.5 *c* = 423 ± 1	[2003Rec]
r-BN	*hR*6	*a* = 250.4 *c* = 999.1	[2003Rec]
Compressed *h*-BN	*mC*4 *C*2/*c* or *Cc*	*a* = 433 *b* = 250 *c* = 310 to 330 β = 92-95°	[2003Rec]
$Al_xB_{1-x}N$	*cF*8 $F\bar{4}3m$ ZnS	*a* = 361 *a* = 364.4 *a* = 361 ± 0.5	at *x* = 0 at *x* = 0.333 [1977But] at *x* = 0
$Al_xB_{1-x}N$		*a* = 361.2 ± 0.5 *a* = 362.7 ± 0.5 *a* = 363.5 ± 0.5	at *x* = 0.05 at *x* = 0.09 at *x* = 0.25 [1983But]

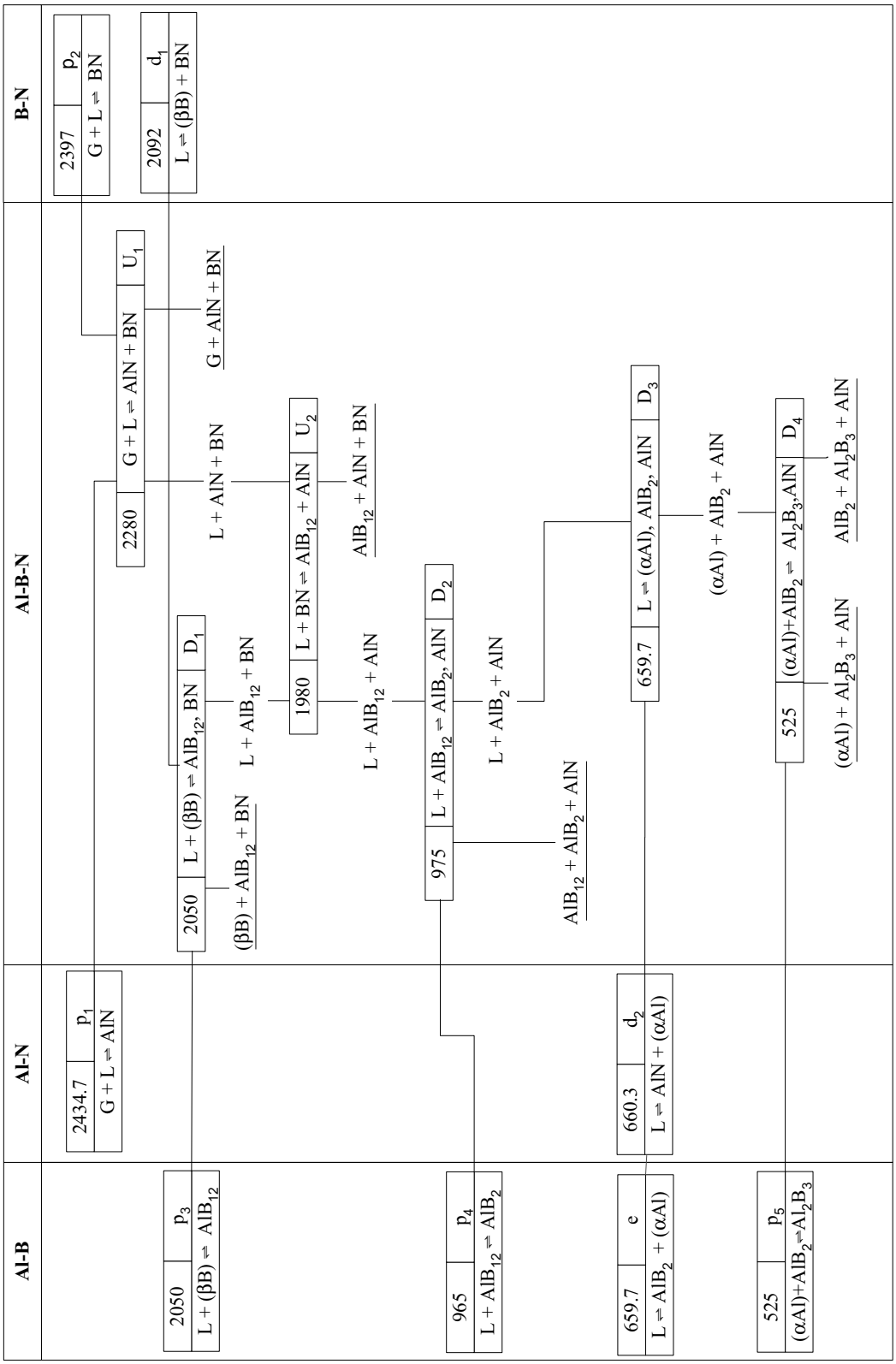

Fig. 1: Al-B-N. Reaction scheme after [1993Wen] with some modifications regarding the accepted binary diagrams from [2003Gry, 2002Fer, 2003Rec]

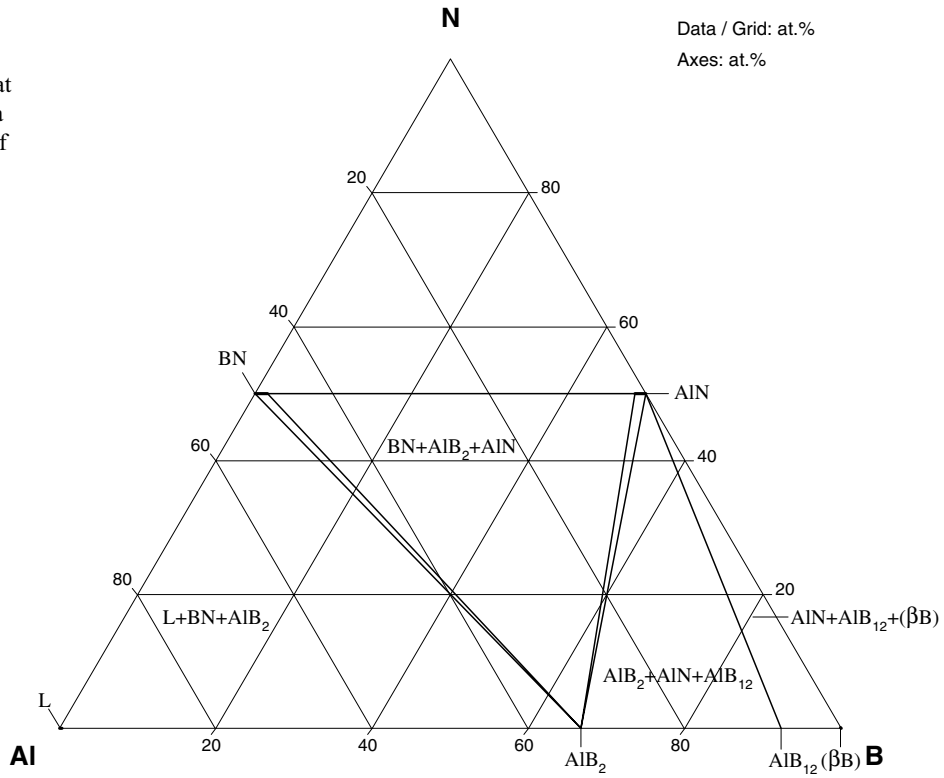

Fig. 2: Al-B-N. Isothermal section at 900°C under 10^5 Pa argon (in absence of external nitrogen) [1991Rem]

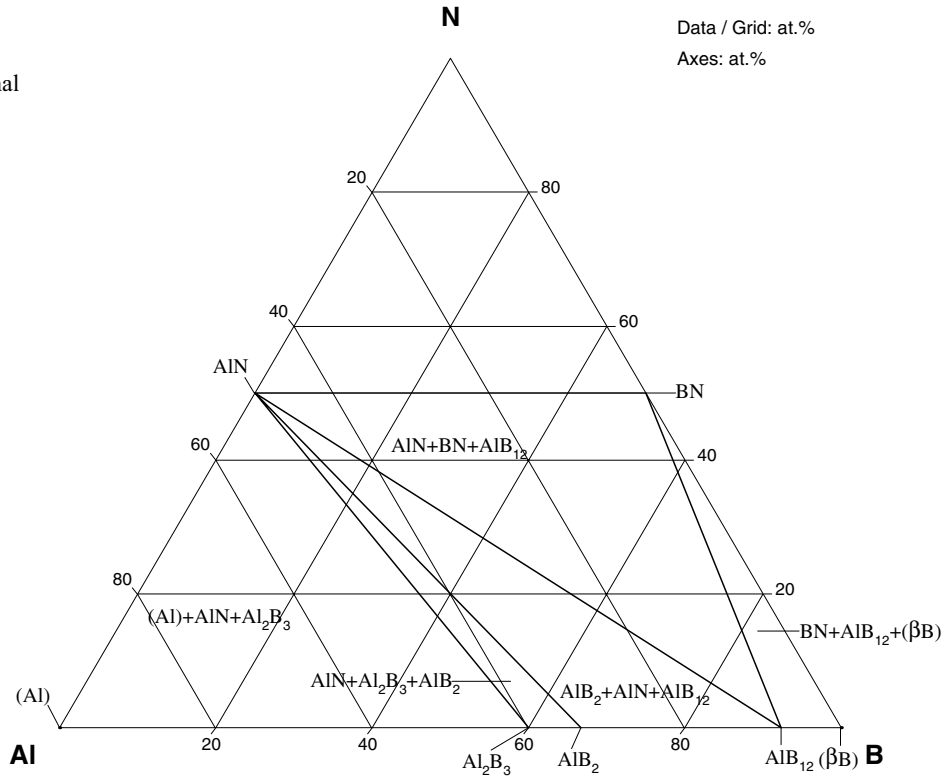

Fig. 3: Al-B-N Calculated isothermal section at 230°C

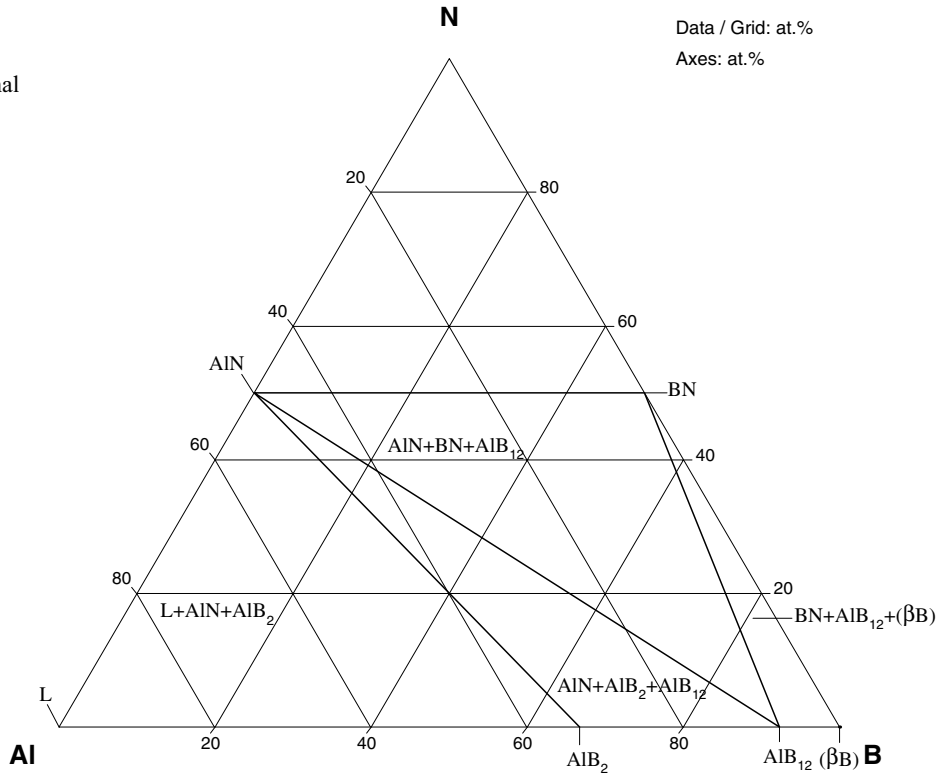

Fig. 4: Al-B-N.
Calculated isothermal section at 730°C

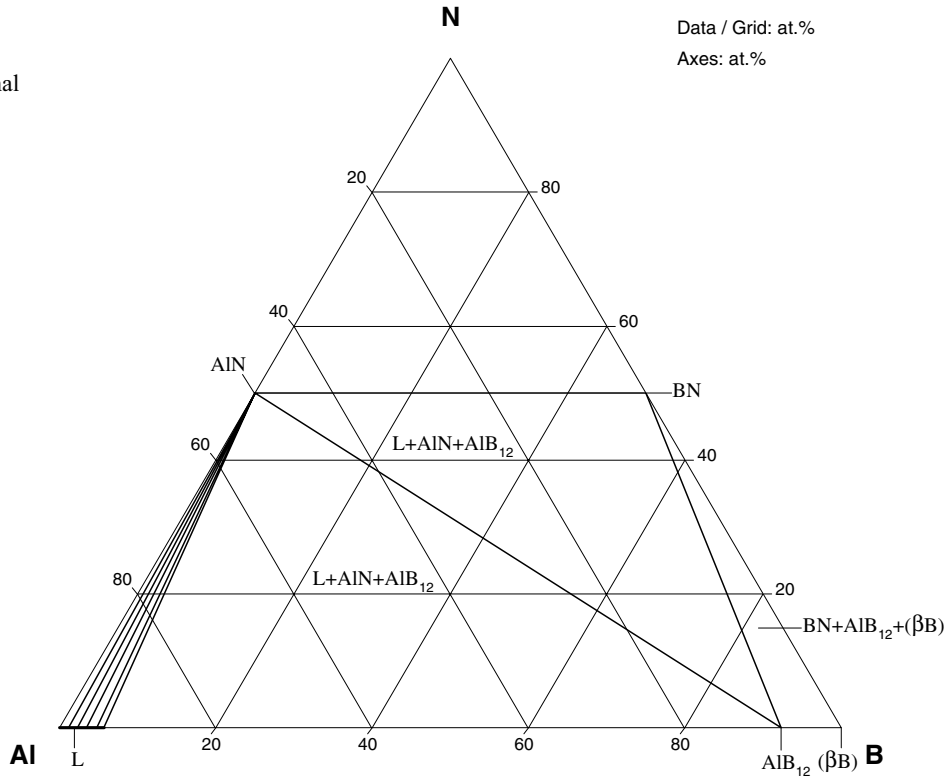

Fig. 5: Al-B-N.
Calculated isothermal section at 1230°C

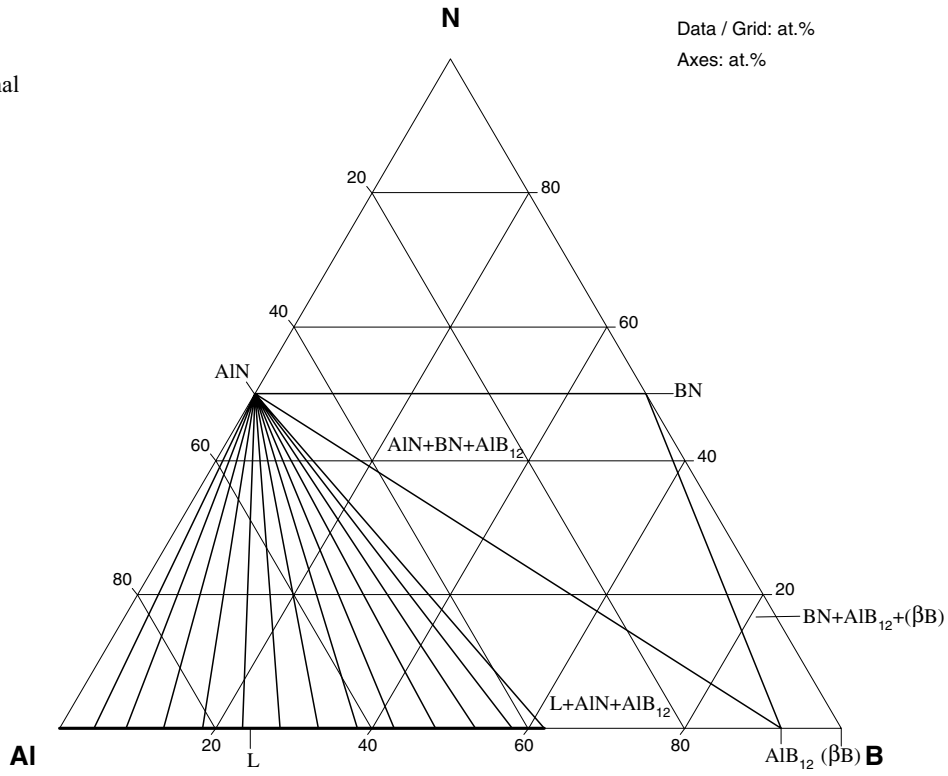

Fig. 6: Al-B-N. Calculated isothermal section at 1730°C

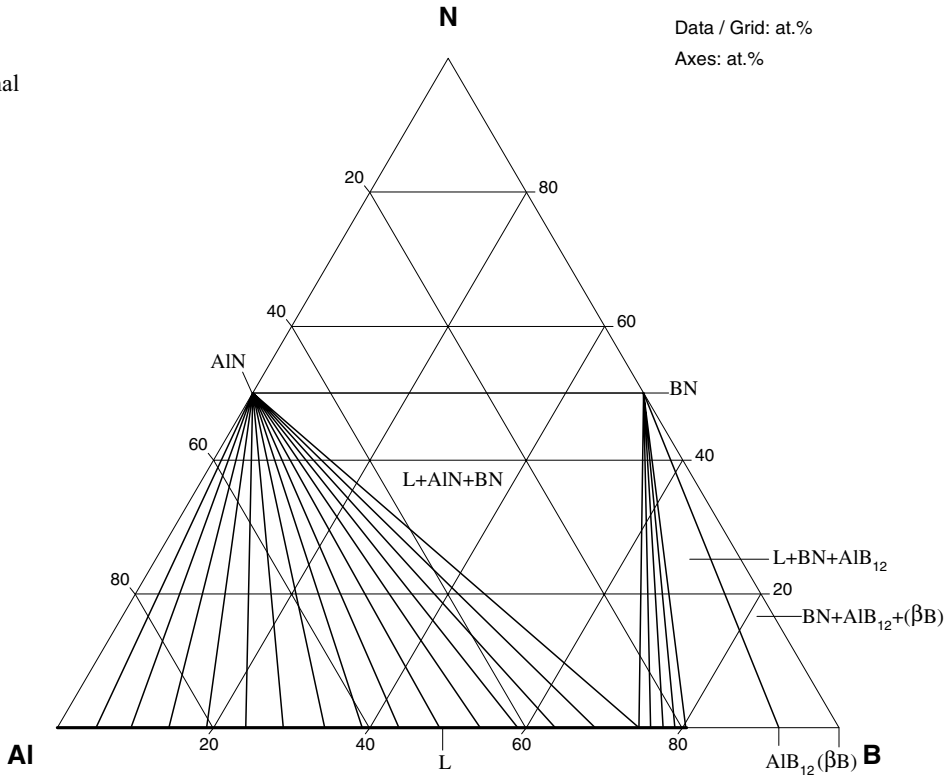

Fig. 7: Al-B-N. Calculated isothermal section at 2060°C

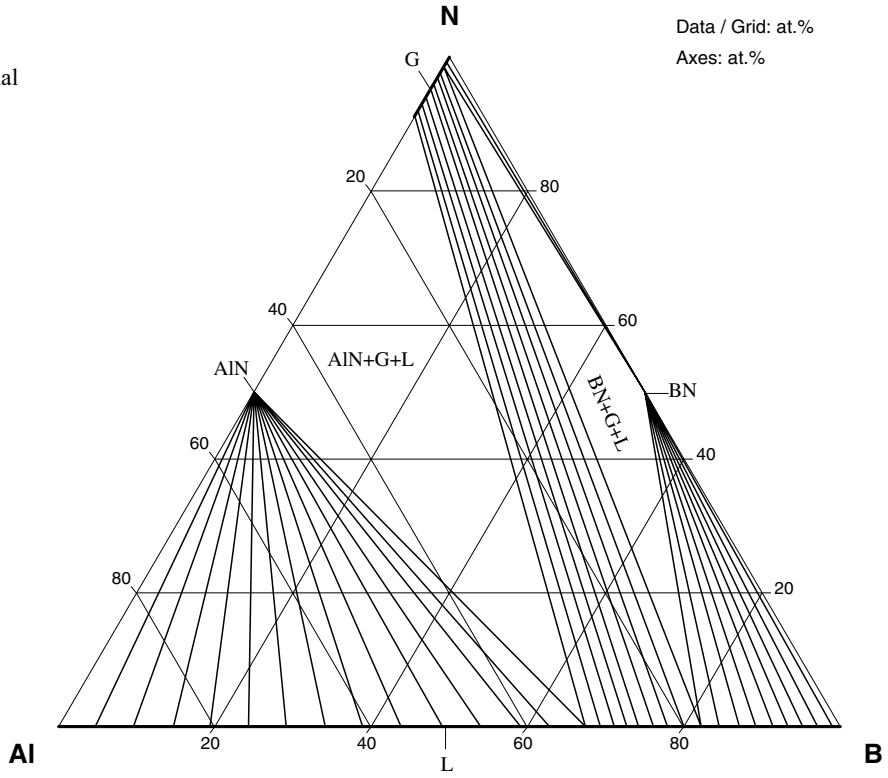

Fig. 8: Al-B-N.
Calculated isothermal section at 2330°C

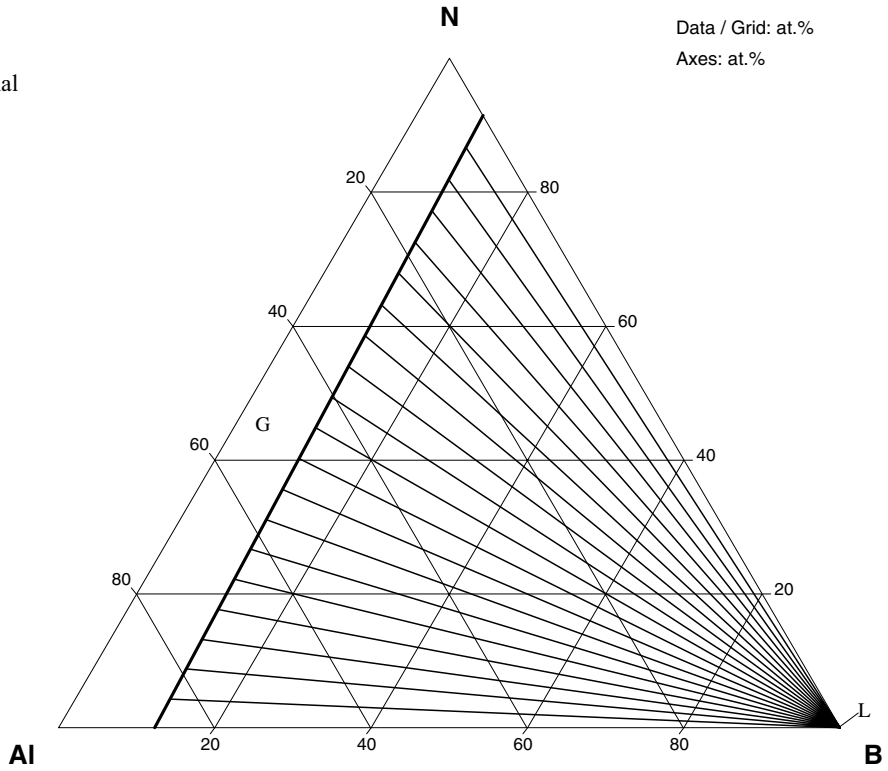

Fig. 9: Al-B-N.
Calculated isothermal section at 3430°C