Aluminium – Boron – Titanium

Anatoliy Bondar

Literature Data

The Al-rich corner in the system has been of great interest due to the fact that Ti and B additions are widely used as grain refiner in the aluminium casting industry. The extensive literature on the phase relationship including Al-base phase was repeatedly assessed by Hayes & Lukas [1991Hay, 1990Hay, 1989Hay], Abdel-Hamid et al. [1986Abd, 1985Abd1, 1985Abd2] and others. However there were some confusions and contradicting conclusions. The main concern whether the $(Ti,Al)B_2$ solid solution is stable or metastable. The cogent evidences of [1999Fje, 1999Zup, 1998Zup1, 1998Zup2, 1994Tok] have confirmed instability of mixed diboride $(Ti,Al)B_2$ in agreement with data of Abdel-Hamid et al. [1986Abd, 1985Abd1, 1985Abd2, 1984Abd] and others. Hayes & Lukas [1991Hay, 1990Hay, 1989Hay] stated that their computed results show compatibility of the mixed boride phase $(Al,Ti)B_2$ existence with all the experimental results in the literature. However, their isopleth at 98 mass% Al and 1300°C liquidus isotherm are not affected by whether the continuous solid solution $(Al,Ti)B_2$ is stable or not.

Fjellstedt et al. [2001Fje, 1999Fje] prepared samples from pure Al (99.998 mass% purity), TiB_2 (97 %), and AlB_2 (98 %) in a high-frequency induction furnace. The alloys were heated in Al_2O_3 crucible at 1530°C for ~1 h, then they were heat treated at 700, 800, and 900°C for 240-600 h. The samples were examined with optical microscopy and SEM equipped with EDS. Besides, the Ti and B solubility in the (Al) melt was calculated using a subregular solution model.

Zupanic et al. [1999Zup, 1998Zup1, 1998Zup2] prepared alloys by arc melting in purified Ar and aluminothermal synthesis at 1050-1100°C. Some alloys were heated and cooled at a rate of 0.1-10 $K \cdot min^{-1}$ from 500 to 1400°C in alumina crucibles. The specimens were annealed at 800 ± 2°C for 1000 h, being put into alumina crucibles and sealed into evacuated silica tubes, followed by quenching in water bath, as well as from 650 to 1000°C for 70 h and at 1600°C 10 h followed by cooling at 60 $K \cdot min^{-1}$. The samples were studied with X-ray powder diffractometer, light microscopy, and SEM (with EDS).

Stolz et al. [1995Sto, 1994Sto] used pure Al of 99.999 mass% purity and commercial master-alloys (~99.7 %). The samples were produced by casting in Ar and heat treated at 577°C for 20 days. They were examined with XRD, DTA, Auger electron spectroscopy and SEM supplemented with EDS equipment.

Abdel-Hamid et al. [1985Abd1,1985Abd2, 1984Abd] used Al of 99.995 or 99.98 mass% purity, powder B (99.7 %) and Ti. The samples prepared in the range from 700 to 1000°C were studied by optic microscopy, SEM (with EPMA), and TEM, as well as melt composition was determined using electromagnetic separation or decantation.

The Ti-rich alloys were investigated in [2002Art, 1992Gra, 1991Hym, 1991Sch, 1990Hym, 1989Hym, etc.] not so comprehensively as the Al-rich one. In [2002Art] alloys were studied by methods of metallography, XRD, DTA, EPMA, microhardness and hot hardness.

Hyman et al. [1991Hym, 1989Hym] studied arc melted and splat-quenched samples made of high-purity Ti (<200 ppm O), Al (99.99 mass% Al), and nitrogen-free B powder (99.7 %). Optical microscopy, SEM, and TEM were used to study structure.

In [1991Sch] two samples were studied with TEM using EDX analysis and high-resolution imaging. Flakes of Ti-25Al-4B and Ti-48Al-5B (at.%) compositions were produced by electron beam melting and splat quenching, and in addition they were annealed in quartz capsules at 800, 1000, and 1200°C for 1 h.

Binary Systems

The binary systems used were as followed: Al-B [2000Hal, 1994Dus], Al-Ti [1997Zha] and B-Ti [1986Mur, 1987Mur]. For invariant equilibria of (βTi), (αTi) and γ phases with melt the [1997Zha] data were used (recently experimentally confirmed for the $l_p + (\beta Ti) \rightleftharpoons (\alpha Ti)$ equilibrium by [1999Jun]).

Nevertheless, somewhat less Ti contents for the l_p + $TiAl_3$ ⇌ (αAl) equilibrium (0.1 at.% or 0.18 mass% Ti for l_p [2001Fje, 2000Ohn, 1992Kat]) seem to be preferred as more close to experimental data, as well close to [E], [S], etc.

Solid Phases

No stable ternary phases have been reported. The binary phases, relevant to phase equilibria under consideration, are listed in Table 1. Hayes & Lukas [1991Hay, 1990Hay, 1989Hay] reported that all of the experimental evidence to date is consistent with complete solid solubility between AlB_2 and TiB_2 to form $(Ti,Al)B_2$. Namely the continuous solid solution $(Ti_{1-x}Al_x)B_2$ was found in [1998Joh] to be in commercial master alloys. This is the case that the mixed diboride $(Ti,Al)B_2$ was synthesised by the reaction of molten Al 99.99 with K_2TiF_6 and KBF_4 at 750 and 1050°C in [1999Zup]. However, the mixed diboride $(Ti,Al)B_2$ was shown to approach slowly toward the compositions of pure diborides at 800°C. At 800 and 1600°C apparently pure diborides or TiB_2 and αAlB_{12}, respectively, are in equilibrium with Al melt. Besides, the almost pure diborides crystallise from the melt at cooling rates as slow as 0.1°C/min [1999Zup]. The same result was reported before already in [1984Abd]. Crystallisation was also found in [1999Fje, 1998Zup1] to yield titanium diboride not richer in Al than $(Ti_{\sim 0.99}Al_{\sim 0.01})B_2$. In the same time EDS analysis of [1999Fje] showed that in samples annealed at 800 and 900°C, prepared by melting in crucible at 1630°C, the Al solubility in TiB_2 was on the level of standard deviations (on average 0.11±0.10 at.% Al) and the same was for AlB_{12} and AlB_2 (on average 0.03±0.02 and 0.05±0.04 at.% Ti). The close EDS data were obtained in [1998Zup1].

In [1998Zup1] a special study was devoted to the problem of mutual solubility of TiB_2 and AlB_2. Two alloys prepared by arc melting were heated and cooled at rates of 0.1-10 $K \cdot min^{-1}$ from 500 to 1400°C in alumina crucibles. The specimens were annealed at 800 ± 2°C for 1000 h, being put into alumina crucibles and sealed into evacuated silica tubes, followed by quenching in water bath. In any case the compositions of Al and Ti rich diborides were quite close to pure TiB_2 and AlB_2. The situation was not changed even after annealing at 800°C for 1000 h.

In [1992Gra] conventional and high resolution TEM were applied to study the as-cast alloy Ti-40.9Al-0.97B (at.%) prepared with arc-melting on water-cooled copper hearth in Ar (< 0.1 ppb O_2) using pure initial materials (the ingot of 35 g mass). Two monoborides were identified as having the FeB and CrB crystal structure types. The former contains thin layers of the latter and in the latter there were found nanoscale intergrowths of Ti_3B_4 and TiB_2 of Ta_3B_4 and AlB_2 crystal structure types, respectively. Clear orientation relationships were revealed in all cases. Examination of sample annealed at 1150°C for 100 h evidenced that the CrB crystal structure monoboride is metastable. The metastable TiB was postulated in [1992Gra] to form instead of the stable Ti_3B_4 and TiB_2 due to promoting kinetic factors.

Data on boron solubility in titanium aluminides are rare: [1984Sig, 1977Gur] reported unrealistic high solubility of B in $TiAl_3$ (1 and 8 mass% B, respectively) at unchanged lattice parameters. There is relevant theoretical consideration [1991Kho] (using linearized combination of muffin-tin orbitals total energy calculations) that boron atoms in γ phase should be accommodated substitutionally into aluminium sites.

A sputter deposition of Ti-7Al-7B (at.%) alloy on Ta substrate was single phase, it was identified with TEM and XRD as metastable fcc structure [1995Loe]. A 900°C annealing yields the TiB dispersion embedded in a single phase hcp matrix (αTi).

A rapidly solidified alloy Al-5Ti-0.2B (mass%) contained diboride and metastable $TiAl_3$ intermetallide of $AuCu_3$ structure type [1994Chu].

Invariant Equilibria

The reaction scheme (Fig. 1 and Table 2) for the Ti rich region is based on data of [2002Art, 1991Hym, 1990Hym]. Then there is a lack for phase fields between γ + TiB_2 and $TiAl_3$ + TiB_2. The Al-rich portion is based on data of [2001Fje, 1998Zup2, 1985Abd1].

The examination of samples in the region Al-TiB_2-AlB_2, which were annealed at 800 and 900°C, showed the four-phase invariant equilibrium L + αAlB_{12} ⇌ AlB_2 + TiB_2 to be between the above-mentioned temperatures [2001Fje]. A thermodynamic modelling, where the excess Gibbs energy calculated by

interpolating between the three binary systems, resulted in 880°C [2001Fje]. It is consistent with [1998Zup2] where the αAlB_{12} phase was stable at 900°C and its sizes and volume fraction decreased during annealing at 800°C, with its decomposition being not complete even after 1000 h exposure.
Thus, in the Al-B-Ti system there are two cascades of monovariant and invariant solidification reactions that are originated in the B-Ti side and quasibinary eutectic e_2 and come to the end in the Al-B side (e_4 eutectic point at 659.7°C). Besides, as found in [1998Zup2], at conventional cooling rates the AlB_2 diboride does not crystallize and a metastable four-phase equilibrium L + TiB_2 ⇌ (αAl) + αAlB_{12} takes place, which is involved with a binary metastable three-phase equilibrium l ⇌ (αAl) + αAlB_{12} at ~655°C.
There are some contrary versions of solidification scheme in the Al-rich corner. As mentioned above Hayes & Lukas [1991Hay, 1990Hay, 1989Hay] calculated the phase diagram on the assumption of stability of mixed diboride $(Ti,Al)B_2$. Their temperature of the invariant equilibrium L + $TiAl_3$ ⇌ (αAl) + TiB_2 was found to be 664.73°C. Stolz et al. [1994Sto, 1995Sto] accepted the diboride $(Ti,Al)B_2$ stability and, basing on two DTA effects of 660 and 666°C obtained for the three-phase (αAl) + TiB_2 + $TiAl_3$ alloys, reported existence of the ternary peritectic reaction L + $TiAl_3$ + TiB_2 ⇌ (αAl) at 666°C and x_{Ti} = 99.942 ± 0.04 mass %. Although these temperature effects are consistent with careful measurements of Bäckerud et al. [1993Joh, 1991Bae1, 1991Bae2] (obtained as temperatures of incipient solidification and grain growth), however, the ternary peritectic reaction existence dictates more boron content in solid (αAl) than in Al melt that seems improbable. Besides, there are DTA data of Maxwell & Hellawell [1972Max], which are lower only by 1°C, consistent with the L + $TiAl_3$ ⇌ (αAl) + TiB_2 invariant equilibrium proposed (Figs. 1, 4d, and 8). Some other variants are criticized elsewhere [1985Abd1, 1985Abd2].

Liquidus and Solidus Surfaces. Phase Equilibria at Melting (Solidification)

The phase equilibria at alloy melting were reported for the Ti-rich region, from (βTi) + TiB to γ+TiB_2 phase fields [2002Art, 1989Hym, 1990Hym, 1991Hym], and for the $TiAl_3$ - TiB_2 - αAlB_{12} - Al portion [2001Fje, 1998Zup2, 1989Hay, 1986Sig, 1985Abd1, 1984Sig, 1976Jon].
The Ti-rich solidus surface projection after [2002Art] is presented in Fig. 2 and characterised by the extensive two-phase (βTi) + TiB field containing a maximum that corrensponds to the quasi-binary eutectic L_e ⇌ $(Ti_{\sim 0.8}Al_{\sim 0.2})$ + TiB at ~1560°C. Close to the B-Ti side the combined eutectic crystallisation of (βTi) and TiB phases takes place practically at constant B content (around 7.5-7.0 at.%) (Fig. 3). In the vicinity of the quasi-binary $(Ti_{\sim 0.8}Al_{\sim 0.2})$+TiB eutectic and at higher Al content the liquidus curve of combined metal-metallide/boride crystallization smoothly goes down to ~1 at.% B at 45-55 at.% Al [1990Hym, 1991Hym]. In what follows the liquidus line reaches as little B content as $\sim 10^{-4}$ at.% in the Al-corner [1989Hay, 1985Abd1].
The above-mentioned data are in agreement with [1991Sch] where a Ti-25Al-4B (at.%) flake sample, prepared by electron beam melting and splat quenching, contained faceted TiB dispersoids free of Al, which had distinct orientation with the (αTi) matrix. The Ti-48Al-5B (at.%) sample prepared in the same manner was three-phase γ + α_2 + TiB_2, with no orientation relationship being found.
Liquidus isotherms of the Al-corner from thermodynamic calculation of [2001Fje, 1989Hay] are shown in Fig. 4. The TiB_2 solubility after [2001Fje] practically follows the dependence
$log\,Ti \cdot B^2 = A + B/T$
(where A and B are constants and T is temperature in K). The [2001Fje] data may be digitised as:
$log\,B = -0.504\,log\,Ti + 2.15 - 6820/T$
(where Ti and B are in at.%) that gives A = 4.28 and $B = -1.36 \cdot 10^4$. After transformation of Ti and B from at.% to mass % the parameters A = 3.74 and $B = -1.36 \cdot 10^4$ are seen to be between the data of Stolz [1995Sto, 1994Sto] (A = 2.70 ± 0.01 and $B = -1.27 \cdot 10^{-4} \pm 1 \cdot 10^{-2}$) and Finch [1972Fin] ($A$ = 5.22 and $B = -1.62 \cdot 10^4$) as well as Hayes and Lukas [1989Hay]. In comparison with the above mentioned, data of Kolesov et al. [1990Kol] seem to be too overestimed, what is presumably related to the presence of solid TiB_2 in molten Al samples taken for chemical analysis.
As shown in Fig. 4a the liquidus curves of double saturation are so close to the Al-Ti and Al-B sides that only logarithmic scales enable presentation of phase equilibria in the Al-corner in a single diagram (Fig. 4d). Some features of logarithmic phase diagram were outlined elsewhere [1976Jon]. Here it is worth to

note that co-lines in a logarithmic phase diagram should connect phase compositions under equilibrium with a curve (see Fig. 6) instead of straight line (as in Figs. 5 and 7).
The concept of the (αAl) phase solidification becomes clear from Figs. 5 to 9 (along with Figs. 1, 4b and Table 2). Corrections for instability of the $(Ti,Al)B_2$ continuous solid solution were introduced in Fig. 5 (thick dashed lines), but the overestimated boron solubility in $TiAl_3$ was kept unchanged in both Figs. 5 and 7.

Isothermal Sections

The 1000°C isothermal section (Fig. 10) was constructed in the Ti-rich portion of the system by Rogl et al. [1994Rog] based on EPMA data for three alloys levitation melted and annealed at 1000°C for 250 h. Initial materials were powder Al, Ti (both of 99.9 mass% minimum purity), and B of 99.8 mass% purity.
[1994Tok] reported equilibrium at 1100°C between α_2, TiB and TiB_2 (X-ray and EPMA data), repeating the 1000°C section of [1994Rog].
Data of [1964Rie] on phase equilibria at 1200°C are rather scarce, negligible solubility of B in titanium aluminides and Al in titanium borides and existence of the TiB_2 + TiB + (Ti) phase field.
In [1991Sch] Ti-25Al-4B and Ti-48Al-5B (at.%) samples, produced by electron beam melting and splat quenching followed by annealing in quartz capsules at 800, 1000, and 1200°C for 1 h, contained α_2+TiB (the former) and γ+TiB_2+α_2 (the latter) in agreement with [1994Rog, 1994Tok].
In [1999Li] an alloy Ti-46Al-0.1B (at.%) was studied in the temperature range 1000 to 1250°C. A 0.1 at.% B addition was found to bias the $\alpha(\alpha_2)/\alpha(\alpha_2) + \gamma$ and $\alpha(\alpha_2) + \gamma/\gamma$ boundaries to the Al-rich side by ~0.5 at.%, with decreasing the $(\alpha Ti) \rightleftharpoons \alpha_2 + \gamma$ equilibrium by 18°C.

Temperature – Composition Sections

A vertical section at constant 98 mass% Al (Fig. 11) was calculated in [1989Hay] on the two assumptions of two separate diborides and mixed diboride $(Ti,Al)B_2$, respectively. The only difference is: in the case of mixed diboride the field L+TiB_2+AlB_2 does not exist, and liquid Al coexist with either the mixed diboride $(Al,Ti)B_2$ or the two separate diborides TiB_2 and AlB_2, respectively. The metastable section TiB_2 - AlB_2 was constructed in order to explain qualitatively experimental data [1998Zup1, 1998Zup2] (Fig. 12) and takes into account the absence of AlB_2 in as-cast alloys.

Thermodynamics

Thermodynamic modeling in the Al-B-Ti system was restricted to equilibria of Al-based phases (solid and liquid) [2001Fje, 1991Hay, 1994Sto, 1995Sto, 1990Hay, 1989Hay, 1986Sig, 1984Sig, 1976Jon]. Only Sigworth's work [1986Sig] took into consideration a parameter of interaction between Ti and B as $\epsilon = 1500$ (at 820°C). The ϵ parameter influence may be seen in Fig. 7. In other works an interpolation between the three binary systems was applied. Thermodynamic parameters used in [2001Fje] are represented in Tables 3 and 4.

Notes on Materials Properties and Applications

In situ titanium matrix composites reinforced with TiB were produced in [1991Sob, 1994Sob] using plasma-arc-melting/centrifugal atomization. Powders were compacted by heating at 1065°C for 2 h followed by extrusion. Composites contained 0.11-0.12 mass% O, 0.07-0.13 mass% C, 0.005-0.027 mass% N, and 11-29 ppm H. Their tensile properties are presented in Table 5.
In [2002Art] Vickers hardness was measured on as-cast eutectic and hypoeutectic (Ti) + TiB alloys. A marked growth of hardness was found with Al alloying. The difference in the hardness of the alloy $Ti_{79.7}Al_{12.8}B_{7.5}$ and the binary $Ti_{92.5}B_{7.5}$ eutectic is about 2 GPa in the temperature interval from RT to 600°C. At 800°C this difference is smaller (~0.5 GPa) but still four times higher then in the basic binary alloy.
Al-based in-situ composites reinforced with TiB_2 particles were recently reviewed by Tjong & Ma [2000Tjo]. Stir casting technique was used in [2000Tee] to produce in-situ aluminium matrix composite,

containing (αAl) + TiB_2 + $TiAl_3$. Elemental Ti of 99.5 mass% purity and B of 99.5 mass% in stoichiometric composition corresponding to 15 vol.% TiB_2 were added to molten Al at 1040°C (18 min. exposition) and 1080°C (12 min.). Its room temperature tensile properties were as UTS = 225 MPa, $_{0.2\%}\sigma_y$ = 167 MPa, Young modulus E = 85 GPa, and elongation of 3.4 %. Aluminium matrix composite reinforced by TiB_2 (as well as by oxides Al_2O_3 and TiO_2) was obtained via the in situ reaction Al + TiO_2 + B_2O_3 ⇌ Al_2O_3 + TiB_2 [2001Lue].
In [2000Lu] a $Ti_{66.3}Al_{18.7}B_{15}$ powder mixture was blended via MA (mechanical alloying) technique. Along with elemental Ti and Al, a number of phases (γ, α_2, $TiAl_3$, TiB, and TiB_2) were detected after MA and annealing at 720 and 850°C. The analogical technique, MA followed by HIP, was used to prepare composites TiAl - (0, 10, 15, and 20) vol.% TiB_2 in [1999Och] (for all the samples strain rate sensitivity exponent was 0.3 at 1100°C).

Miscellaneous

Boron additions from ~0.03 to 0.1-0.2 at.% had an influence on lamellar formation on TiAl alloys [2002Zha].
In [1996Har] Al-Ti-B alloys suitable for Al grain refining were obtained from oxide precursors, B_2O_3 and TiO_2 by reduction with Al in the presence of cryolite.
The grain refinement of Al alloys with Al-Ti-B master-alloys has been extensively studied for more than a half of century. Detailed review of experimental results and a number of theories to explain them (in particular, cumulative action of TiB_2 and excess Ti) are out of the frame of the present issue and they are in detail described elsewhere [1999Eas1, 1999Eas2, 1998Sch, 1995Moh, 1993Joh, 1991Bae1, 1991Bae2]. Only modern experimental observations and theoretical justifications are outlined below.
As shown AlB_2 is a weak grain refiner for unalloyed aluminium alloys. Furthermore, a grain refinement test showed that boride particles with a wide distribution in both composition (being on average at [Ti]/[B] < 2.2 in mass%) and size give a poorer grain-refining effect [1998Joh]. On the other hand, intermetallide $TiAl_3$ is accepted as strong refiner, although some doubts are cast whether it acts alone, even in quite pure Al alloys. So, the TiB_2 nucleant was revealed by SEM study (using EDS) in an Al-0.115 mass% Ti alloy produced of Al of 99.99 mass% purity containing $5\cdot10^{-5}$ mass% B as contamination, where Ti was introduced from K_2TiF_6 (data could not themselves exclude (Ti,Al)B_2 mixed diboride) [2002Mik1].
Data on grain refining efficiency of pure TiB_2 have no single meaning, although an Al-2.2Ti-1B (mass%) master alloy is taken for granted to be inefficient refining addition for unalloyed Al. Introduction of synthetic TiB_2 crystals shows that they do not nucleate Al grains alone [1995Moh]. In presence of excess 0.01 mass% Ti, effectiveness of the same TiB_2 crystals was observed and $TiAl_3$ was detected at excess 0.05 mass% Ti.
So, the cumulative refining effect of TiB_2 and excess Ti is established unambiguously. An Al-5Ti-1B (mass%) master alloy is accepted as the most effective in Al grain refining. As found in [1993May] (TEM, scanning Auger microscopy, etc.) it contains duplex aluminide $TiAl_3$ particles as either rough or faceted blockies and entrained diboride platelets.
Incipient Ti content ensuring acceptance level of refinement for Al grains was found to be much below the binary Al-Ti peritectic composition (0.1 at.% Ti or 0.18 mass% Ti [2000Ohn]), depending on the purity of Al:
[2000Mik] found that ~0.05 mass% Ti (from K_2TiF_6) has sufficient effect for 99.7 % purity Al (~$2\cdot10^{-4}$ mass% B as contamination);
an Al-5Ti-1B (mass%) addition becomes effective at 0.1 % content, e.i. at ~0.005 mass% Ti and ~0.001 mass% B (~0.003 at.% Ti and ~0.002 at.% B) for 99.7 % purity Al [1976Jon, 2000Mik];
in [1999Eas2] aluminium of 99.97 mass% purity was refined at 0.01 mass% Ti and 0.03 mass % TiB_2 (demonstrating cumulative action as addition of only Ti needs 0.055 mass%);
an analogical result was obtained in [1992Joh] where master alloys Al-4.8Ti-1B, Al-5.3Ti-0.1B, and Al-6.2Ti-0.003B (mass%) added to Al of 99.995mass% purity showed effectiveness in increasing order of boron content (the 0.5% addition of the Al-5Ti-1B master alloy effectively refines the 99.995 % Al, 0.025 mass% Ti and 0.005mass% B [1991Bae2]).

The results obtained and reviewed were considered by Mohanty & Gruzleski [1995Moh] as experimental validation of the hypernucleation theory of Jones [1988Jon], which suggests that excess titanium segregates in the TiB_2/melt interface and results in precipitation of a thin layer of $TiAl_3$ and hence activation of the TiB_2 refining ability. Really, such a $TiAl_3$ interlayer was observed between the surface of TiB_2 particles and (αAl) phase in [1998Sch], where a $Al_{85}Y_8Ni_5Co_2$ alloy containing Al-4.5Ti-1.8B (mass%) refiner and excess Ti up to ~0.1 at.% was studied with TEM after rapid quenching from 1300°C (along with the three phases, the samples contained an amorphous matrix). In the three phases the close packed planes (and corresponding directions) were reported to be parallel: $\{0001\}_{TiB2}\|\{112\}_{TiA3}\|\{111\}_{(\alpha Al)}$. Based on these data Schumancher et al. [1998Sch] proposed a duplex nucleation theory, *per se* being concretization of Jones' hypernucleation theory. In [2001Mik], however, an intermediate layer of ~10 nm thickness, detected at the boundary between (αAl) and intermetallide of composition $(Ti_{0.8}Zr_{0.2})_{0.22}Al_{0.78}$, was found to be close to amorphous (in an alloy Al-0.24Ti-0.18Zr (mass%) prepared from Al of 99.7 mass% purity).

In light of the necessity of excess titanium regarding the TiB_2 stoichiometry, it is appropriate to mention here that the TiB_2 particles are poorly wetted by molten Al, the contact angle was measured to be 114° at 1000°C in vacuum or Ar [1966Yas]. A slightly different result was reported by [1972Sam]: 98° at 900°C in vacuum.

Another interpretation of the role of excess Ti was proposed in [1999Eas1, 1999Eas2, 1996Sig, 1993Joh, 1992Joh] involving crystal growth stage. The solute titanium is required to slow down the growth of (αAl) grains. So, Easton & StJohn [1999Eas1, 1999Eas2] state that the excess Ti provides constitutional undercooling in front of the growing interface so that in the constitutionally undercooled layer further nucleation can take place more easily. At high ratio Ti/B the Ti partition was found to be similar in the binary Al-Ti and ternary Al-B-Ti systems [2002Mik2]. The EMPA data of [2002Mik2] for an Al-0.053 mass% Ti as-cast alloy produced of Al of 99.7 mass% purity (that suggests B contamination of $\sim 2 \cdot 10^{-4}$ mass%, e.i. in total 0.030 at.% Ti and $\sim 5 \cdot 10^{-4}$ at.% B; solidification at cooling rate of 1 K/s) point out that the maximum Ti content reaches 0.33 mass% Ti (0.19 at.%) inside (αAl) grains. Concerning the constitutional undercooling resulting from the action of excess Ti, Jones & Pearson [1976Jon] estimated it for the binary Al-Ti alloys as ~0.07 K that means its effect should play a secondary part.

Thus, the hypernucleation theory of Jones [1988Jon] seems to get experimental validation. Concerning arguments of Sigworth [1996Sig] against the theory, they would not have seemed so forcible if the author had used the ternary phase diagram instead of treating data for ternary and even more multicomponent alloys with the Al-Ti binary one. Just what is required to be taken into consideration is the appropriate phase diagram at solidification of Al alloys (in the manner of [1986Sig], [1976Jon], [1975Max], [1971Mar] and others). And in the case of "a peritectic metastable reaction" of [1993Joh], which "can occur a few degrees above the stable peritectic point" (relatively to the binary Al-Ti system), it turns out to be a phase transformation between ternary solidus and liquidus surfaces. Although the state of the art Al-B-Ti phase diagram is far from perfection, it appears to be applicable in treating data on grain refinement of Al with Ti+B additions in most cases.

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Table 1: Crystallographic Data of Solid Phases

Phases/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/Referenses
(αAl) < 665	*cF*4 *Fm*$\bar{3}$*m* Cu	*a* = 404.96	at 25°C [Mas2] Temperature from [1997Zha] at 0.8 at.% Ti
(βB) <2092	*hR*333 *R*$\bar{3}$*m* βB	*a* = 1093.30 *c* = 2382.52	[Mas2, 1993Wer]
(αTi) < 1490	*hP*2 *P*6$_3$/*mmc* Mg	*a* = 295.06 *c* = 468.35	[Mas2]
(βTi) 1670- 882	*cI*2 *Im*$\bar{3}$*m* W	*a* = 330.65	[Mas2]
AlB_2 980 to <400	*hP*3 *P6/mmm* AlB_2	*a* = 300.5 *c* = 325.7	[2002Riz]
αAlB_{12} 2050 to <500	*tP*216 $P4_12_12$ αAlB_{12}	*a* = 1016.1 *c* = 1428.3	[2000Hig]
α_2, Ti_3Al < 1166	*hP*8 *P*6$_3$/*mmc* Ni_3Sn	*a* = 577.5 *c* = 465.5	[V-C2]
γ, TiAl < 1463	*tP*4 *P4/mmm* AuCu	*a* = 400.0 *c* = 407.5 *a* = 398.4 *c* = 406.0	at 50.0 at.% Al [2001Bra] at 62.0 at.% Al [2001Bra]
$TiAl_2$ < 1215	*tI*24 *I*4$_1$/*amd* $HfGa_2$	*a* = 397.0 *c* = 2497.0	[2001Bra]
$TiAl_3$ (h) 1387-735	*tI*8 *I4/mmm* $TiAl_3$(h)	*a* = 384.9 *c* = 860.9	[2001Bra]
$TiAl_3$ (l) < 950 (Ti-rich)	*tI*32 *I4/mmm* $TiAl_3$ (l)	*a* = 387.7 *c* = 3382.8	[2001Bra]
$TiAl_3$ metastable	*cP*4 *Pm*$\bar{3}$*m* $AuCu_3$	*a* = 397.2 ± 0.1	[1994Bra, 1994Chu]

Phases/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/Referenses
TiB < 2180	*oP*8 *Pnma* FeB	*a* = 610.5 *b* = 304.8 *c* = 454.2	[1987Mur]
TiB Metastable	*oC*8 *Cmcm* CrB		[1992Gra]
Ti_3B_4 < 2200	*oI*14 *Immm* Ta_3B_4		[1987Mur]
TiB_2 < 3225	*hP*3 *P6/mmm* AlB_2	*a* = 302.8 to 304.0 *c* = 322.8 to 323.4 *a* = 303.006 *c* = 323.009	for the binary system binary [1987Mur] for the ternary Al-40B-17.5Ti (mass%) as-cast alloy [1998Zup1]
$(Ti_{1-x}Al_x)B_2$ metastable	*hP*3 *P6/mmm* AlB_2	*a* = 302.64 ± 0.05 *c* = 323.18 ± 0.09 (extracted from Al-2.6Ti-1.4B (mass%) master alloy [1992Joh]	$0 \le x \le 1$, metastable [1999Fje, 1999Zup, 1998Zup1, 1998Zup2, 1994Tok, 1986Abd, 1985Abd1, 1985Abd2]
$Ti_{86}Al_7B_7$ metastable	fcc	*a* = 421.0(2)	[1995Loe]

Table 2: Composition of Liquid in Invariant Equilibria in the Al-B-Ti System

Equilibrium	*T* [°C]	Point in Fig. 1	Composition of liquid (at.%)			Comments/ References
			Al	Ti	B	
$L + (\beta B) \rightleftharpoons \alpha AlB_{12} + TiB_2$	unknown	U_1	unknown			presumably *T*<2050°C
$L \rightleftharpoons (\beta Ti) + TiB$	~1560	e_2	20	34.5	5.5	[2002Art]
$L + TiB \rightleftharpoons Ti_3B_4 + (\beta Ti)$	<1545	U_2	44	54.6	1.4	[1990Hym]
$L + Ti_3B_4 \rightleftharpoons TiB_2 + (\beta Ti)$	below U_2	U_3	45	53.7	1.3	[1990Hym]
$L + (\beta Ti) \rightleftharpoons (\alpha Ti) + TiB_2$	below U_3	U_4	49	50	1.0	[1991Hym]
$L + (\alpha Ti) \rightleftharpoons \gamma + TiB_2$	below U_4	U_5	55.5	43.8	0.7	[1991Hym]
$L + Ti_5Al_{11} \rightleftharpoons TiAl_3(h) + TiB_2$	<1393	U_6	unknown			presumably *T* is ~1390°C
$L + \alpha AlB_{12} \rightleftharpoons AlB_2 + TiB_2$	880	U_7	to balance	$\sim 4 \cdot 10^{-6}$	~2.5	[2001Fje, 1998Zup2]
$L + TiAl_3(h) \rightleftharpoons (\alpha Al) + TiB_2$	~664.5	U_8	to balance to balance	~0.08 0.1015	$6.7 \cdot 10^{-5}$ $1.8 \cdot 10^{-5}$	[1985Abd1] [1989Hay]
$L + TiB_2 \rightleftharpoons (\alpha Al) + AlB_2$	~660	U_9	to balance	$6.7 \cdot 10^{-6}$	~0.06	[1985Abd1]
$L + TiB_2 \rightleftharpoons (\alpha Al) + \alpha AlB_{12}$	≳655	meta-stable	to balance	$\sim 4 \cdot 10^{-6}$	0.05	[1998Zup2]

Table 3: Thermodynamic Stability of Phases Being in Equilibrium with Solid and Liquid Aluminium Phases [2001Fje]

Reaction (Standard State)	$\Delta^0 G_f$ (J·mol)$^{-1}$
Al(l) + 2(βB) ⇌ AlB_2	–119007 + 63.3886 T
Al(l) + 12(βB) ⇌ αAlB_{12}	–286607 + 8.76206 T
Ti(hcp) + 2(βB) ⇌ TiB_2	–331761 + 22.9143 T
3Al(l) + Ti(hcp) ⇌ $TiAl_3$	–185871 + 64.5540 T

Table 4: Optimised Parameters for Al-rich Melt [2001Fje]

Liquid	$^0L_{i,j}$	$^1L_{i,j}$	$^2L_{i,j}$
(Al,B)	–394.627 – 2.02086 T	19322.4	10486.3
(Al,Ti)	–196807 + 54.0763 T	73896.5	
(Ti,B)	–160670 – 37.3860 T	–152116 + 47.0434 T	

Table 5: Tensile Properties of Titanium Matrix Composites at 25°C [1994Sob, 1991Sob]

Composition (mass%)	Annealed at 704°C for 24 h				Annealed at 1200°C for 1 h plus at 600°C for 24 h			Annealed at 815°C for 24 h
	Yield Stress [MPa]	Elongation (%)	Modulus E [GPa]	K_{1c} [MPa·m$^{1/2}$]	Yield Stress [MPa]	Elongation (%)	K_{1c} [MPa·m$^{1/2}$]	K_{1c} [MPa·m$^{1/2}$]
Ti-6Al-0.5B	1055	8.1	135	38	896	3	57	42
Ti-6Al-1B	1158	1.5	142	23			68	16.5
Ti-7.5Al-1B	1241	0		17	1241	3.5	22.5	20

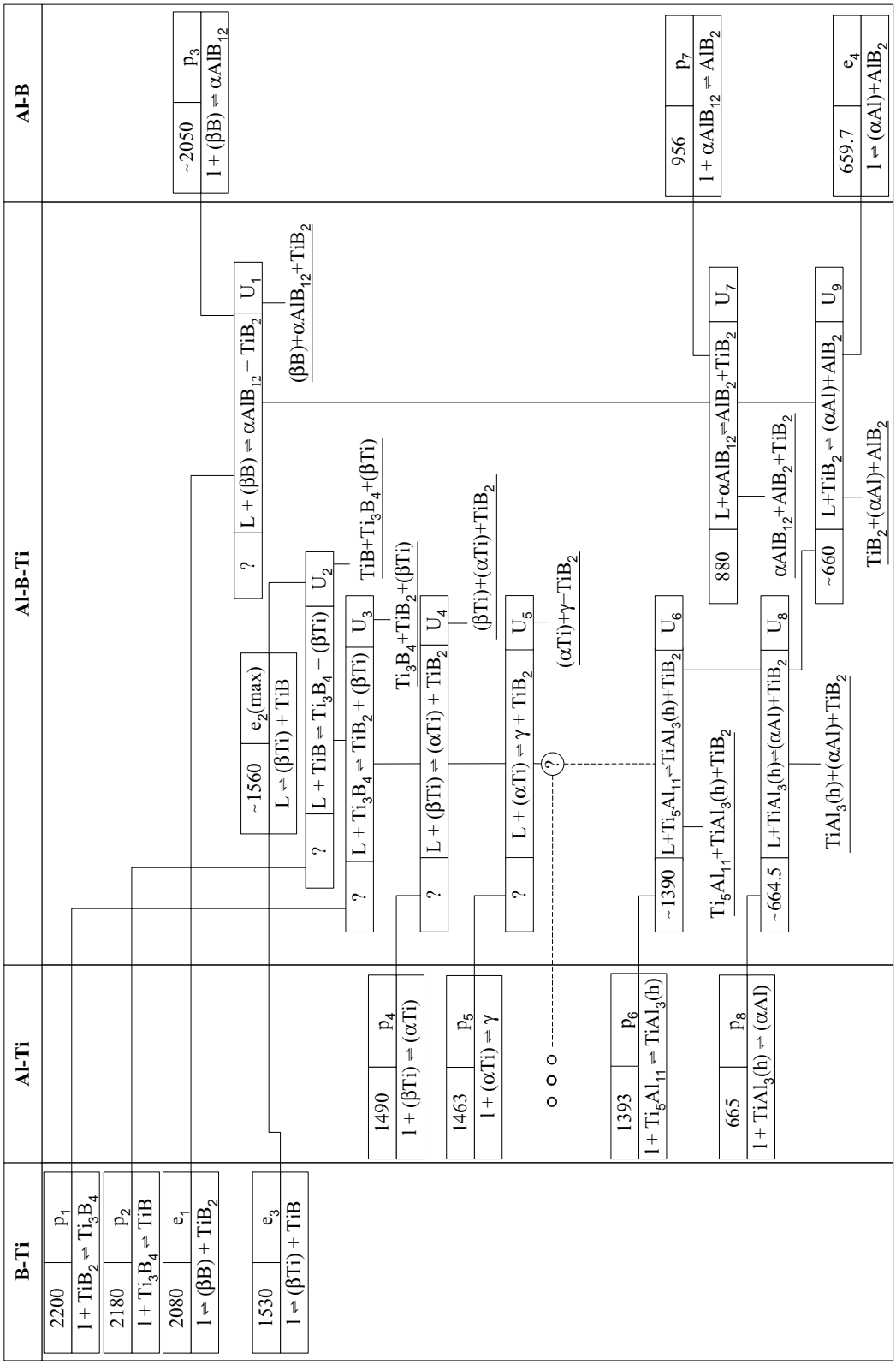

Fig. 1: Al-B-Ti. Reaction scheme at solidification of alloys [2002Art, 2001Fje, 1991Hym, 1990Hym, 1985Abd1]

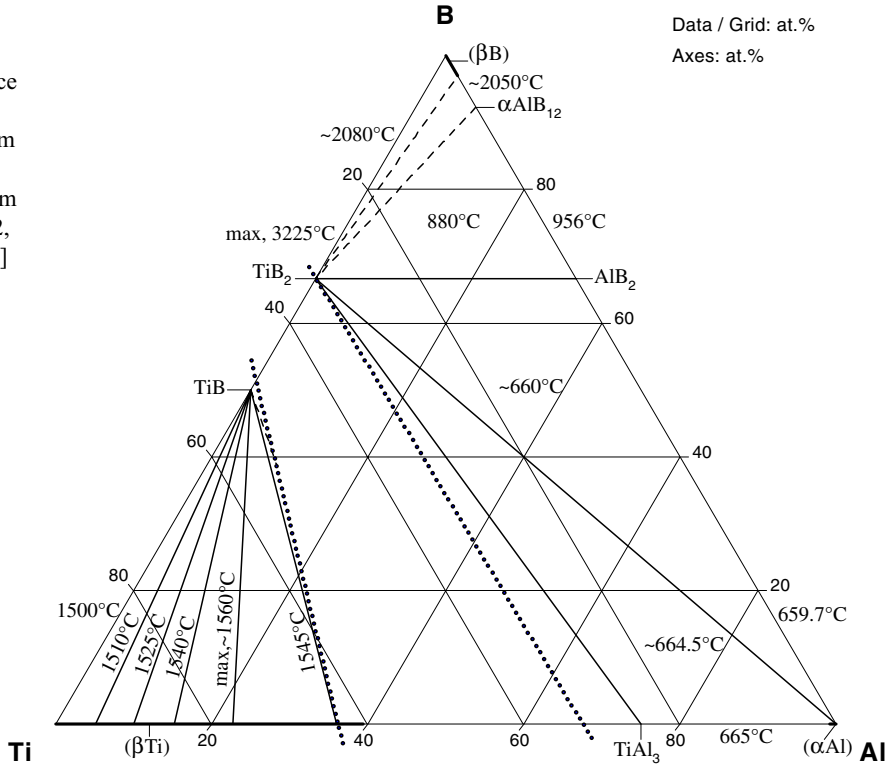

Fig. 2: Al-B-Ti.
Partial solidus surface projection.
Ti-rich region is from [2002Art],
Al-rich region is from [2001Fje, 1998Zup2, 1985Abd1, 1984Sig]

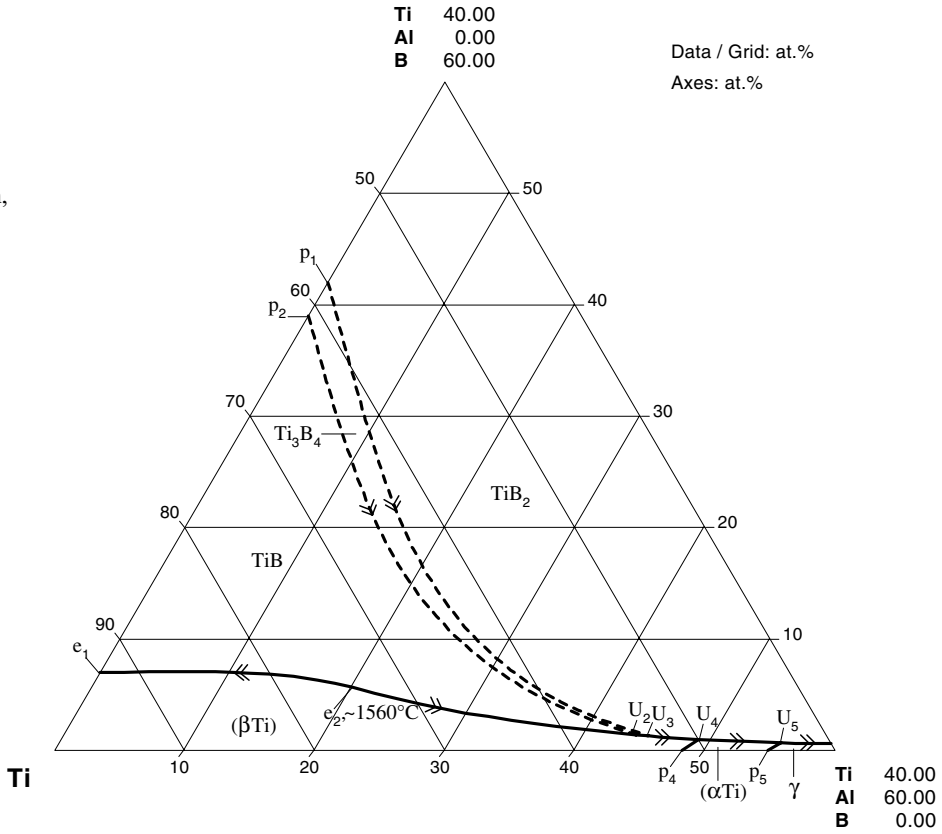

Fig. 3: Al-B-Ti.
Liquidus surface projection in the Ti-rich region [2002Art, 1991Hym, 1990Hym]

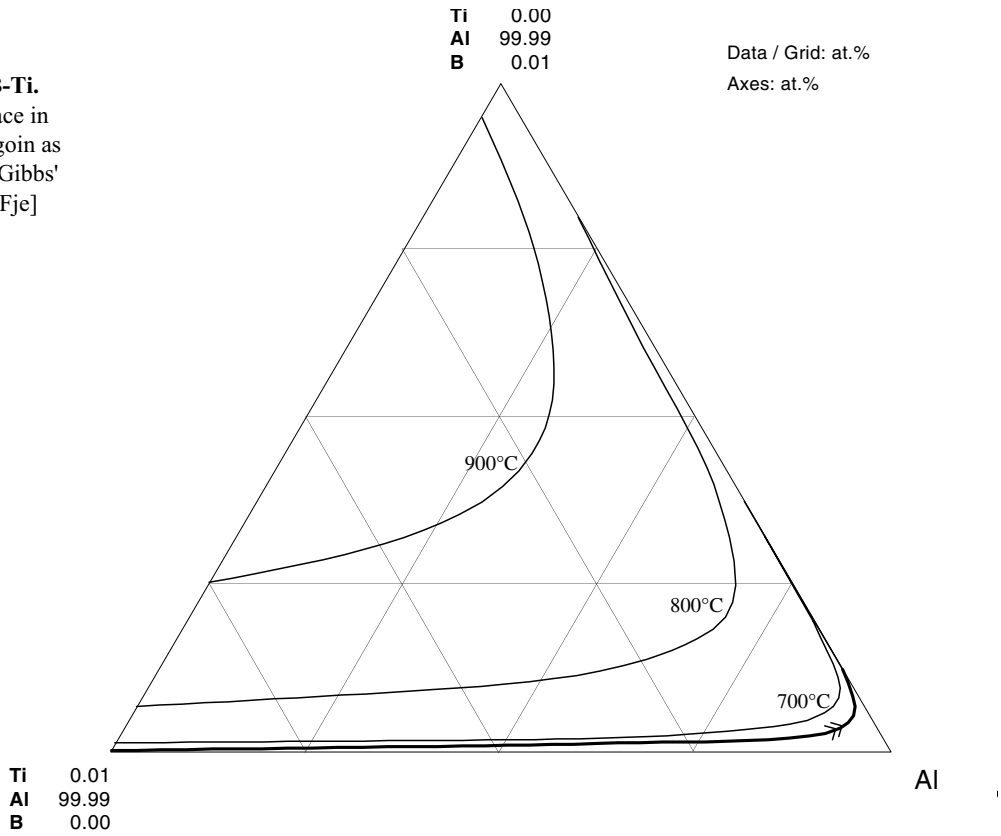

Fig. 4a: Al-B-Ti. Liquidus surface in the Al-rich regoin as projection on Gibbs' triangle [2001Fje]

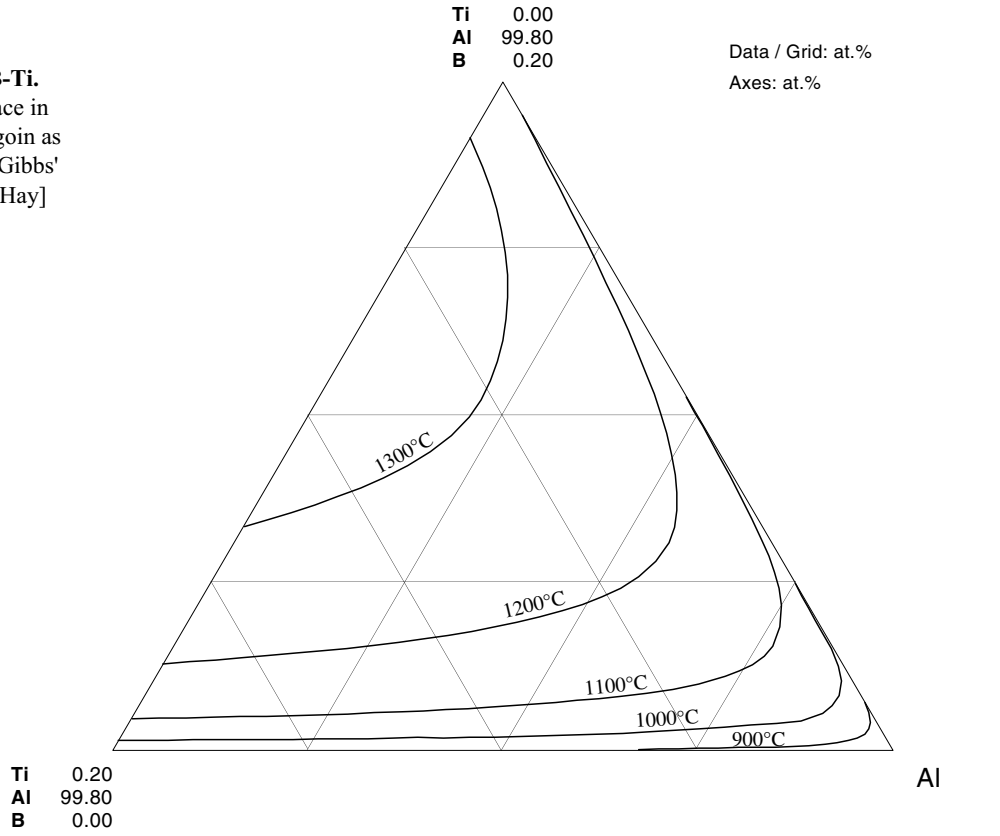

Fig. 4b: Al-B-Ti. Liquidus surface in the Al-rich regoin as projection on Gibbs' triangle [1989Hay]

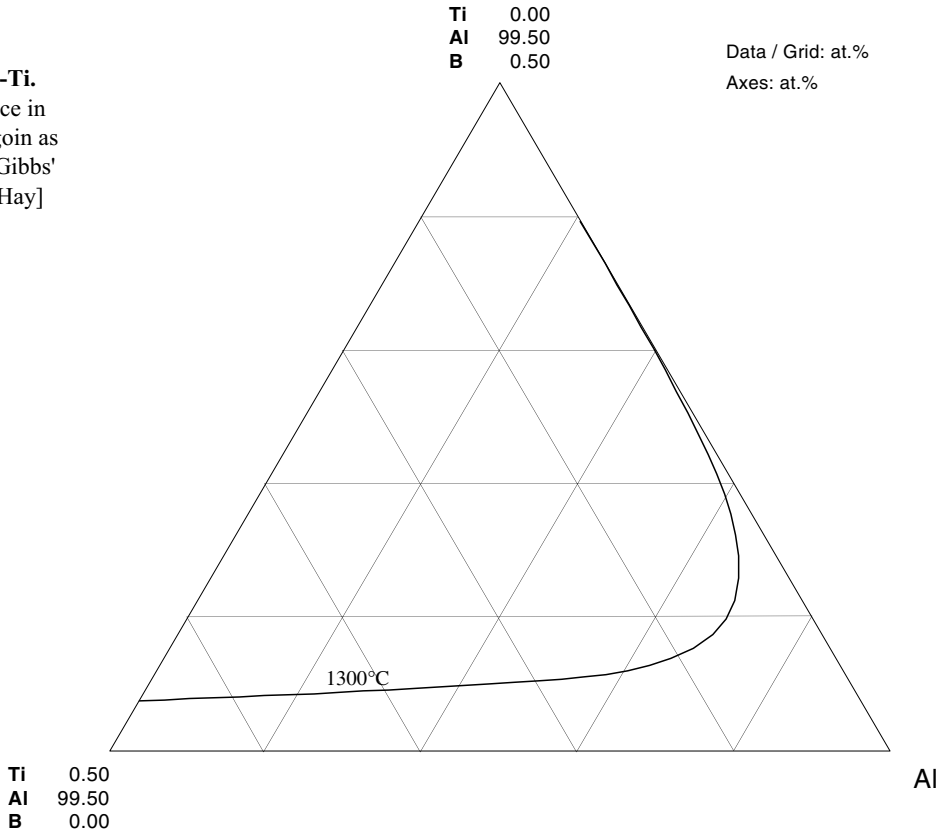

Fig. 4c: Al-B-Ti. Liquidus surface in the Al-rich regoin as projection on Gibbs' triangle [1989Hay]

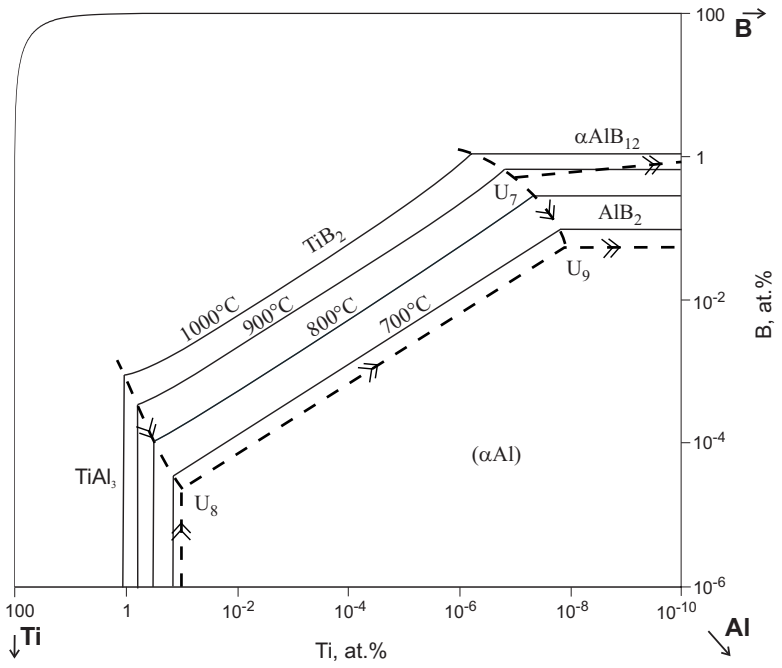

Fig. 4d: Al-B-Ti. Liquidus surface in the Al-rich region as projection on logarithmic scale after [2001Fje]

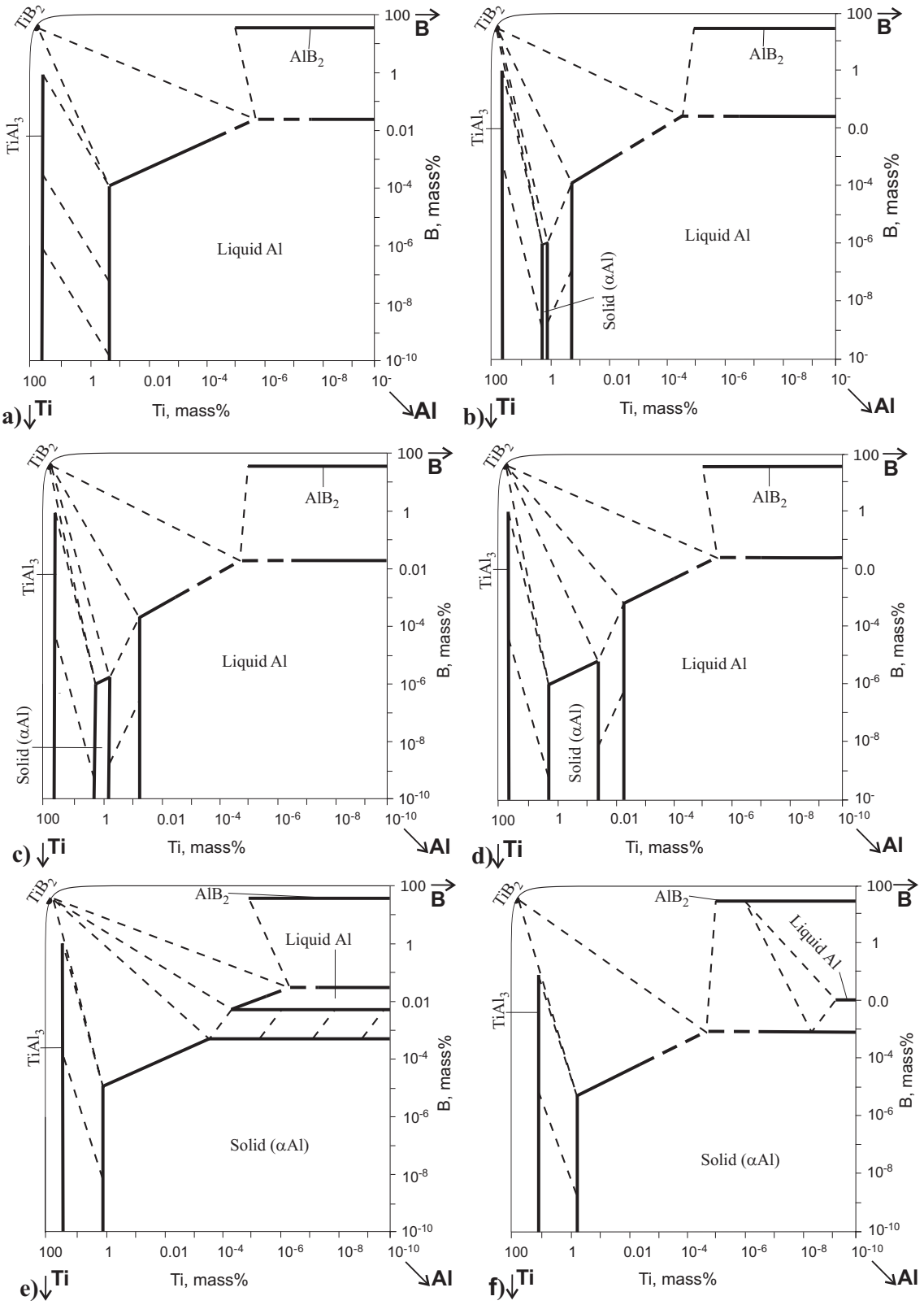

Fig. 5: Al-B-Ti. Phase equilibria in the range of melting/solidification of (Al) phase at 666°C (a), 664°C (b), 662°C (c), 660.2°C (d), 660°C (e) and 659.708°C (f) after [1984Sig]

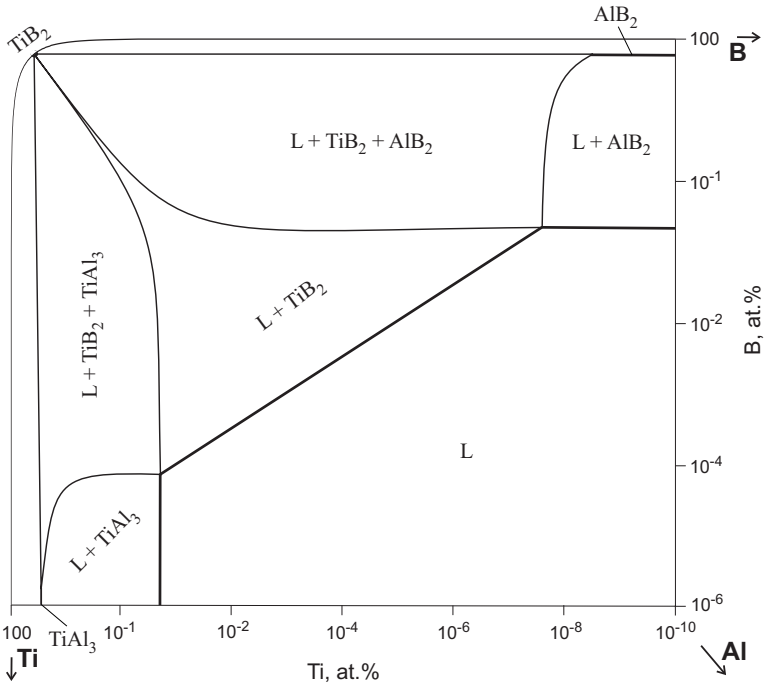

Fig. 6: Al-B-Ti. Partial isothermal section at 727°C [1976Jon]

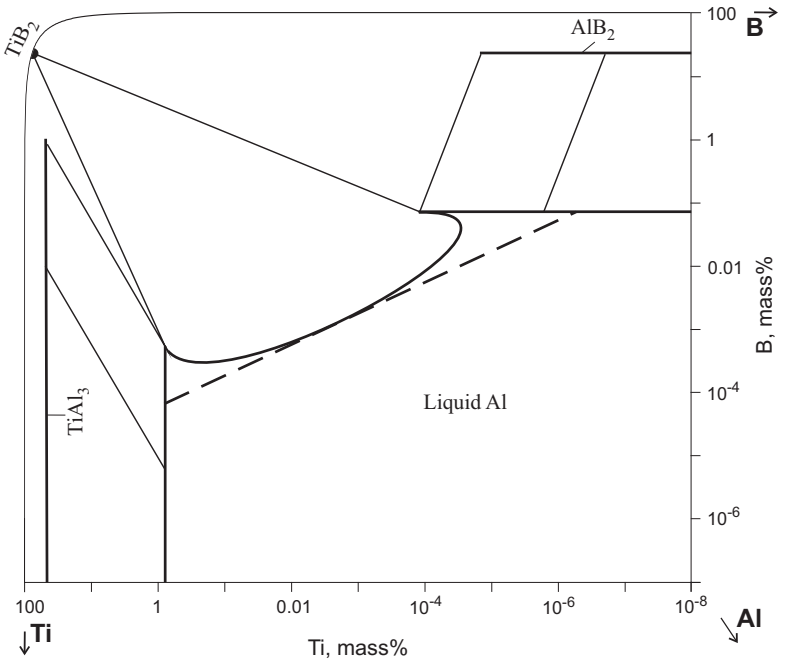

Fig. 7: Al-B-Ti. Partial isothermal section at 820°C [1986Sig].
The solid line gives the TiB_2 solubility calculated taking into account the interaction coefficient of Ti and B as $\varepsilon = -1500$.
The dashed straight line is calculated without interaction between Ti and B

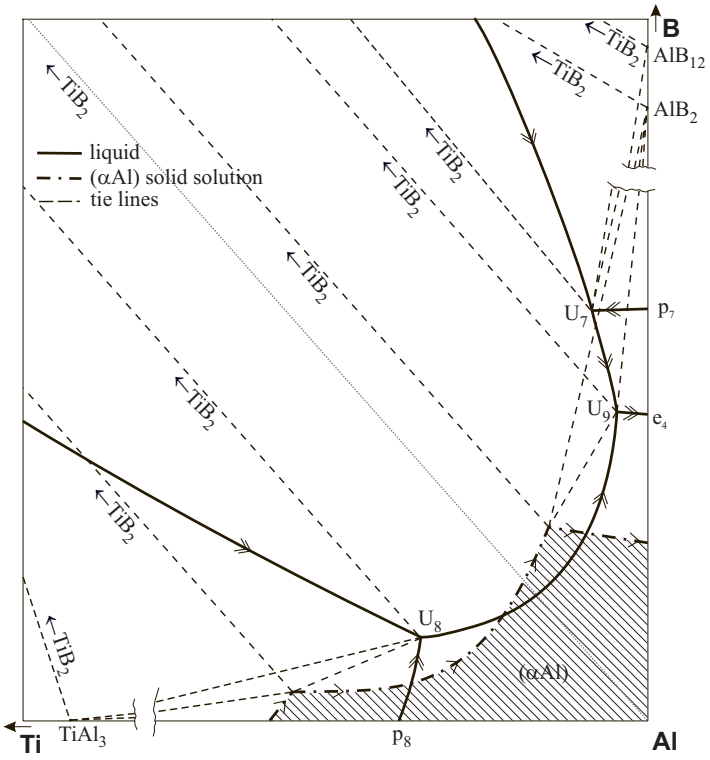

Fig. 8: Al-B-Ti. Schematic representation of invariant and monovariant equilibria including phases of liquid Al and solid (αAl) [1998Zup2, 1985Abd1]

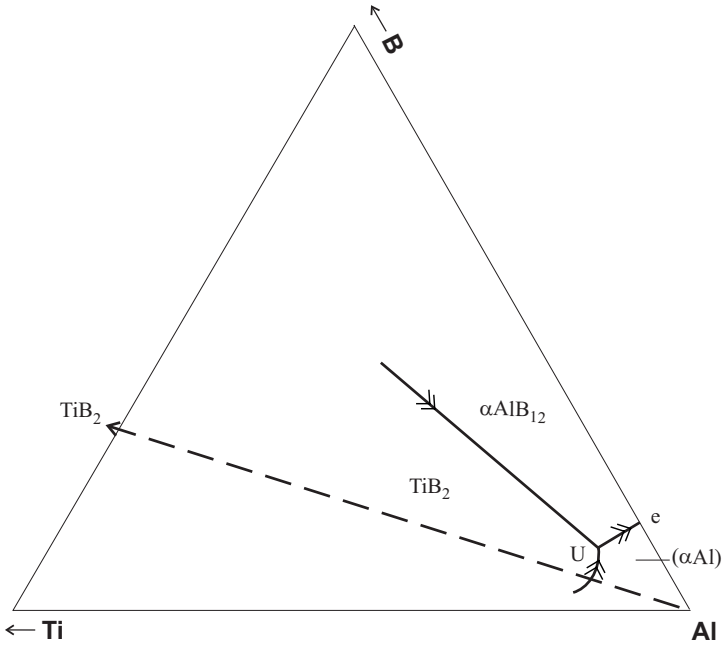

Fig. 9: Al-B-Ti. Schematic representation of metastable liquidus projection in the Al-AlB_{12}-TiB_2 region [1998Zup2]

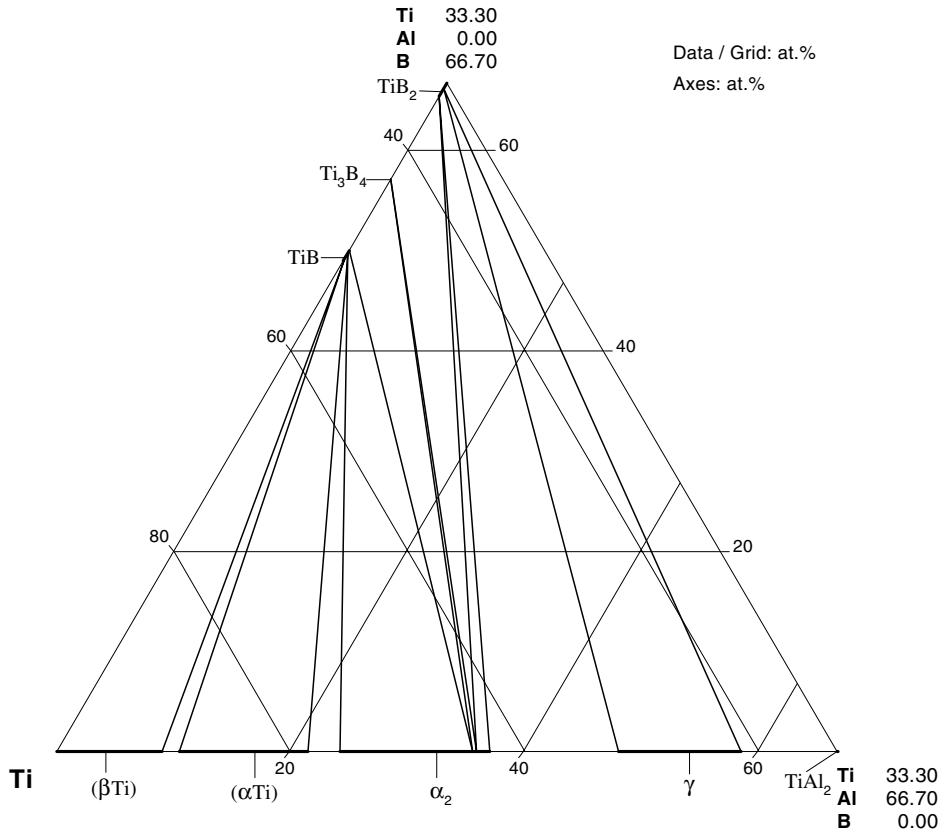

Fig. 10: Al-B-Ti. Partial isothermal section at 1000°C [1994Rog]

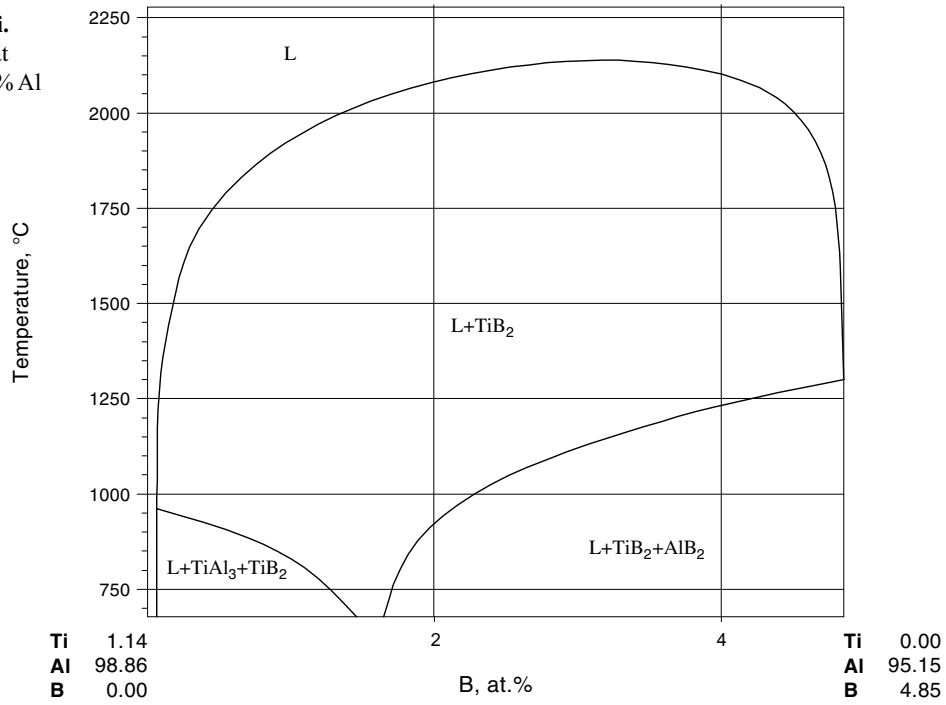

Fig. 11: Al-B-Ti. Vertical section at constant 98 mass% Al [1989Hay]

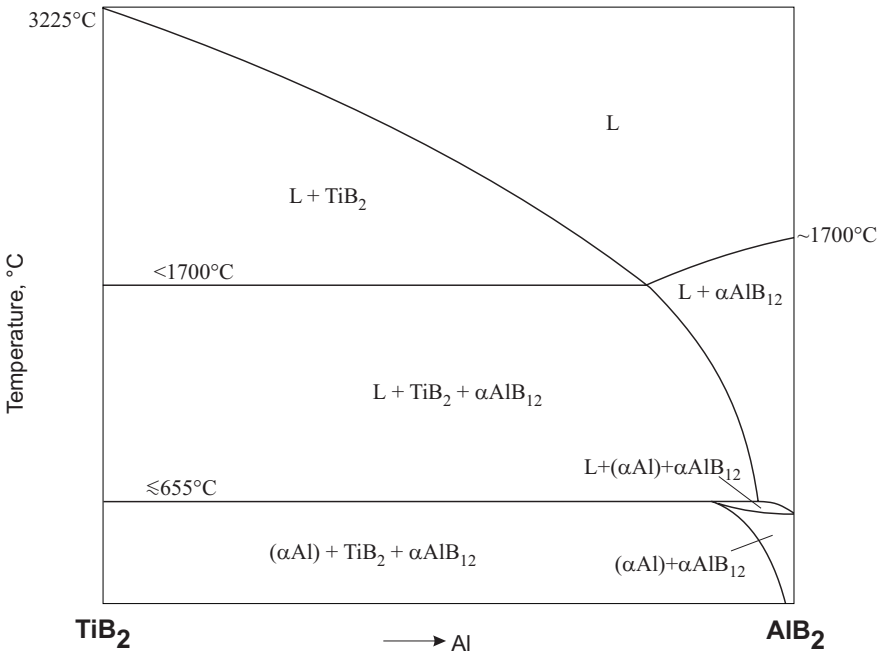

Fig. 12: Al-B-Ti. Qualitative metastable section TiB -AlB [1998Zup2]