

Al-B-Ti (Aluminum-Boron-Titanium)

V. Raghavan

The previous review of this ternary system by [2004Bon] presented partial liquidus and solidus surfaces, partial isothermal sections at 1000, 820, and 727 °C and a vertical section at 98 mass% Al. [2005Rag] reviewed briefly the experimental and calculated results of [2001Fje] and presented for Al-rich alloys a schematic liquidus projection, a reaction scheme and two isothermal sections at 1000 and 800 °C. These reviews concluded that the diborides AlB₂ and TiB₂ do not form a continuous solid solution and that there are no stable ternary phases in the system. In their thermodynamic treatment, [2005Gro] ignored ternary interactions and based their calculations solely on the binary parameters. Their results showed a miscibility gap in the liquid phase, which has no experimental support. Very recently, [2009Wit] carried out additional experiments on selected ternary and binary alloys and used the new results along with selected experimental data from the literature to recalculate in detail the phase equilibria.

Binary Systems

In the Al-B system [2004Mir], two borides are known: AlB₂ (C32, AlB₂-type hexagonal) and AlB₁₂ (AlB₁₂-type tetragonal). The Al-Ti phase diagram [2006Sch] has the following intermediate phases: Ti₃Al (*D*₀₁₉, Ni₃Sn-type hexagonal, denoted α_2), TiAl (*L*₁₀, AuCu-type tetragonal,

denoted γ), TiAl₂ (HfGa₂-type tetragonal, denoted η by [2009Wit]), TiAl₃ (HT) (*D*₀₂₂-type tetragonal, denoted ε by [2009Wit]), and TiAl₃ (LT) (tetragonal, space group *I*4/*mmm*, denoted ε (l) by [2009Wit]). Based on their own assessment [2008Wit2], [2009Wit] included two previously known compounds: Ti_{2+x}Al_{5-x} (tetragonal, space group *P*4/*mmm*, denoted ζ) and Ti₃Al₅ (tetragonal, space group *P*4/*mbm*), which were excluded by [2006Sch] in their assessed diagram. The Ti-B phase diagram [2004Ma, 2008Wit1] shows three intermediate phases: TiB (*B*27, FeB-type orthorhombic), TiB₂ (*C*32, AlB₂-type hexagonal) and Ti₃B₄ (*D*7_b, Ta₃B₄-type orthorhombic).

Ternary Phase Equilibria

With starting metals of 99.99% Al, 99+% B and 99.9% Ti, [2009Wit] arc-melted under Ar atm 10 ternary alloys with B contents up to 2 at.% (with the exception of one alloy with 7.5 at.% B). Five binary alloys free of B were also made with Al/Ti atom ratio of either ~1 or ~3. The alloys were annealed between 1350 and 1400 °C for 4-10 h. The phase equilibria were studied with the scanning electron microscope equipped with energy dispersive x-ray analyzer, x-ray powder diffraction and differential thermal analysis at heating/cooling rate of 20 °C per min. The thermal arrests and the deduced phase changes were listed

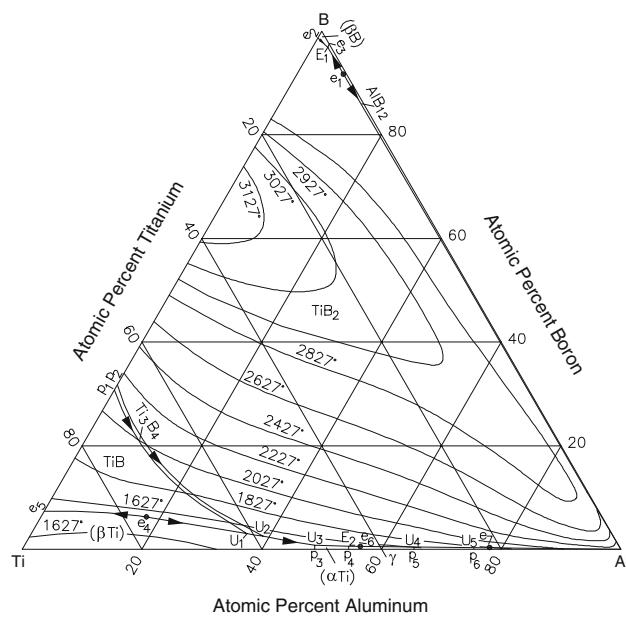


Fig. 1 Al-B-Ti computed liquidus projection [2009Wit]

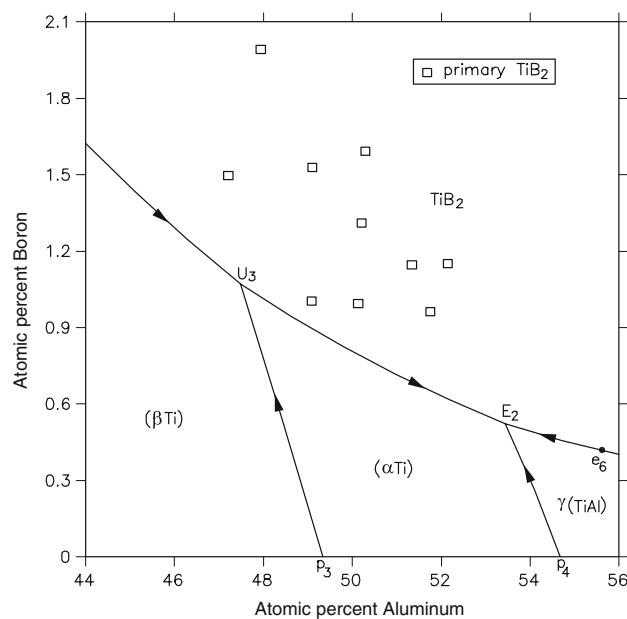


Fig. 2 Al-B-Ti computed partial liquidus projection showing the primary fields of (β Ti), (α Ti) and γ [2009Wit]

for all the alloys and compared with the calculated temperatures.

New results were obtained by [2009Wit] on the solubility of B in Ti-Al phases by energy dispersive analysis and NMR spectroscopy. It was confirmed that the solubility of B in Ti_3Al (α_2) and $TiAl$ (γ) is less than 0.03 and 0.011 at.%, respectively. The B solubility in $TiAl_3$ (ε) is about 0.8 at.%. The solubility of Al in TiB_2 is negligible. There is no continuous solid solution between the isostructural compounds TiB_2 and AlB_2 . These findings are in line with earlier reports.

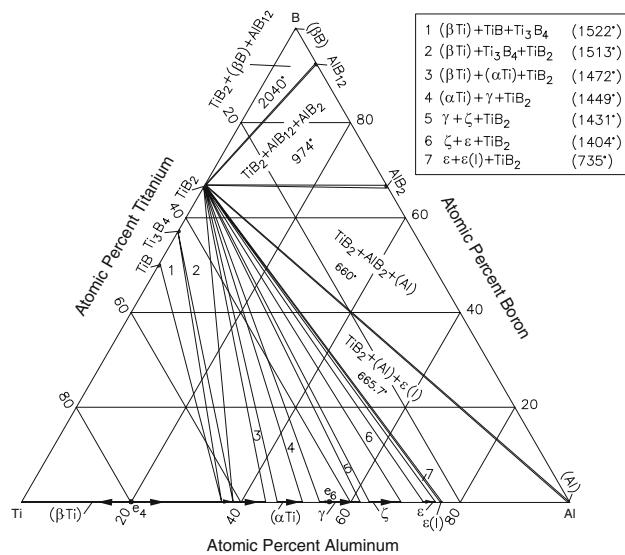


Fig. 3 Al-B-Ti computed solidus projection [2009Wit]

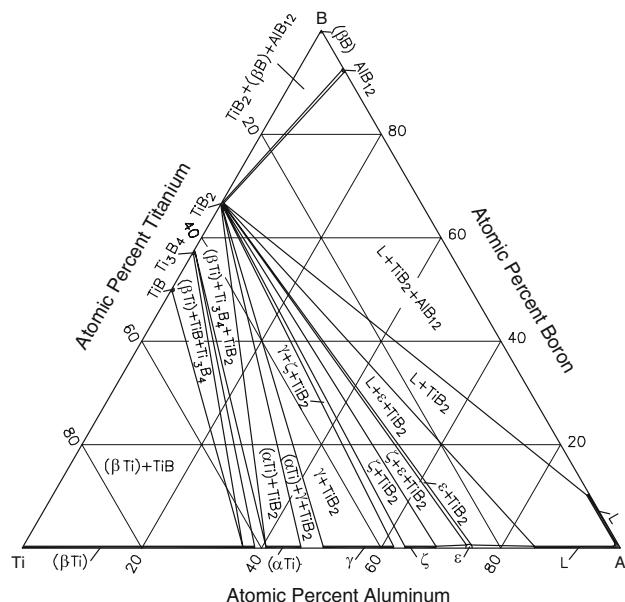


Fig. 4 Al-B-Ti computed isothermal section at 1350 °C [2009Wit]

In their thermodynamic modeling, [2009Wit] used the binary interaction parameters from [2004Mir] (Al-B), [2008Wit1] (B-Ti) and [2008Wit2] (Al-Ti). The liquid phase was modeled as a substitutional solution, with the inclusion of ternary interaction parameters. The bcc, fcc and cph phases were described by a two sublattice model, with B (along with vacancies) residing in the second sublattice. The binary compounds were described by appropriate sublattice models. The newly derived interaction parameters were listed along with those adopted from literature.

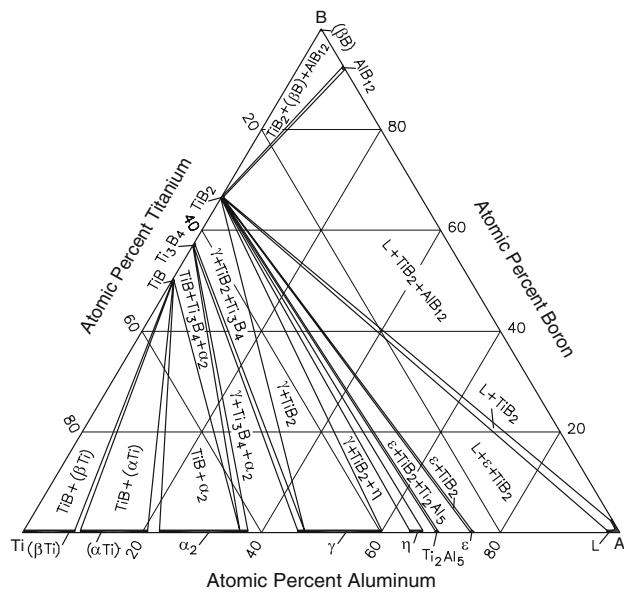


Fig. 5 Al-B-Ti computed isothermal section at 1000 °C [2009Wit]

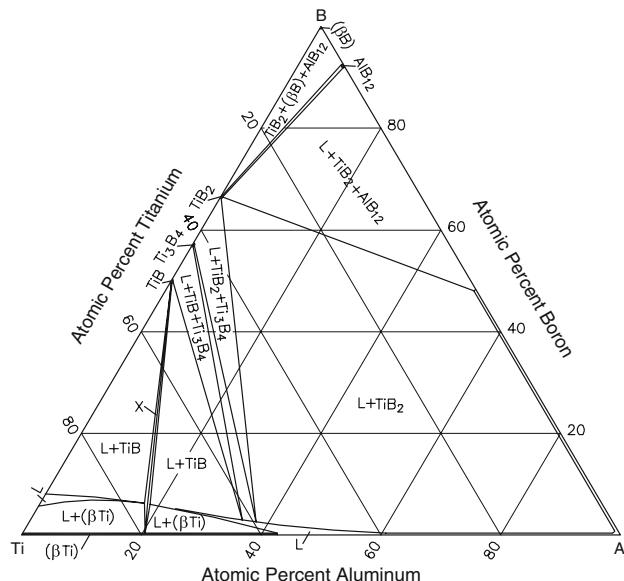


Fig. 6 Al-B-Ti computed isothermal section at 1548.8 °C [2009Wit]

Section II: Phase Diagram Evaluations

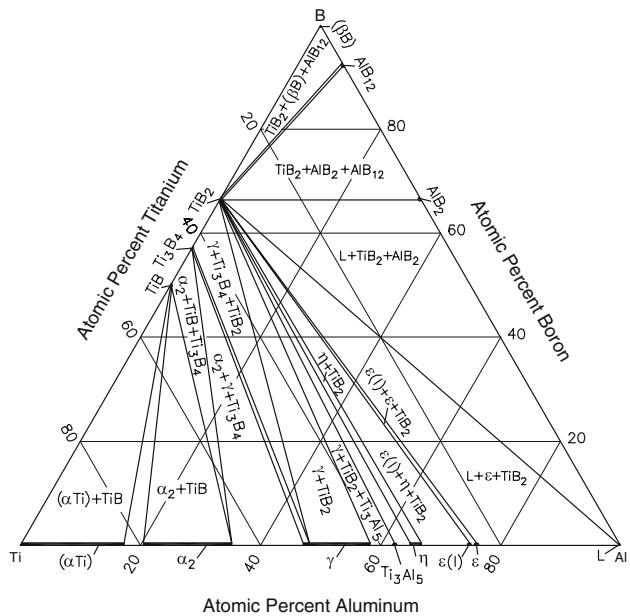


Fig. 7 Al-B-Ti computed isothermal section at 800 °C [2009Wit]. Narrow two-phase regions are omitted

Liquidus and solidus projections, four isothermal sections at 1350, 1000, 1548.8 and 800 °C, six vertical sections at constant contents of 0.5, 1.0, 5.0, and 7.5 at.% B, 47.4 at.% Al, and 24.6 at.% Ti, respectively, and two vertical sections along the $Ti_{89.8}Al_{10.2}$ - $Ti_{67}Al_8B_{25}$ and $Ti_{77.5}Al_{22.5}$ - $Ti_{63.5}Al_{11.5}B_{25}$ joins were computed by [2009Wit]. A full reaction sequence from the computed results was also written. Here, the liquidus projection is shown in Fig. 1. The primary crystallization fields agree with the experimental data (not shown). Near the Al corner, the reactions are too crowded and are not shown in Fig. 1. Fig. 2 shows the primary fields of (β Ti), (α Ti) and TiAl (γ) in greater detail. Figure 3 gives the solidus projection. The temperatures in °C shown in the fields with three solid phases are those of the invariant reactions from which the three-phase fields emerge. The computed isothermal sections at 1350 and 1000 °C shown in Fig. 4 and 5 agree with the scanty experimental data points (not shown). The computed isothermal sections at 1548.8 and 800 °C in Fig. 6 and 7 have no experimental data for comparison. In Fig. 6, the temperature (1548.8 °C) is just below the critical point e_4 in Fig. 1, at which the L + (β Ti) + TiB equilibrium comes into existence. Within the narrow region marked X in Fig. 6, two tie-triangles of L + (β Ti) + TiB exist. With decreasing temperature, these move in opposite directions, one ends at e_5 on the Ti-B side on the left and the other at U_1 on the right, see Fig. 1. At 800 °C (Fig. 7), additional phases AlB_2 and Ti_3Al_5 are present.

The computed vertical section at 0.5 at.% B (not shown here) is in satisfactory agreement with the experimental thermal arrests from [2009Wit] and [2009Bon]. The vertical section at 47.4 at.% Al in Fig. 8 is compared with experimental arrests of [2009Wit]. The agreement is satisfactory. The invariant horizontal corresponding to

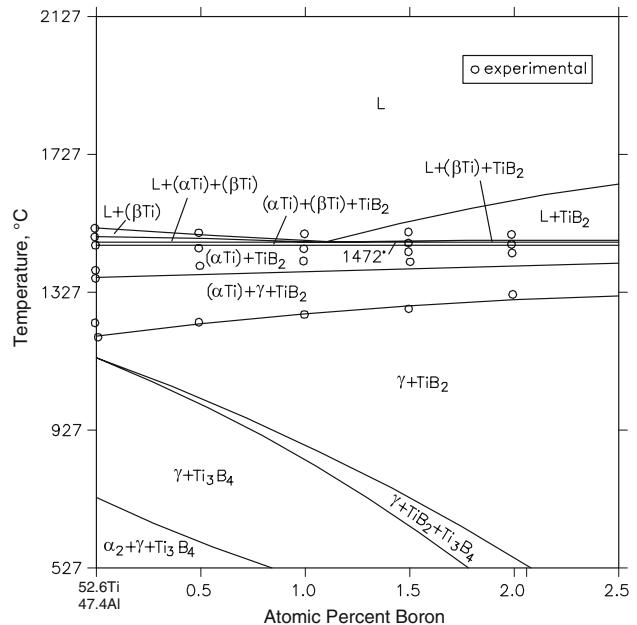


Fig. 8 Al-B-Ti computed vertical section at 47.4 at.% Al [2009Wit]

the reaction $L + (\beta\text{Ti}) \leftrightarrow (\alpha\text{Ti}) + \text{TiB}_2$ is shown at 1472 °C.

The calculated solubility product of TiB_2 in the ternary liquid was found to agree with experimental data at higher temperatures in the range of 1300-1100 °C [2009Wit]. At lower temperatures, the experimental values were consistently higher, pointing to the experimental difficulties in measuring very small concentrations of B and Ti, as well as the lack of attainment of equilibrium.

References

- 2001Fje:** J. Fjellstedt and A.E.W. Jarfors, Experimental and Theoretical Study of the Al-Rich Corner in the Ternary Al-Ti-B System and Reassessment of the Al-Rich Side of the Binary Al-B Phase Diagram, *Z. Metallkd.*, 2001, **92**(6), p 563-571

2004Bon: A. Bondar, Aluminum-Boron-Titanium, *Landolt-Bornstein New Series IV*, G. Effenberg and S. Ilyenko, Ed., Springer-Verlag, Berlin, Vol 11A1, 2004, p 80-101

2004Ma: X. Ma, C. Li , Z. Du, and W. Zhang, Thermodynamic Assessment of the Ti-B System, *J. Alloys Compd.*, 2004, **370**, p 149-158

2004Mir: D. Mirkovic, J. Grobner, R. Schmid-Fetzer, O. Fabrichnaya, and H.L. Lukas, Experimental Study and Thermodynamic Reassessment of the Al-B System, *J. Alloys Compd.*, 2004, **384**, p 168-174

2005Gro: J. Grobner, D. Mirkovic, and R. Schmid-Fetzer, Thermodynamic Aspects of Grain Refinement of Al-Si Alloys Using Ti and B. *Mater. Sci. Eng. A*, 2005, **395**, p 10-21

2005Rag: V. Raghavan, Aluminum-Boron-Titanium, *J. Phase Equilib. Diffus.*, 2005, **26**(2), p 173-174

2006Sch: J.C. Schuster and M. Palm, Reassessment of the Binary Aluminum-Titanium Phase Diagram, *J. Phase Equilb. Diffus.*, 2006, **27**(3), p 255-277

Phase Diagram Evaluations: Section II

2008Wit1: V.T. Witusiewicz , A.A. Bondar, U. Hecht, S. Rex, and T.Y. Velikanova, The Al-B-Nb-Ti System I. Reassessment of the Constituent Binary Systems: B-Nb and B-Ti on the Basis of New Experimental Data, *J. Alloys Compd.*, 2008, **448**, p 185-194

2008Wit2: V.T. Witusiewicz , A.A. Bondar, U. Hecht, S. Rex, and T.Y. Velikanova, The Al-B-Nb-Ti System III. Thermodynamic

Reevaluation of the Constituent Binary System Al-Ti, *J. Alloys Compd.*, 2008, **465**, p 64-77

2009Bon: Unpublished work of A.A. Bondar, quoted by [2009Wit]

2009Wit: V.T. Witusiewicz, A.A. Bondar, U. Hecht, J. Zollinger, L.V. Artyukh, and T.Y. Velikanova, The Al-B-Nb-Ti System V. Thermodynamic Description of the Ternary System Al-B-Ti, *J. Alloys Compd.*, 2009, **474**, p 86-104