



## The Al–B–Nb–Ti system

### V. Thermodynamic description of the ternary system Al–B–Ti

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#### ABSTRACT

The thermodynamic description of the ternary system Al–B–Ti is obtained by modelling the Gibbs energy of all individual phases in the system using the CALPHAD approach. The model parameters have been evaluated using the computer optimization technique PARROT based on the available descriptions of the constituent binary systems Al–B, B–Ti and Al–Ti recently published and relevant experimental information on phase equilibria for the ternary system. For the ternary system Al–B–Ti the reaction scheme, projection of the liquidus, solidus and solvus surfaces, selected vertical and isothermal sections are calculated using the proposed thermodynamic description. An acceptable agreement between the calculations and experimental data is achieved.

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## 1. Introduction

As highlighted in previous parts of the work [1–4], knowledge of phase equilibria and thermodynamic properties of the Al–B–Nb–Ti system is of high technological interest. Firstly, niobium containing TiAl-based alloys, refined by boron additions, are attractive materials for both aero-engine and automotive components [5]. Secondly, composite materials with a titanium-matrix being reinforced with borides have seen rapid development for the last 15 years, and they often contain Al additions [6–10]. Despite of the manifest technological interest the ternary Al–B–Ti phase diagram was not fully modelled by the CALPHAD method. Thus, thermodynamic modelling in the Al–B–Ti system was limited to the Al-rich corner [11–17]. In the most recent work of Gröbner et al. [18] the entire phase diagram Al–Ti–B was modelled by an interpolation from the constituent binary systems. The authors claimed that since no ternary phases or extended solubilities exist in this system, no ternary parameters were necessary for modelling. As a consequence of the approach, the liquidus surface obtained by Ref. [18] shows a miscibility gap of the liquid phase. This is in contradiction with experimental data on the liquidus surface [19–23].

In the present work the thermodynamic description of the ternary system Al–B–Ti is obtained by modelling the Gibbs energy of all individual phases in the system by the CALPHAD method. The

model parameters have been evaluated by means of a computer optimization technique based on the available descriptions of all the constituent binary systems and recently obtained experimental information on phase equilibria for the ternary system [19–23]. Additional experiments, meant to complement already available data, were performed within the frame of the present work. The thermodynamic descriptions of both binary systems with titanium, i.e. Al–Ti and B–Ti, were published in the previous parts of this work [3,1], respectively. The description of the third system, i.e. Al–B was adopted from Ref. [24]. For the ternary system Al–B–Ti several vertical and isothermal sections, projection of the liquidus, solidus and solvus surfaces, as well as reaction scheme, are calculated using the elaborated thermodynamic description. An acceptable agreement between the calculations and experimental data is achieved.

## 2. Experimental information for the ternary Al–B–Ti system

### 2.1. Literature data

The current status of experimental knowledge concerning the Al–B–Ti system has recently been reviewed in detail by Bondar [21]. According to the review, no stable ternary phases have been reported in the Al–B–Ti system. The designation of phases for the Al–B–Ti system and their crystal structure data [1,3,21,24] are given in Table 1.

Hayes and Lukas [14,16] stated that experimental evidence to date confirms the existence of a complete solid solubility between  $AlB_2$  and  $TiB_2$ . However, the ternary mixed diboride  $(Ti,Al)B_2$  was

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**Table 1**

The phase designations most often used in literature for the Al–B–Ti system along with crystal structure data [1,3,21,24] and thermodynamic models used in the present description

Phase (designation)	Pearson symbol	Space group	Strukturbericht designation	Prototype	Sublattice model used in the present description/remark
L <sup>a</sup> , liquid					[Al,B,Ti]
( <b>α</b> Al), (Al), fcc_A1	cF4	<i>Fm</i> $\bar{3}$ <i>m</i>	A1	Cu	[(Al,Ti) <sub>1</sub> :(B,Va) <sub>1</sub> ]
<b>α</b> , (αTi), hcp_A3	hP2	<i>P6</i> <sub>3</sub> / <i>mmc</i>	A3	Mg	[(Al,Ti) <sub>1</sub> :(B,Va) <sub>0.5</sub> ]
<b>α</b> <sub>2</sub> , Ti <sub>3</sub> Al	hP8	<i>P6</i> <sub>3</sub> / <i>mmc</i>	D0 <sub>19</sub>	Ni <sub>3</sub> Sn	[(Al,Ti) <sub>3</sub> :(Al,Ti) <sub>1</sub> :(B,Va) <sub>1</sub> ]
<b>AlB</b> <sub>2</sub> , <b>TiB</b> <sub>2</sub> , (Ti <sub>1-x</sub> Al <sub>x</sub> )B <sub>2</sub> <sup>b</sup>	hP3	<i>P6</i> / <i>mmm</i>	C32	AlB <sub>2</sub>	[(Al,B,Ti) <sub>1</sub> :(B%,Ti) <sub>2</sub> ]
<b>AlB</b> <sub>12</sub> , αAlB <sub>12</sub>	tP216	<i>P4</i> <sub>1</sub> 2 <sub>1</sub> 2	–	AlB <sub>12</sub>	[(Al,Ti) <sub>1</sub> :(B) <sub>12</sub> ]
<b>β</b> , (βTi), bcc_A2	cI2	<i>Im</i> $\bar{3}$ <i>m</i>	A2	W	[(Al,Ti) <sub>1</sub> :(B,Va) <sub>3</sub> ]
<b>β</b> <sub>0</sub> , β', bcc_B2	cI2	<i>Pm</i> $\bar{3}$ <i>m</i>	B2	CsCl	[(Al,Ti) <sub>1</sub> :(B,Va) <sub>3</sub> ] + [(Al,Ti) <sub>0.5</sub> :(Al,Ti) <sub>0.5</sub> :(B,Va) <sub>3</sub> ]
( <b>β</b> B), β-B	hR108	<i>R</i> $\bar{3}$ <i>m</i>	–	β-B	[Al,B,Ti]
γ, γ-TiAl, TiAl	tP4	<i>P4</i> / <i>mmm</i>	L1 <sub>0</sub>	AuCu	[(Al%,Ti) <sub>1</sub> :(Al,Ti%) <sub>1</sub> :(B,Va) <sub>1</sub> ]
ε, TiAl <sub>3</sub> , TiAl <sub>3</sub> (h)	tI8	<i>I4</i> / <i>mmm</i>	D0 <sub>22</sub>	TiAl <sub>3</sub> (h)	[(Al,B;Ti) <sub>3</sub> :(Al,Ti) <sub>1</sub> ]
ε(I), TiAl <sub>3</sub> (I)	tI32	<i>I4</i> / <i>mmm</i>	–	TiAl <sub>3</sub> (I)	[(Al,B;Ti) <sub>3</sub> :(Al,Ti) <sub>1</sub> ]
ζ, Ti <sub>2+x</sub> Al <sub>5-x</sub>	tP28	<i>P4</i> / <i>mmm</i>	–	Ti <sub>2</sub> Al <sub>5</sub>	[(Al,Ti) <sub>5</sub> :(Al,Ti) <sub>2</sub> :(B,Va) <sub>1</sub> ]
η, TiAl <sub>2</sub>	tI24	<i>I4</i> <sub>1</sub> / <i>amd</i>	–	HfGa <sub>2</sub>	[(Al,Ti) <sub>2</sub> :(Al,Ti) <sub>1</sub> :(B,Va) <sub>1</sub> ]
<b>Ti</b> <sub>3</sub> <b>Al</b> <sub>5</sub>	tP32	<i>P4</i> / <i>mbm</i>	–	Ti <sub>3</sub> Al <sub>5</sub>	[(Al) <sub>5</sub> :(Ti) <sub>3</sub> :(B,Va) <sub>1</sub> ]
<b>TiB</b>	oP8	<i>Pnma</i>	B27	FeB	[(Al,Ti) <sub>1</sub> :(B,Ti) <sub>1</sub> ]
TiB	oC8	<i>Cmcm</i>	B <sub>f</sub>	CrB	Metastable, not considered
<b>Ti</b> <sub>3</sub> <b>B</b> <sub>4</sub>	oI14	<i>Immm</i>	D7 <sub>b</sub>	Ta <sub>3</sub> B <sub>4</sub>	[(Al,Ti) <sub>3</sub> :(B) <sub>4</sub> ]
Ti <sub>86</sub> Al <sub>7</sub> B <sub>7</sub> <sup>c</sup>	c***	?	–	?	Metastable, not considered

<sup>a</sup> Designations given in bold letters are used throughout the present work.

<sup>b</sup> Metastable at 0.01 ≤ *x* < 1.

<sup>c</sup> Ternary phase.

shown to de-mix slowly into the practically pure diborides at 1073 K. From 1073 to 1873 K apparently pure diborides or a mixture of TiB<sub>2</sub> and AlB<sub>12</sub>, respectively, are in equilibrium with the Al melt. Moreover, almost pure diborides crystallise from the melt at cooling rates as slow as 0.1 K min<sup>-1</sup> [25,26]. Crystallization was also reported to yield titanium diboride not richer in Al than (Ti<sub>1-0.99</sub>Al<sub>~0.01</sub>)B<sub>2</sub> [27,28]. In the same time energy dispersive X-ray (EDS) analysis of the aluminium content in titanium diboride, in samples annealed at 1073 and 1173 K showed that the Al solubility in TiB<sub>2</sub> was very small, e.g. 0.11 ± 0.10 at.%, and that the solubility of Ti in AlB<sub>12</sub> and AlB<sub>2</sub> was virtually zero, e.g. 0.03 ± 0.02 and 0.05 ± 0.04 at.%, respectively [27]. Similar results were also obtained by EDS and reported in [28] where an exclusive study was dedicated to the problem of mutual solubility of TiB<sub>2</sub> and AlB<sub>2</sub>. Based on these results the authors concluded that the mixed diboride (Ti<sub>1-x</sub>Al<sub>x</sub>)B<sub>2</sub> is metastable for 0.01 ≤ *x* < 1.

Data on boron solubility in titanium aluminides are rare. The authors of [12,29] reported rather high solubility of B in TiAl<sub>3</sub> (1 and 8 wt.% B, respectively) with no influence on the lattice parameters.

The solubility of TiB<sub>2</sub> in liquid aluminium, usually expressed as the solubility product ([wt.% Ti]·[wt.% B]<sup>2</sup>), was experimentally measured by Finch [30], Cibula [31], Morimune et al. [32], Abdel-Hamid and Durand [33] as well as Yoshikawa and Morita [34]. The solubility product in the temperature range 973–1573 K varied from 10<sup>-10</sup> to 5 × 10<sup>-5</sup>.

In Ref. [35] high-resolution transmission electron microscopy (TEM) was used to study the as-cast alloy Ti–40.9Al–0.97B (at.%). Two monoborides were identified as having the FeB and CrB crystal structure types. Further examination of the sample annealed at 1423 K for 100 h confirmed that the TiB monoboride with the CrB crystal structure is metastable. Therefore the metastable TiB was postulated to form instead of the stable phases Ti<sub>3</sub>B<sub>4</sub> and TiB<sub>2</sub>, due to kinetic effects [35].

The isothermal section at 1273 K was constructed in Ref. [36] based on experimental data obtained for three alloys prepared by a levitation technique and annealed at 1273 K for 250 h. The as-cast alloys Ti–12Al–25B and Ti–15Al–35B (at.%) consisted of borides TiB<sub>2</sub> (primary crystallized), Ti<sub>3</sub>B<sub>4</sub> and TiB inside the α and α<sub>2</sub> matrices Ti<sub>0.79</sub>Al<sub>0.21</sub> and Ti<sub>0.685</sub>Al<sub>0.315</sub>, respectively. After the annealing, the alloy Ti–15Al–35B (at.%) retained its phase constituents, with-

out reaching thermodynamic equilibrium. The third as-cast alloy Ti–30Al–25B (at.%) contained primary crystallized TiB<sub>2</sub> inside the lamellar two-phase matrix α<sub>2</sub> + γ, and after the annealing the phase constituents were the same, with the intermetallic phases being α<sub>2</sub>-Ti<sub>0.58</sub>Al<sub>0.42</sub> and γ-Ti<sub>0.52</sub>Al<sub>0.48</sub>, respectively.

In Ref. [37] the authors investigated the phase equilibria at 1373 K between α<sub>2</sub>, TiB and TiB<sub>2</sub> with the results being similar to the ones for the isothermal section at 1273 K reported in Ref. [36]. Data on phase equilibria at 1473 K [38] reveal a negligible small solubility of B in titanium aluminides and of Al in titanium borides and the existence of the β + TiB + TiB<sub>2</sub> phase field. In Ref. [39] two alloys Ti–25Al–4B and Ti–48Al–5B (at.%) were prepared and annealed at 1073, 1273, and 1473 K for 1 h. The alloys were shown to contain α<sub>2</sub> + TiB and α<sub>2</sub> + γ + TiB<sub>2</sub>, respectively, which is in agreement with Refs. [36,37]. In Ref. [40] an alloy Ti–46Al–0.1B (at.%) was studied in the temperature range from 1273 to 1523 K. The addition of 0.1 at.% B was found to shift the α<sub>2</sub> + γ and α + γ phase regions to the Al-rich side by ~0.5 at.%, leading to a decrease of the α ↔ α<sub>2</sub> + γ transformation temperature by 18 K.

The solid/liquid phase equilibria were studied in more details for the TiAl<sub>3</sub>–TiB<sub>2</sub>–AlB<sub>12</sub>–Al portion of the ternary system in [11–14,17,41,42]. The examination of samples annealed at 1073 and 1173 K in the region Al–TiB<sub>2</sub>–AlB<sub>2</sub> showed that the temperature of the four-phase invariant reaction L<sub>U</sub> + AlB<sub>12</sub> ↔ AlB<sub>2</sub> + TiB<sub>2</sub> is between the above-mentioned temperatures [17]. This is consistent with Ref. [41] where the AlB<sub>12</sub> phase was stable at 1173 K and its size and volume fraction decreased during annealing at 1073 K, with its decomposition being incomplete even after 1000 h exposure.

Different versions of the solidification scheme were proposed for the Al-rich corner of the ternary system. Thus, Hayes and Lukas [14,16] calculated the phase diagram on the assumption that the mixed diboride (Ti,Al)B<sub>2</sub> is stable. The temperature of the U-type invariant equilibrium L<sub>U</sub> + ε ↔ (αAl) + TiB<sub>2</sub> was reported to be 937.9 K. Stolz et al. [15] investigated three-phase (αAl) + TiB<sub>2</sub> + ε alloys by differential thermal analysis (DTA) and observed two effects at 933 and 939 K, that were thought to prove the existence of a ternary peritectic reaction L<sub>p</sub> + ε + TiB<sub>2</sub> ↔ (αAl) at 939 K and 99.942 ± 0.04 wt.% Al. Though these results are consistent with careful measurements of Bäckerud et al. [43–45], the existence of the ternary peritectic reaction implies that the boron content in

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