JPEDAV (2005) 26:624-628
DOI: 10.1361/154770305X74520
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Al-Si-Ti (Aluminum-Silicon-Titanium)

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The compilation of data on this ternary system by [1995Vil] includes a partial liquidus projection; full isothermal sections at 1200 °C from [1962Sch], 700 °C from [1965Ram], and 25 °C from [1968Age]; and vertical sections at 2 and 6 wt.% Al and 10, 12, and 14 wt.% Si. Much of the above data need revision, due to the recent modifications of the constituent binary systems. New results reviewed here include the thermodynamic description of the system by [2002Aze] and the experimental data by [2004Bul].

Binary Systems

The Al-Si system is of the simple eutectic type, with the eutectic temperature at 577 °C and 12.2 at.% (12.6 wt.%) Si. The updated version of the Al-Ti phase diagram [2005Rag] depicts a number of intermediate phases. $TiAl_3$ has two crystal modifications: $TiAl_3$ (HT) ($D0_{22}$-type tetragonal) forms peritectically at 1387 °C and decomposes eutectoidally at 735 °C. $TiAl_3$ (LT) (tetragonal) forms at ~950 °C and is stable at low temperatures. Ti_5Al_{11} is a superstructure based on the AuCu-type tetragonal phase. It forms peritectically at 1416 °C and decomposes eutectoidally at 995 °C to $TiAl_2$ and $TiAl_3$ (HT). $TiAl_2$ ($HfGa_2$-type tetragonal) forms congruently at 1215 °C from Ti_5Al_{11} and is stable at low temperatures. $Ti_{1-x}Al_{1+x}$ (AuCu-type tetragonal) is stable between 1445 and 1170 °C. Ti_3Al_5 is a low-temperature phase stable below 810 °C. TiAl, often designated γ, has the $L1_0$, AuCu-type tetragonal structure and forms peritectically at 1460 °C. (βTi) (bcc, also denoted β) and liquid undergo a peritectic reaction at 1490 °C to yield (αTi) (cph, also denoted α). Ti_3Al, commonly labeled α_2, has the $D0_{19}$, Ni_3Sn-type hexagonal structure and forms congruently from (αTi) at 1176 °C. The Si-Ti phase diagram [Massalski2, 2004Bul] shows five intermediate phases: Ti_3Si (Ti_3P-type tetragonal), Ti_5Si_3 ($D8_8$, Mn_5Si_3-type hexagonal), Ti_5Si_4 (αTi_5Si_4: Zr_5Si_4-type tetragonal below 1815 °C and βTi_5Si_4: Sm_5Ge_4-type orthorhombic above 1815 °C), TiSi (αTiSi: TiSi-type orthorhombic below ~800 °C and βTiSi: $B27$, FeB-type orthorhombic above ~800 °C), and $TiSi_2$ (α$TiSi_2$: $C54$, $TiSi_2$-type orthorhombic below ~1200 °C and β$TiSi_2$: $ZrSi_2$-type orthorhombic above ~1200 °C). For a recent thermodynamic description of this system, see [1996Sei].

Ternary Compounds and Phases

There are several reports of a $ZrSi_2$-type orthorhombic compound denoted by the formula $Ti(Al_xSi_{1-x})_2$ (labeled TC by [2004Bul]). It appears to be the high-temperature β$TiSi_2$, stabilized by the addition of Al. At 1250 °C, it has a composition range of $TiSi_{1.7\text{-}1.4}Al_{0.3\text{-}0.6}$ [2004Bul]. The

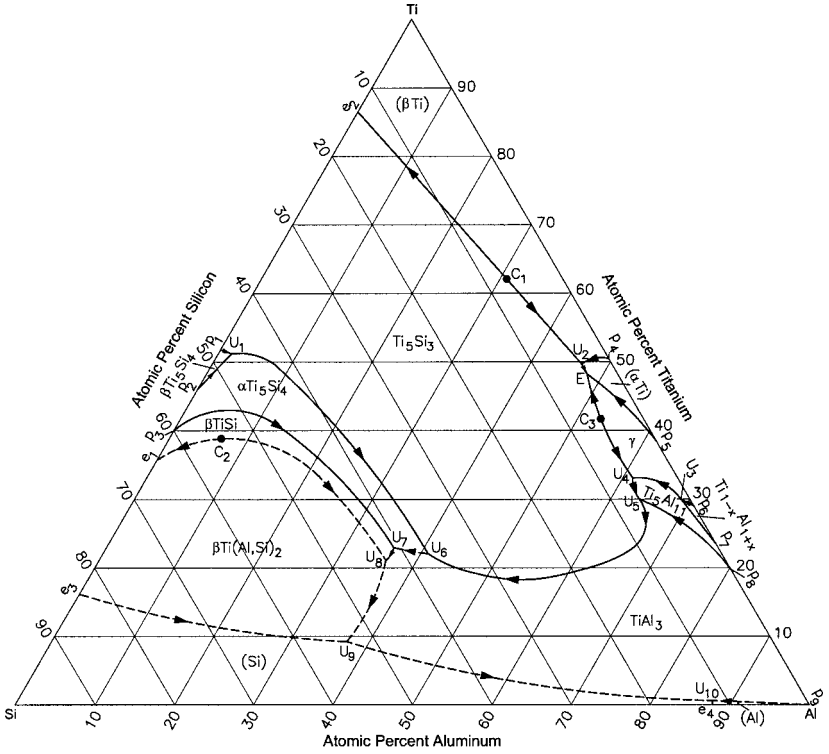
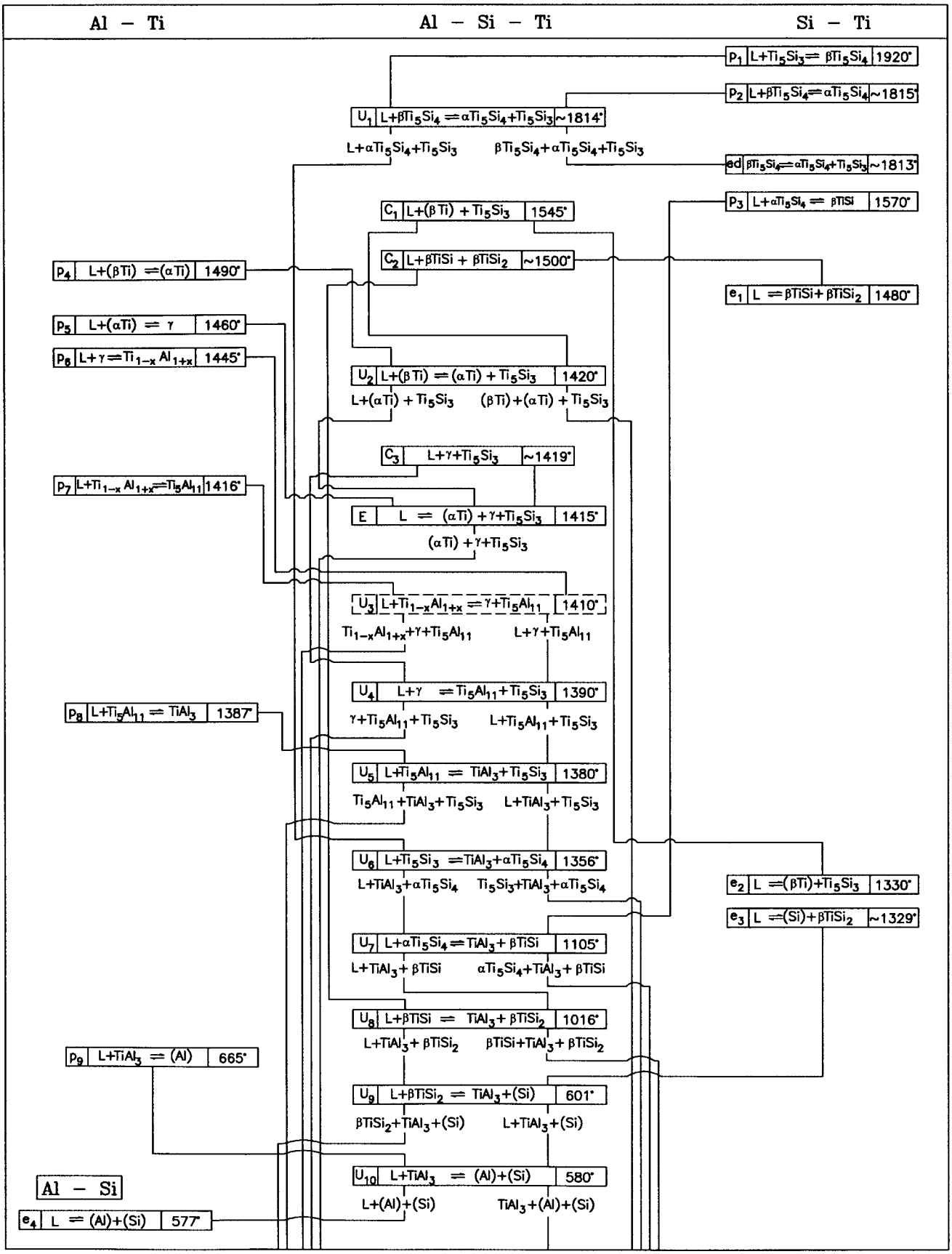


Fig. 1 Al-Si-Ti liquidus projection [after 2004Bul]

Table 1 Al–Si–Ti reaction sequence during solidification [2004Bul]



reported O phase Ti_2AlSi_3 [1965Ram] also has the $ZrSi_2$-type orthorhombic structure. At 16.7 at.% Al, the compositions of $Ti(Al_xSi_{1-x})_2$ and Ti_2AlSi_3 are identical. The existence of other reported compounds such as $TiAlSi_2$, $Ti_2Al_3Si_2$, and $Ti_7Al_5Si_{12}$ has not been firmly established. [2004Bul] pointed out that the questions of the number of ternary compounds in this system, their structure, and the temperature ranges of stability are still open.

The solubility of Si in γ and Ti_5Al_{11} is 0.5 at.% or less. The solubility of Si in $TiAl_3$ is about 15 at.%. The solubility of Al in Ti_5Si_3 is about 8 at.%. The Al solubility in Ti_5Si_4 and TiSi phases is ~0.5 at.% [2004Bul]. The solubility of Al in TiSi was, however, reported to be between 9 and 12 at.% in previous studies. The solubility of Al in $\beta TiSi_2$ or TC is about 16 at.% [2004Bul].

Solidification Equilibria

[1990Wu] and [1994Wu] determined partially the eutectic liquidus line corresponding to the L + (βTi) + Ti_5Si_3 equilibrium in ternary alloys. The liquidus temperatures listed by [1994Wu] indicate a maximum on this line between 13 and 20 at.% Al. [1994Man] also found a maximum point on this line. They postulated two U-type invariant reactions during solidification of alloys in this region: L + (βTi) ↔ (αTi) + Ti_5Si_3 and L + (αTi) ↔ γ + Ti_5Si_3. [1997Bul] experimentally determined two invariant reactions on the above liquidus line. The first reaction is the same as above [1994Man], but the second reaction was found to be a ternary eutectic: L ↔ (αTi) + γ + Ti_5Si_3.

With starting metals of 99.995% Al, 99.999% Si, and 99.85% Ti, [2004Bul] arc-melted under Ar atm about 40 ternary alloys. Differential thermal analysis was done at a heating/cooling rate of 30 °C per min. The phase equilibria were studied by metallography, x-ray diffraction, and electron probe microanalysis (EPMA). With grain size/spot ratio > 10 in EPMA, the measured composition was taken to be that of the corresponding phase. When the ratio is less, the measured value was accepted as the average composition of a mixture of the coexisting phases. Combining their results with those of [1997Bul], [2004Bul] constructed a liquidus projection. This is redrawn in Fig. 1 to agree with the accepted binary data. The phases of primary crystallization (the notation used by [2004Bul] is given in brackets following the notation used here) marked in Fig. 1 are (βTi) (β), (αTi) (α), γ, $Ti_{1-x}Al_{1+x}$, Ti_5Al_{11} (ξ), $TiAl_3$ (ε), (Al), (Si), Ti_5Si_3 (Z), αTi_5Si_4 (α5/4), βTi_5Si_4 (β5/4), βTiSi (β1/1), and $\beta TiSi_2$ (β1/2).

The ternary phase $\beta Ti(Al_xSi_{1-x})_2$ (TC) and the isostructural binary phase $\beta TiSi_2$ were shown as separate phases of primary crystallization by [2004Bul]. The peritectic reaction L + $\beta TiSi_2$ ↔ $\beta Ti(Al_xSi_{1-x})_2$ postulated by [2004Bul] remains doubtful. It is more likely that a peritectic reaction L + βTi(Al,Si) ↔ $\beta Ti(Al,Si)_2$ originates at the critical maximum C_2 (Fig. 1). The liquidus line from C_2 moving towards the Ti-Si binary side can change character and end at the binary eutectic reaction e_1 (Fig. 1). This would mean that the high-temperature modification of $TiSi_2$ has a wide homogeneity range, as seen in the isothermal section at 1200 °C [1962Sch], and there is no separate ternary phase.

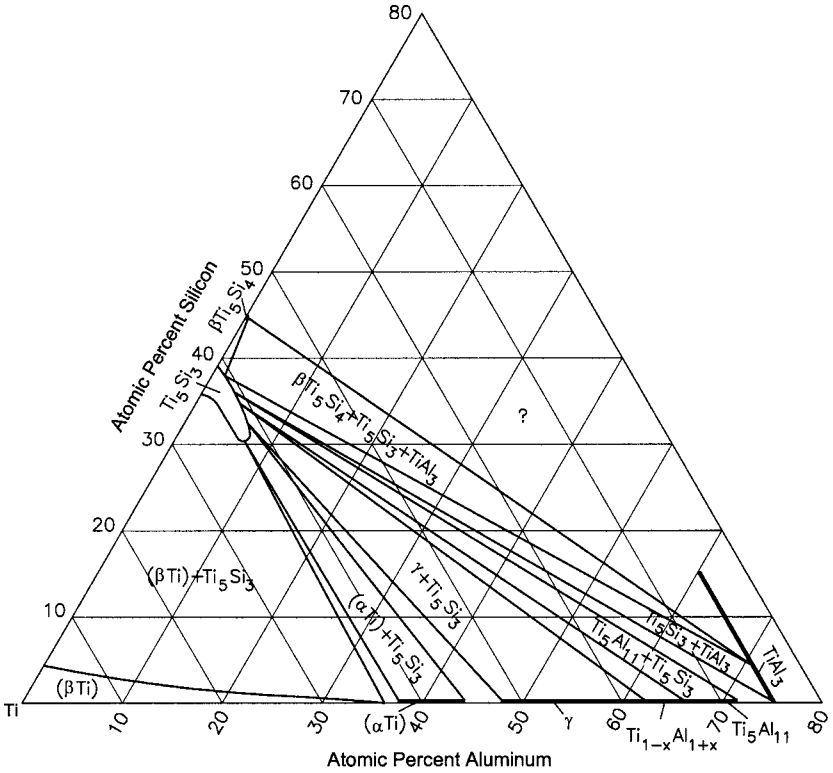


Fig. 2 Al-Si-Ti partial isothermal section at 1250 °C [2004Bul]

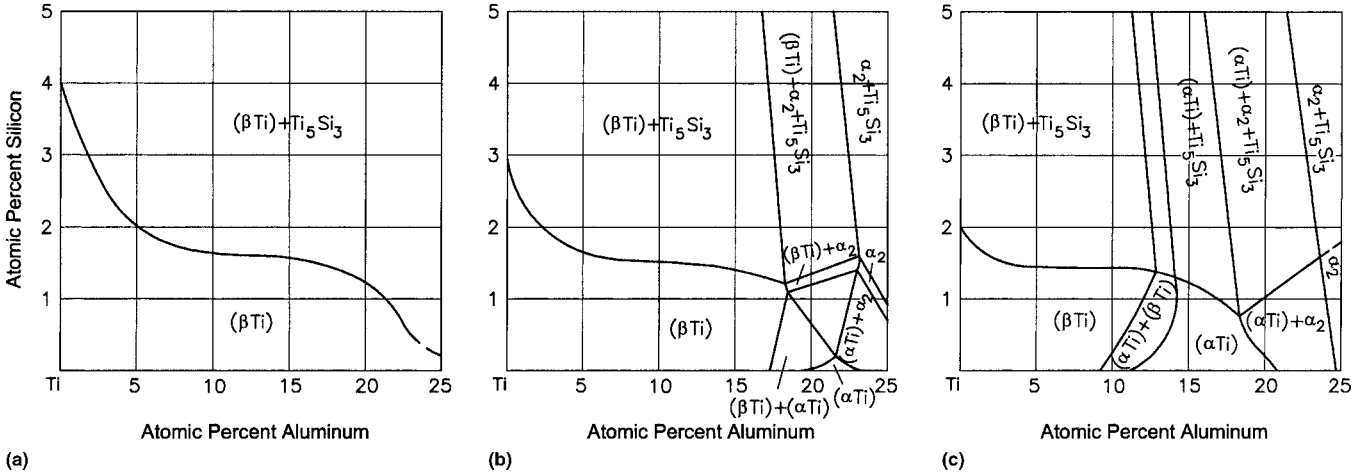


Fig. 3 Al-Si-Ti computed isothermal sections at (a) 1200 °C, (b) 1100 °C, and (c) 1000 °C [2002Aze]

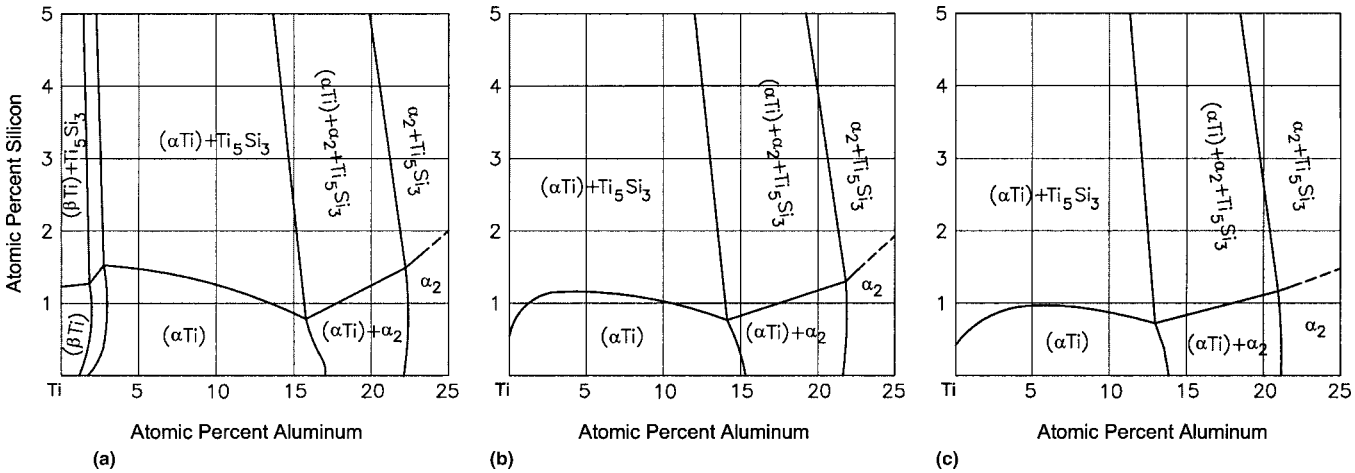


Fig. 4 Al-Si-Ti computed isothermal sections at (a) 900 °C, (b) 800 °C, and (c) 700 °C [2002Aze]

In that case, the invariant reactions U_3: L + $\beta TiSi_2 \leftrightarrow \beta TiSi$ + $\beta Ti(Al,Si)_2$ (TC) and U_7: L + $\beta TiSi_2 \leftrightarrow \beta Ti(Al,Si)_2$ (TC) + (Si) listed by [2004Bul] will stand deleted. At temperatures below the $\beta TiSi_2 \rightarrow \alpha TiSi_2$ transition, the Al-stabilized $\beta TiSi_2$ may recede into the ternary region and may appear as a ternary island-like phase. Clearly, more experimental data are required in this region to resolve this question. In Fig. 1, the invariant reactions U_3 and U_7 listed by [2004Bul] (which have no experimental support) are omitted. The other reactions are renumbered sequentially in order of decreasing temperature. The low temperature modification of $TiAl_3$ is not considered. Table 1 shows the reaction sequence corresponding to the liquid-solid reactions in Fig. 1. A more complete reaction scheme including the solid-state reactions is given by [2004Bul].

Isothermal Sections

The isothermal sections at 700 and 25 °C from the earlier literature compiled by [1995Vil] depict unconfirmed ternary compounds. Recent work on isothermal sections pertains to Ti-rich alloys and includes experimental sections at 1300 °C [1997Bul], 1270 °C and 1250 °C [2004Bul], a computed section at 1523 °C [1994Man], and six computed sections between 1200 and 700 °C [2000Aze, 2002Aze]. The partial experimental section of [2004Bul] at 1250 °C is redrawn in Fig. 2 to agree with the accepted binary data.

[1999Aze], [2000Aze], and [2002Aze] prepared four alloy compositions containing 16Al-3.5Si, 16Al-1Si, 22Al-3.5Si, and 22Al-1Si. The alloys were annealed at 1200-700 °C for 4 h to 36 days and quenched in iced water. The phase equilibria were studied by optical and electron metallography. The compositions of the coexisting phases were determined using the energy dispersive x-ray spectroscopy. The listed compositions were used in the thermodynamic optimization. Six isothermal sections were computed for Ti-rich alloys at 1200, 1100, 1000, 900, 800, and 700 °C [2000Aze, 2002Aze]. These are redrawn in Fig. 3 and 4, without any modification for agreement with the accepted binary data.

Vertical Sections

Experimental vertical sections at 10 at.% Si [1997Bul], 5 at.% Si, and 50 at.% Ti [2004Bul] and computed vertical sections at 2, 3.5, and 5 at.% Si [1994Man] are known.

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