



# Experimental investigation of Ti–Al–Si phase equilibria at 800–1200 °C

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## ABSTRACT

Five partial isothermal sections of the Ti–Al–Si system up to 70 at% Al and 40 at% Si have been determined experimentally between 800 and 1200 °C. Seven alloys were heat-treated for 24–1504 h and characterized utilizing scanning electron microscopy, electron probe microanalysis, X-ray diffraction, and differential thermal analysis. No ternary phase was found and  $\alpha$ Ti,  $\beta$ Ti, Ti<sub>3</sub>Al, TiAl, TiAl(1d-APS), TiAl<sub>2</sub>, TiAl<sub>3</sub> are in equilibrium with Ti<sub>5</sub>Si<sub>3</sub>. A partial vertical section at 9 at% Si shows that all determined data are consistent with each other.

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## 1. Introduction

TiAl-based alloys are by now an established class of high-temperature materials. Low-pressure turbine blades manufactured from TiAl-based alloys are used in GENx™ commercial aircraft engines since more than a decade. The application of TiAl-based alloys in aero engines successfully decreased the amount of fuel consumption, thereby substantially reducing gas emissions [1]. This success is due to the low density of TiAl-based alloys compared to Ni-based superalloys, which they have replaced. TiAl-based alloys show similar specific strength to Ni-based superalloys, which enables them to replace superalloys at application temperatures between 600–800 °C [2]. In order to enable even higher application temperatures, their creep and high-temperature oxidation resistance have to be improved which can be achieved through tailoring the microstructure and alloying [2,3].

The oxide scale which forms on TiAl-base alloys is a multilayer that consists of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [3]. TiO<sub>2</sub> is porous and therefore cannot inhibit the metal surface from further oxidation. Alloying with Si can improve the oxidation resistance through different mechanisms. Si refines TiO<sub>2</sub> particles, which results in the formation of a more compact oxide scale [3]. Si also facilitates Al diffusion in the scale and hinders the outward diffusion of Ti<sup>4+</sup>, thereby prohibiting further formation of TiO<sub>2</sub>. About 10 at% Si are sufficient for the preferential formation of Al<sub>2</sub>O<sub>3</sub>, which forms a protective oxide scale [4]. Even higher Si contents promote the formation of SiO<sub>2</sub> in the

oxide scale. It is assumed that the lower diffusion coefficient of oxygen in SiO<sub>2</sub> compared to TiO<sub>2</sub> and the formation of a TiN layer between the base material and the oxide scale lead to a decrease in the oxidation rate [5,6].

Moreover, Si is known to be beneficial in improving the creep resistance through the formation of fine-scaled Ti<sub>5</sub>Si<sub>3</sub> precipitates [7,8]. Adding about 0.3 at% Si can lead to the formation of Ti<sub>5</sub>Si<sub>3</sub> at the Ti<sub>3</sub>Al/TiAl lamellar interface. Ti<sub>5</sub>Si<sub>3</sub> particles substantially increase the creep resistance by hindering the movement of dislocations. For an alloy with about 0.6 at% Si, a ten times higher creep rate has been achieved compared to its Si-free counterpart [7,8]. On the other hand, a small excess amount of Si deteriorates the microstructure, thus reducing fracture toughness and creep resistance [7]. Though there is an apparent discrepancy between the optimum Si contents for improving creep and oxidation resistance at the same time only by Si, it was observed recently that of two alloys produced by powder metallurgy and containing 21 and 28 at% Si, the alloy with the higher amount of Si showed a lamellar structure coupled with larger silicides, which yielded a better toughness [9].

For the development of new TiAl-based alloys with improved properties, the knowledge of the constituent phases and phase transformations in dependence on temperature and composition is crucial. As commercial alloys usually comprise a large number of elements, CALPHAD (CALCulation of PHASE Diagram) modeling is usually employed to envisage phase equilibria of higher-order systems [10]. The results can be used to predict e.g. compositions, which yield a specific volume fraction of Ti<sub>5</sub>Si<sub>3</sub> for improving the creep resistance, or windows for thermomechanical processing or heat treatments to generate individual microstructures. Since CALPHAD relies on the extrapolation of thermodynamic data from

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binary and ternary systems, the reliability of the results crucially depends on the underlying database, i.e. the availability and quality of experimental results from the constituent binary and ternary systems [10].

### 1.1. Literature review

The Ti–Al–Si system has been thoroughly assessed within the MSI Ternary Phase Diagram Evaluation scheme [11,12], considering references for the ternary system up to 2002 and has been reviewed by Raghavan [13,14], covering references up to 2008. In the following, a summary of investigations focusing on phase equilibria in the Ti-rich part of the system is given.

Bulanova et al. [15,16] established three partial isothermal sections at 1250, 1270 and 1300 °C, a liquidus and solidus diagram for the complete Ti–Al–Si system, four vertical sections at 5 and 10 at% Si, 50 at% Ti, 40 at% Al and a reaction scheme using metallography, differential thermal analysis (DTA), X-ray diffraction (XRD), and electron probe microanalysis (EPMA) of annealed and as-cast alloys. Based on XRD of samples annealed for 6–12 h, Schob et al. [17] established a complete isothermal section at 1200 °C. Turner and Crossley [18,19] established partial isothermal sections of the Ti corner at 600, 800, 900, 1000, 1100, and 1200 °C and two partial vertical sections for 2 and 6 wt% Al from light optical microscopy. Li et al. [20,21] established a partial vertical section for 0.3 at% Si from EPMA measurements showing the Ti<sub>3</sub>Al/TiAl and αTi/TiAl phase boundaries between 1000 and 1250 °C. Azevedo and Flower [22–24] carried out a comprehensive study of the Ti-rich part of the system employing XRD, scanning and transmission electron microscopy (SEM, TEM), both combined with energy-dispersive spectroscopy (EDS). They established partial isothermal sections at 700, 800, 900, and 1100 °C [22] and calculated partial isothermal sections for the temperature range 700–1200 °C [23,24]. From XRD and EPMA results of a single sample and data from literature Viala et al. [25] created a simplified isothermal section at 1000 °C. Gupta [26] studied the phase equilibria in the temperature range 700–1000 °C employing ternary diffusion couples between pure titanium and a eutectic Al–Si alloy. Compositions of the phases were established through EPMA. An isothermal section at 1000 °C was constructed and phase equilibria at the remaining temperatures were discussed. Liu et al. [27] established an isothermal section at 1000 °C and a partial isothermal section at 900 °C focusing on the Al-rich side utilizing EDS measurements of heat-treated alloys. Additionally, they determined the liquidus surface by performing DTA up to 1500 °C. A complete isothermal section at “about 700 °C” was determined employing metallography and XRD of annealed alloys by Raman & Schubert [28]. Apparently, the term “about” was chosen because the authors realized that annealing times of 48–120 h may have been too short to attain equilibrium in all investigated alloys. Based on the work of Raman & Schubert [28], Gröbner et al. [29] calculated the isothermal section at 700 °C. More recently, a complete isothermal section at 700 °C has been established by XRD and EDS on alloys that were homogenized at 1100 °C for 40 h and then equilibrated at 700 °C for 1080 h [30]. Based on a number of experimental data from Al–Si-rich alloys, complete isothermal sections at 550, 585, 590, 650, 727 and 900 °C were calculated by Li et al. [31]. A complete isothermal section at 550 °C was established by Wang et al. [32] using SEM, EDS and XRD on annealed alloys. Finally, a complete isothermal section at 20 °C was presented by Kamei et al. [33] from microstructures and XRD of as-cast alloys.

Despite all the investigations mentioned above, data on phase equilibria are at least partially controversial. For instance for the solid solubility of Si in TiAl at 1000 °C, reported data vary between 0.1 [20] and about 3 at% [26,27] and data for the solid solubility of Al in Ti<sub>5</sub>Si<sub>3</sub> vary between 2 [22] and 11 at% [27]. It is noted that in alloys produced through powder metallurgy even much higher Al contents

up to more than 20 at% Al have been observed in Ti<sub>5</sub>Si<sub>3</sub> [34–36], but it is assumed that these compositions are metastable [36]. However, the knowledge of the precise solid solubilities of both phases in dependence on temperature is essential for the design of more creep resistant TiAl-based alloys, because this information yields the volume fraction of Ti<sub>5</sub>Si<sub>3</sub> at a certain temperature for a given composition.

In order to improve these and other thermodynamic data, which are relevant for the development of TiAl alloys with improved properties, several Ti–Al–X(–Y) systems are investigated within the large-scale European project ADVANCE to set up the next generation of advanced CALPHAD databases for Ti–Al alloys [37]. As a part of this project, phase equilibria between the Ti–Al phases and Ti<sub>5</sub>Si<sub>3</sub> between 800 and 1200 °C, the temperature range where the alloys are processed and maybe applied, were experimentally investigated.

## 2. Materials and methods

From elements of high purity (Ti: 99.995%; Al: 99.999%; Si: 99.99%) seven alloys were prepared by crucible-free levitation melting (Fives Celes) [38] or advanced arc melting (PINK GmbH Vakuumtechnik). These techniques have been chosen in view that phase equilibria in Ti–Al(–X) are crucially affected by impurities, especially oxygen [39]. In contrast to conventional arc melters, the advanced device is equipped with a manipulator, which allows overturning the solidified material without opening the device, thereby maintaining a good vacuum during the whole melting process. Moreover, the alloys do not solidify on the cold copper hearth but are cast into a Cu mold. Advanced arc melting has been used for alloys S2 and S3 (Table 1), which could not be fully molten by levitation melting. Rods of 15–18 mm in diameter and 150 mm in length were produced by both methods by casting into cold copper molds. Wet-chemical analysis of slices taken from the top and bottom of the alloys showed that the alloys were homogeneous within standard error. Alloys produced by crucible-free levitation melting showed an average amount of about 100 wt% ppm O, while those produced by advanced arc melting contained 260 and 430 wt% ppm oxygen. Overall compositions of the alloys and impurity contents have been determined by wet-chemical analysis, employing inert gas fusion (NCS Fusion Master ONH) for oxygen and nitrogen, combustion gas analysis (NCS Combustion Master CS) for carbon, and inductively coupled plasma optical emission spectroscopy (PerkinElmer Optima 8300 ICP-OES) for all other elements. The results are summarized in Table 1.

For heat-treatments at 800–1100 °C, slices of the alloys were encapsulated in high-purity quartz capsules back-filled with Ar and using Ti as a getter. Heat-treatments at 1200 °C, where quartz capsules are not any longer gas-tight [40], were performed under flowing dry Ar using a double-crucible technique [38,41]. After annealing at 1200 °C/24 h, 1100 °C/165–200 h, and 800–1000 °C/1000–1504 h, all samples were quenched to room temperature.

Microstructures were inspected using a SEM (Zeiss LEO 1550 VP). Phases were identified by XRD (Bruker Advance D8) using powders with a particle size of < 90 μm. XRD measurements were performed

**Table 1**  
Wet-chemical analyses of the as-cast alloys.

Alloy	Ti (at%)	Al (at%)	Si (at%)	O (wt. ppm)	N (wt. ppm)	C (wt. ppm)
S1	37.5	55.0	7.5	110	< 50	92
S2	43.5	47.4	9.1	260	< 50	100
S3	50.7	40.4	8.9	430	< 50	120
S4	60.2	32.7	7.1	85	< 50	75
S5	71.0	20.4	8.6	70	< 50	97
S6	75.8	14.7	9.5	105	< 50	110
S7	80.7	9.7	9.6	130	< 50	129

**Table 2**  
Crystallographic data of solid phases.

Phase	Pearson Symbol, Space Group, Prototype	Lattice Constants (nm)	Ref.
$\beta$ Ti	cI2, $Im\bar{3}m$ , W	$a_0 = 0.33112$	[48]
$\alpha$ Ti	hP2, $P6_3/mmc$ , Mg	$a_0 = 0.29503$ , $c_0 = 0.46810$	[48]
Ti <sub>3</sub> Al	hP8, $P6_3/mmc$ , Ni <sub>3</sub> Sn	$a_0 = 0.5765$ , $c_0 = 0.4625$	[49]
TiAl	tP4, $P4/mmm$ , AuCu	$a_0 = 0.4000$ , $c_0 = 0.4075$	[50]
TiAl (1d-APS)	one-dimensional, tetragonal ordered superstructures of AuCu $P4/mmm$ , tP28, Ti <sub>2</sub> Al <sub>5</sub>	$a_0 = 0.39053$ , $c_0 = 2.91921$	[51]
TiAl <sub>2</sub>	tI24, $I4_1/amd$ , HfGa <sub>2</sub>	$a_0 = 0.3971$ , $c_0 = 2.4312$	[52]
TiAl <sub>3</sub> (h)	tI8, $I4/mmm$ , TiAl <sub>3</sub> (h)	$a_0 = 0.3849$ , $c_0 = 0.8610$	[53]
Ti <sub>5</sub> Si <sub>3</sub>	hP16, $P6_3/mmc$ , Mn <sub>5</sub> Si <sub>3</sub>	$a_0 = 0.7452$ , $c_0 = 0.5142$	[54]

in Bragg-Brentano geometry in the range of  $20^\circ < 2\theta < 120^\circ$  using Co-K $\alpha$  ( $\lambda = 0.178897$  nm) radiation. Phases were identified using the X'Pert HighScore software together with the Powder Diffraction File™ (PDF-2) provided from the International Center for Diffraction Data (ICDD) [42]. Lattice constants were calculated using TOPAS (Bruker AXS-Version 5). Compositions of the coexisting phases were established with EPMA (JEOL JXA-8100) using metallographic sections. To check the presence of any impurities, qualitative analyses were performed at 15 kV, 400 nA with a beam width of 3  $\mu$ m. For quantitative analysis, standards of the pure elements have been used and analyses were performed at 15 kV, 20 nA with a focused beam. At least 12 measurements for each phase were carried out at least at five different places of the samples. Final compositions were obtained through ZAF matrix correction. In a few cases, specifically for samples annealed at 800 °C, phases were so fine-scaled that within the spatial resolution of the EPMA a fraction of the measured composition may come from neighbouring or underlying grains of another phase. In those cases, all analyses were plotted in a Gibbs triangle and only those data, which corresponded to the very end of a tie-line or the corners of a tie-triangle, i.e. the extreme values, were considered as equilibrium compositions. For these extreme values, no standard deviation can be given. Phase transformation temperatures were measured on bulk samples by DTA (NETZSCH STA 449 F3 Jupiter, NETZSCH DSC 404 C) under a stream of pure Ar and using alumina crucibles. Samples in as-cast and heat-treated condition were heated up to a maximum of about 1400 °C for at least two times and cooled down to room temperature at 10 K/min. Transformation temperatures were evaluated from the first heating cycle. By calibrating with the melting temperatures of pure elements, the experimental uncertainty was  $\pm 2$  °C.

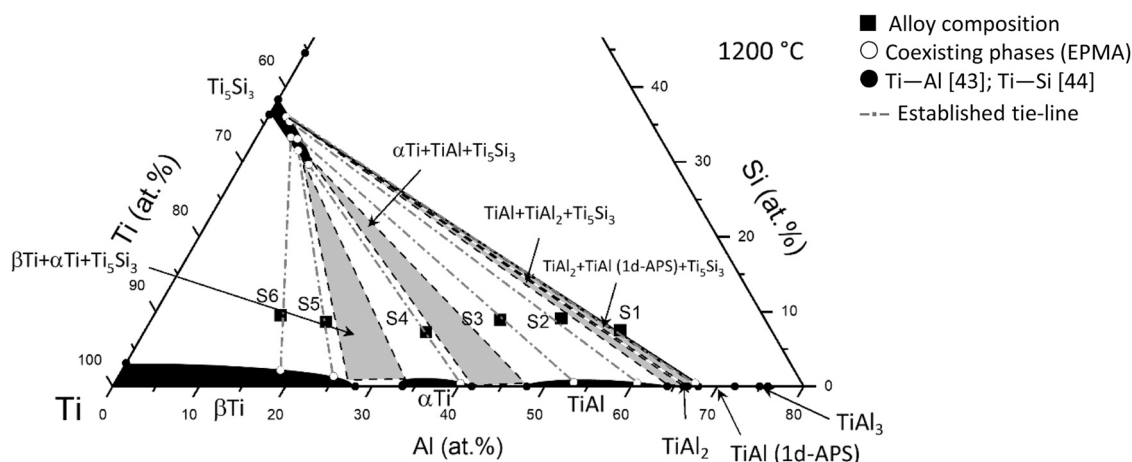
### 3. Results and discussion

To establish the partial isothermal sections, compositions of the phase boundaries in the binary systems were taken from recent

assessments. For Ti–Al the updated version [43] of the comprehensive assessment by Schuster & Palm [39] is chosen. The update settles the dispute about the peritectoid or congruent formation of Ti<sub>3</sub>Al. While experiments show a peritectoid formation of Ti<sub>3</sub>Al, all CALPHAD calculations predict a congruent formation of Ti<sub>3</sub>Al. As detailed in [43], also the CALPHAD calculations show the peritectoid reaction  $\alpha$ Ti +  $\beta$ Ti  $\leftrightarrow$  Ti<sub>3</sub>Al at 1200 °C, if substitutional vacancies are included in the CALPHAD calculations. In consequence, the phase field of  $\alpha$ Ti is interrupted between 1170 and 1200 °C by the equilibrium  $\beta$ Ti + Ti<sub>3</sub>Al, i.e. no continuous phase field of  $\alpha$ Ti exists up to the melt. The Ti–Si binary was adopted from the latest thermodynamic assessment by Fiore et al. [44]. They conclude that the long ongoing debate whether the line compound Ti<sub>3</sub>Si exists between the Ti solid solution and Ti<sub>5</sub>Si<sub>3</sub> or whether this phase is stabilised by impurities cannot be settled from the existing evidence. The Al–Si binary is taken from Lukas & Lebrun [45]. It is a simple eutectic system containing no intermetallic phases.

The partial isothermal sections determined here comprise compositions up to 70 at% Al and 40 at% Si. The crystallographic data of the solid phases observed within this composition range are listed in Table 2. No ternary phase was detected within the investigated temperature and composition range. Additionally, Ti<sub>3</sub>Si (tp32,  $P4_2/n$  [44,46]), whose existence is still under debate [44], was not detected in the present investigation. This phase was observed in the Ti–Al–Si system by Li et al. [30] and Gupta [26], but not in other studies [15,16,18,19,32,36,47]. Nevertheless, investigated compositions in the present work could be outside the composition range where equilibria with this phase may occur. Therefore, phase equilibria with Ti<sub>3</sub>Si are indicated by dashed tie-triangle.

Comparison with the liquidus projection [27] shows that all alloy compositions are located within the primary field of high-melting Ti<sub>5</sub>Si<sub>3</sub> ( $T_m = 2130$  °C), except S7. Therefore, S1–S6 contained varying amounts of large idiomorphic grains of primary Ti<sub>5</sub>Si<sub>3</sub> in the as-cast state. These grains are too big to equilibrate within reasonable annealing times. Therefore, all compositions measured by EPMA were



**Fig. 1.** Partial Ti–Al–Si isothermal section at 1200 °C.

**Table 3**

Compositions of coexisting phases measured with EPMA; figures for HT denote length of heat-treatment and figures shown in bold are extreme values (see text); n.d.: not determined.

Temp.	1200 °C				1100 °C				1000 °C				
	Alloy	Phases	Ti	Al	Si	Phases	Ti	Al	Si	Phases	Ti	Al	Si
HT (h)	24												
S1	Ti <sub>5</sub> Si <sub>3</sub>	61.9 ± 0.4	2.1 ± 0.4	36.0 ± 0.4	Ti <sub>5</sub> Si <sub>3</sub>	62.2 ± 0.2	1.1 ± 0.3	36.7 ± 0.2	Ti <sub>5</sub> Si <sub>3</sub>	61.2 ± 0.2	1.5 ± 0.4	37.3 ± 0.5	
	TiAl (1d-APS)	32.3 ± 0.6	67.2 ± 0.6	0.5 ± 0.1	TiAl (1d-APS)	30.1 ± 0.2	69.6 ± 0.2	0.3 ± 0.04	TiAl <sub>3</sub>	26.7 ± 0.5	72.7 ± 0.7	0.6 ± 0.2	
					TiAl <sub>2</sub>	34.6 ± 0.2	65.0 ± 0.2	0.4 ± 0.04	TiAl <sub>2</sub>	34.6 ± 0.4	65.0 ± 0.4	0.4 ± 0.1	
HT* (h)	24				200				1000				
S2	Ti <sub>5</sub> Si <sub>3</sub>	61.8 ± 0.3	2.8 ± 0.6	35.4 ± 0.5	Ti <sub>5</sub> Si <sub>3</sub>	61.2 ± 0.5	3.2 ± 0.5	35.6 ± 0.2	Ti <sub>5</sub> Si <sub>3</sub>	61.5 ± 0.5	3.9 ± 0.7	34.6 ± 0.5	
	TiAl	39.0 ± 0.4	60.5 ± 0.4	0.5 ± 0.06	TiAl <sub>2</sub>	34.8 ± 0.5	65.0 ± 0.5	0.2 ± 0.1	TiAl <sub>2</sub>	35.1 ± 0.5	64.6 ± 0.6	0.3 ± 0.1	
					TiAl	38.8 ± 0.4	60.8 ± 0.4	0.4 ± 0.1	TiAl	42.3 ± 0.4	57.5 ± 0.4	0.2 ± 0.1	
HT* (h)	24				200				1000				
S3	Ti <sub>5</sub> Si <sub>3</sub>	62.1 ± 0.3	4.9 ± 0.5	33.1 ± 0.5	Ti <sub>5</sub> Si <sub>3</sub>	61.8 ± 0.2	4.0 ± 0.2	34.2 ± 0.3	Ti <sub>5</sub> Si <sub>3</sub>	61.2 ± 0.5	7.1 ± 0.7	31.7 ± 0.7	
	TiAl	46.4 ± 0.3	53.1 ± 0.4	0.5 ± 0.2	TiAl	46.0 ± 0.3	53.7 ± 0.3	0.3 ± 0.04	TiAl	45.5 ± 0.3	54.1 ± 0.3	0.4 ± 0.1	
					TiAl				TiAl				
HT* (h)	24				200				1000				
S4	Ti <sub>5</sub> Si <sub>3</sub>	62.5 ± 0.2	7.7 ± 0.6	29.8 ± 0.6	Ti <sub>5</sub> Si <sub>3</sub>	62.8 ± 0.3	6.7 ± 0.6	30.5 ± 0.6	Ti <sub>5</sub> Si <sub>3</sub>	62.4 ± 0.3	7.4 ± 0.5	30.2 ± 0.3	
	αTi	59.6 ± 0.3	40.0 ± 0.3	0.4 ± 0.04	TiAl	54.6 ± 0.6	45.2 ± 0.6	0.2 ± 0.01	TiAl	53.3 ± 0.3	46.5 ± 0.3	0.2 ± 0.1	
					Ti <sub>3</sub> Al	61.8 ± 0.4	37.8 ± 0.4	0.4 ± 0.04	Ti <sub>3</sub> Al	64.0 ± 0.7	35.5 ± 0.7	0.5 ± 0.1	
HT* (h)	24				200				1000				
S5	Ti <sub>5</sub> Si <sub>3</sub>	62.8 ± 0.4	5.7 ± 0.2	31.5 ± 0.5	Ti <sub>5</sub> Si <sub>3</sub>	62.9 ± 0.2	5.4 ± 0.2	31.7 ± 0.3	Ti <sub>5</sub> Si <sub>3</sub>	62.8 ± 0.4	5.9 ± 0.2	31.3 ± 0.5	
	βTi	73.8 ± 0.3	24.9 ± 0.2	1.3 ± 0.3	Ti <sub>3</sub> Al	74.0 ± 0.4	24.5 ± 0.3	1.5 ± 0.2	Ti <sub>3</sub> Al	73.6 ± 0.4	24.9 ± 0.2	1.5 ± 0.5	
					Ti <sub>3</sub> Al				Ti <sub>3</sub> Al				
HT* (h)	24				200				1000				
S6	Ti <sub>5</sub> Si <sub>3</sub>	62.7 ± 0.3	4.0 ± 0.4	33.3 ± 0.5	Ti <sub>5</sub> Si <sub>3</sub>	62.9 ± 0.2	3.5 ± 0.3	33.6 ± 0.4	Ti <sub>5</sub> Si <sub>3</sub>	63.0 ± 0.2	3.5 ± 0.8	33.5 ± 0.8	
	βTi	79.7 ± 0.4	18.3 ± 0.4	2.0 ± 0.3	βTi	80.8 ± 0.4	17.8 ± 0.4	1.4 ± 0.04	Ti <sub>3</sub> Al	78.1 ± 0.6	20.1 ± 0.7	1.8 ± 0.2	
									αTi	82.0 ± 0.5	17.1 ± 0.5	0.9 ± 0.03	
HT* (h)									1000				
S7									Ti <sub>5</sub> Si <sub>3</sub>	62.7 ± 0.4	2.0 ± 0.3	35.3 ± 0.5	
									αTi	86.3 ± 0.2	12.4 ± 0.2	1.3 ± 0.1	
Temp. Alloy	900 °C				800 °C								
	Phases	Ti	Al	Si	Phases	Ti	Al	Si					
HT* (h)	1000				1000								
S1	Ti <sub>5</sub> Si <sub>3</sub>	61.4 ± 0.4	2.2 ± 0.5	36.4 ± 0.4	Ti <sub>5</sub> Si <sub>3</sub>	<b>62.1</b>	<b>2.0</b>	<b>35.9</b>					
	TiAl <sub>3</sub>	n.d.	n.d.	n.d.	TiAl <sub>3</sub>	<b>26.0</b>	<b>73.1</b>	<b>0.9</b>					
	TiAl <sub>2</sub>	34.6 ± 0.3	65.2 ± 0.3	0.2 ± 0.1	TiAl <sub>2</sub>	<b>34.0</b>	<b>65.8</b>	<b>0.2</b>					
HT* (h)	1504				1000								
S2	Ti <sub>5</sub> Si <sub>3</sub>	61.8 ± 0.2	2.9 ± 0.1	35.3 ± 0.2	Ti <sub>5</sub> Si <sub>3</sub>	<b>61.9</b>	<b>3.1</b>	<b>35.0</b>					
	TiAl <sub>2</sub>	35.7 ± 0.2	64 ± 0.2	0.3 ± 0.1	TiAl <sub>2</sub>	<b>35.0</b>	<b>64.8</b>	<b>0.2</b>					
	TiAl	43.5 ± 0.3	56.3 ± 0.3	0.2 ± 0.1	TiAl	44.6 ± 0.2	54.5 ± 0.5	0.9 ± 0.2					
HT* (h)	1504				1000								
S3	Ti <sub>5</sub> Si <sub>3</sub>				Ti <sub>5</sub> Si <sub>3</sub>	62.5 ± 0.1	5.1 ± 0.3	32.4 ± 0.3					
	TiAl				TiAl	46.1 ± 0.2	53.1 ± 0.3	0.8 ± 0.1					
HT* (h)	1000				1000								
S4	Ti <sub>5</sub> Si <sub>3</sub>	63.0 ± 0.3	6.5 ± 0.3	30.5 ± 0.4	Ti <sub>5</sub> Si <sub>3</sub>	62.6 ± 0.2	8.0 ± 0.7	29.4 ± 0.8					
	TiAl	53.8 ± 0.5	46.0 ± 0.6	0.2 ± 0.1	TiAl	<b>54.1</b>	<b>45.7</b>	<b>0.2</b>					
	Ti <sub>3</sub> Al	65.1 ± 0.4	34.5 ± 0.5	0.4 ± 0.2	Ti <sub>3</sub> Al	<b>64.4</b>	<b>34.1</b>	<b>1.5</b>					
HT* (h)	1000				1000								
S5	Ti <sub>5</sub> Si <sub>3</sub>	63.3 ± 0.3	5.9 ± 0.4	30.8 ± 0.5	Ti <sub>5</sub> Si <sub>3</sub>	62.8 ± 0.3	5.6 ± 0.2	31.6 ± 0.4					
	Ti <sub>3</sub> Al	74.6 ± 0.5	24.1 ± 0.5	1.3 ± 0.1	Ti <sub>3</sub> Al	74.5 ± 0.3	24.1 ± 0.3	1.4 ± 0.1					
HT* (h)	1000				1000								
S6	Ti <sub>5</sub> Si <sub>3</sub>	62.9 ± 0.2	4.7 ± 0.4	32.4 ± 0.4	Ti <sub>5</sub> Si <sub>3</sub>	62.0 ± 0.2	4.7 ± 0.1	33.3 ± 0.2					
	Ti <sub>3</sub> Al	78.2 ± 0.3	20.2 ± 0.3	1.6 ± 0.1	Ti <sub>3</sub> Al	<b>78.5</b>	<b>20.1</b>	<b>1.4</b>					
	αTi	83.2 ± 0.3	16.0 ± 0.2	0.8 ± 0.1	αTi	<b>83.0</b>	<b>15.5</b>	<b>1.5</b>					
HT* (h)	1000				1000								
S7	Ti <sub>5</sub> Si <sub>3</sub>	63.7 ± 0.8	2.4 ± 0.3	33.9 ± 0.8	Ti <sub>5</sub> Si <sub>3</sub>	63.5 ± 1.1	1.8 ± 0.4	34.7 ± 1.1					
	αTi	86.8 ± 0.2	12.4 ± 0.2	0.8 ± 0.1	αTi	87.1 ± 0.7	12.3 ± 0.7	0.6 ± 0.1					

obtained from small, spherical Ti<sub>5</sub>Si<sub>3</sub> grains, which are assumed to have formed at the annealing temperatures.

### 3.1. Partial isothermal section at 1200 °C

Fig. 1 depicts the partial isothermal section at 1200 °C. All investigated alloys are located within two-phase fields at this temperature. The compositions of coexisting phases measured with EPMA are summarised in Table 3 and identification of the phases by XRD is shown in Table 4. All binary Ti–Al phases show a limited solid solubility for Si, while the maximum Al content observed in Ti<sub>5</sub>Si<sub>3</sub> is about 8 at%. It is noted that in alloys where βTi is stable at 1200 °C, αTi is observed at room temperature, instead. The βTi ↔ αTi transformation in Ti–Al alloys cannot be suppressed even by quenching [41,49,55] and also not in Ti–Al–Si alloys [11,22]. Likewise, the ordering reaction αTi ↔ Ti<sub>3</sub>Al (α<sub>2</sub>) cannot be suppressed during cooling

in binary Ti–Al alloys, even by quenching the alloys to room temperature [49,56]. The same has been observed for the Ti–Al–Si alloys [22]. Finally, Al-rich TiAl cannot be preserved by quenching, but forms a sequence of long-periodic one-dimensional antiphase domain structures during cooling, denoted as 1d-APS [57]. Depending on the composition, different crystallographic structures are observed at room temperature, identified as Ti<sub>2</sub>Al<sub>5</sub> in the present case.

In Fig. 2 the present isothermal section is compared with previously reported data [17–22,24,58,59]. The outline of the βTi phase field at 1200 °C has been investigated before [17,19,22] and the present investigation agrees with the previous ones in that the solid solubility for Si in βTi decreases with increasing Al content. Quantitatively, the solid solubility for Si in βTi is somewhat higher than previously determined, e.g. 2.0 at% Si at about 20 at% Al compared to about 1.5 at% Si [17,22]. Only Schob et al. [17] investigated a more extended composition range at 1200 °C. They observed an extended

**Table 4**  
Lattice constants of the constituent phases;  $\alpha\text{Ti}^*$  denotes formation from  $\beta\text{Ti}$  during quenching to room temperature.

Alloy	1200 °C			1100 °C			1000 °C		
	Phase	Lattice constant (nm)		Phase	Lattice constant (nm)		Phase	Lattice constant (nm)	
		$a_0$	$c_0$		$a_0$	$c_0$		$a_0$	$c_0$
S1	Ti <sub>5</sub> Si <sub>3</sub>	0.74596 (1)	0.51470 (2)	Ti <sub>5</sub> Si <sub>3</sub>	0.74545(2)	0.51478(1)	Ti <sub>5</sub> Si <sub>3</sub>	0.74533 (2)	0.51495 (2)
	Ti <sub>2</sub> Al <sub>5</sub>	0.393519 (1)	2.8932 (1)	Ti <sub>2</sub> Al <sub>5</sub>	0.39158(2)	2.9125(3)	TiAl <sub>3</sub>	0.38523 (2)	0.86009 (6)
S2	Ti <sub>5</sub> Si <sub>3</sub>	0.74641(1)	0.51520 (1)	TiAl <sub>2</sub>	0.39704(3)	2.4310(7)	TiAl <sub>2</sub>	0.397041(7)	2.43098(7)
	TiAl	0.39782(1)	0.40593 (2)	Ti <sub>5</sub> Si <sub>3</sub>	0.74644(1)	0.51521(2)	Ti <sub>5</sub> Si <sub>3</sub>	0.74688(2)	0.51554(2)
S3	Ti <sub>5</sub> Si <sub>3</sub>	0.74794 (1)	0.51637 (2)	TiAl <sub>2</sub>	0.39848(3)	2.4373(6)	TiAl <sub>2</sub>	0.39737(2)	2.4317(2)
	TiAl	0.39846 (1)	0.40773 (2)	TiAl	0.4020(5)	0.3974(3)	TiAl	0.39882(3)	0.40796(3)
S4	Ti <sub>5</sub> Si <sub>3</sub>	0.74991 (2)	0.51824 (2)	Ti <sub>5</sub> Si <sub>3</sub>	0.74778(5)	0.51611(4)	Ti <sub>5</sub> Si <sub>3</sub>	0.74767 (2)	0.51605 (2)
	$\alpha\text{Ti}$	0.29138(1)	0.46222(2)	TiAl	0.40412(6)	0.3978 (1)	TiAl	0.39855 (2)	0.40844 (3)
S5	Ti <sub>5</sub> Si <sub>3</sub>	0.74790 (2)	0.51721(1)	Ti <sub>5</sub> Si <sub>3</sub>	0.75062(9)	0.51816(8)	Ti <sub>5</sub> Si <sub>3</sub>	0.75053 (2)	0.51768 (2)
	$\alpha\text{Ti}^*$	0.28974 (1)	0.46384 (2)	TiAl	0.4030(1)	0.3955(1)	TiAl	0.40650(4)	0.39795(3)
S6	Ti <sub>5</sub> Si <sub>3</sub>	0.74758 (3)	0.51629 (2)	Ti <sub>3</sub> Al	0.57691(8)	0.4628 (1)	Ti <sub>3</sub> Al	0.56160(7)	0.46279(3)
	$\alpha\text{Ti}^*$	0.28997 (1)	0.46465 (2)	Ti <sub>5</sub> Si <sub>3</sub>	0.74878(9)	0.51695(8)	Ti <sub>5</sub> Si <sub>3</sub>	0.74958(8)	0.51737(8)
S7				Ti <sub>3</sub> Al	0.5770 (1)	0.4646 (2)	Ti <sub>3</sub> Al	0.57913(6)	0.46403(4)
				Ti <sub>5</sub> Si <sub>3</sub>	0.7483(1)	0.5164(1)	Ti <sub>5</sub> Si <sub>3</sub>	0.74818 (3)	0.51566 (3)
				$\alpha\text{Ti}^*$	0.29157 (5)	0.4658 (1)	Ti <sub>3</sub> Al	0.5796 (1)	0.4648(7)
							$\alpha\text{Ti}$	0.29171(5)	0.4673 (1)
							Ti <sub>5</sub> Si <sub>3</sub>	0.74771 (2)	0.51543 (2)
							$\alpha\text{Ti}$	0.29231 (1)	0.46629 (3)

Lattice constants of the constituent phases in the annealed Ti–Al–Si alloys

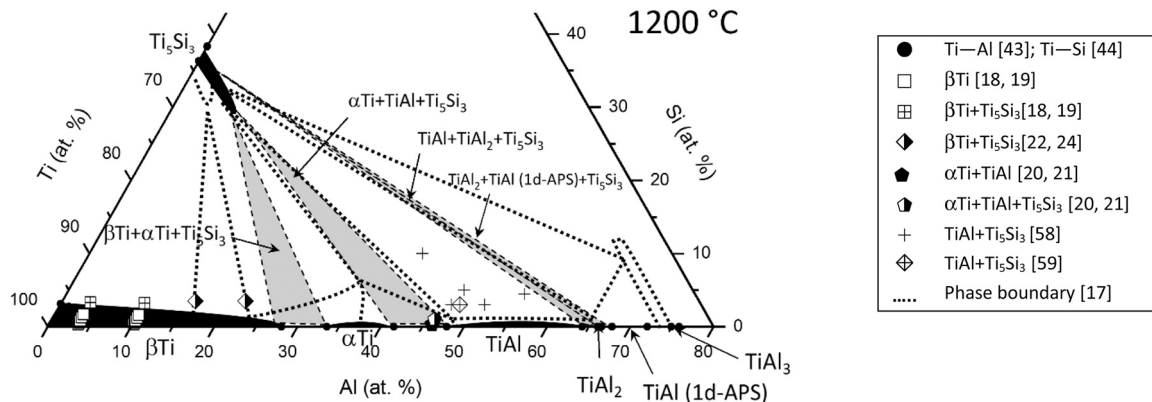
Alloy	900 °C			800 °C		
	Phase	Lattice constant (nm)		Phase	Lattice constant (nm)	
		$a_0$	$c_0$		$a_0$	$c_0$
S1	Ti <sub>5</sub> Si <sub>3</sub>	0.74522 (1)	0.51473 (2)	Ti <sub>5</sub> Si <sub>3</sub>	0.74533 (5)	0.51529(6)
	TiAl <sub>3</sub>	0.38510(7)	0.86017 (5)	TiAl <sub>3</sub>	0.38524(7)	0.86050(5)
	TiAl <sub>2</sub>	0.39682(1)	2.43124 (7)	TiAl <sub>2</sub>	0.39701 (7)	2.43147(2)
S2	Ti <sub>5</sub> Si <sub>3</sub>	0.74531(4)	0.51500(4)	Ti <sub>5</sub> Si <sub>3</sub>	0.74695(4)	0.51569(4)
	TiAl <sub>2</sub>	0.37579(2)	2.56815(8)	TiAl <sub>2</sub>	0.39791(3)	2.4425(3)
	TiAl	0.39701(2)	0.40527(3)	TiAl	0.39835(5)	0.40544(9)
S3	Ti <sub>5</sub> Si <sub>3</sub>	0.74675(4)	0.51548(4)	Ti <sub>5</sub> Si <sub>3</sub>	0.74806(6)	0.51642(6)
	TiAl	0.39800(2)	0.40708(4)	TiAl	0.39919(3)	0.40768(5)
S4	Ti <sub>5</sub> Si <sub>3</sub>	0.75022(5)	0.51792(5)	Ti <sub>5</sub> Si <sub>3</sub>	0.75078(5)	0.51828(5)
	TiAl	0.40073(4)	0.40579(6)	TiAl	0.40080(4)	0.40622(6)
S5	Ti <sub>3</sub> Al	0.57690(5)	0.46295(6)	Ti <sub>3</sub> Al	0.57760(5)	0.46354(7)
	Ti <sub>5</sub> Si <sub>3</sub>	0.74954(7)	0.51713(6)	Ti <sub>5</sub> Si <sub>3</sub>	0.74997(7)	0.51753(7)
S6	Ti <sub>3</sub> Al	0.57951(5)	0.46424(4)	Ti <sub>3</sub> Al	0.57921(5)	0.46423(4)
	Ti <sub>5</sub> Si <sub>3</sub>	0.74704 (2)	0.51609(2)	Ti <sub>5</sub> Si <sub>3</sub>	0.7486(3)	0.5169(3)
S7	Ti <sub>3</sub> Al	0.5787(2)	0.4646(1)	Ti <sub>3</sub> Al	0.58072(3)	0.46641(3)
	$\alpha\text{Ti}$	0.29188(5)	0.4668(2)	$\alpha\text{Ti}$	0.29131(1)	0.46396(2)
S7	Ti <sub>5</sub> Si <sub>3</sub>	0.74713(6)	0.51555(6)	Ti <sub>5</sub> Si <sub>3</sub>	0.74711(8)	0.51557(8)
	$\alpha\text{Ti}$	0.29274(2)	0.46651(3)	$\alpha\text{Ti}$	0.29272(3)	0.46648(4)

homogeneity range for Ti<sub>3</sub>Al, denoted as Ti<sub>3-2</sub>Al in their investigation, which showed a solid solubility of up to about 6 at% Si. However, by now it is clear that Ti<sub>3</sub>Al exists only below 1200 °C, as it forms at that temperature on cooling by the peritectic reaction  $\beta\text{Ti} + \alpha\text{Ti} \leftrightarrow \text{Ti}_3\text{Al}$  [39,43]. Instead of Ti<sub>3</sub>Al,  $\alpha\text{Ti}$  is stable in that composition range at 1200 °C and its solubility for Si at that temperature is limited to about 0.5 at% (Fig. 1). Additionally, as TiAl<sub>2</sub> had not been

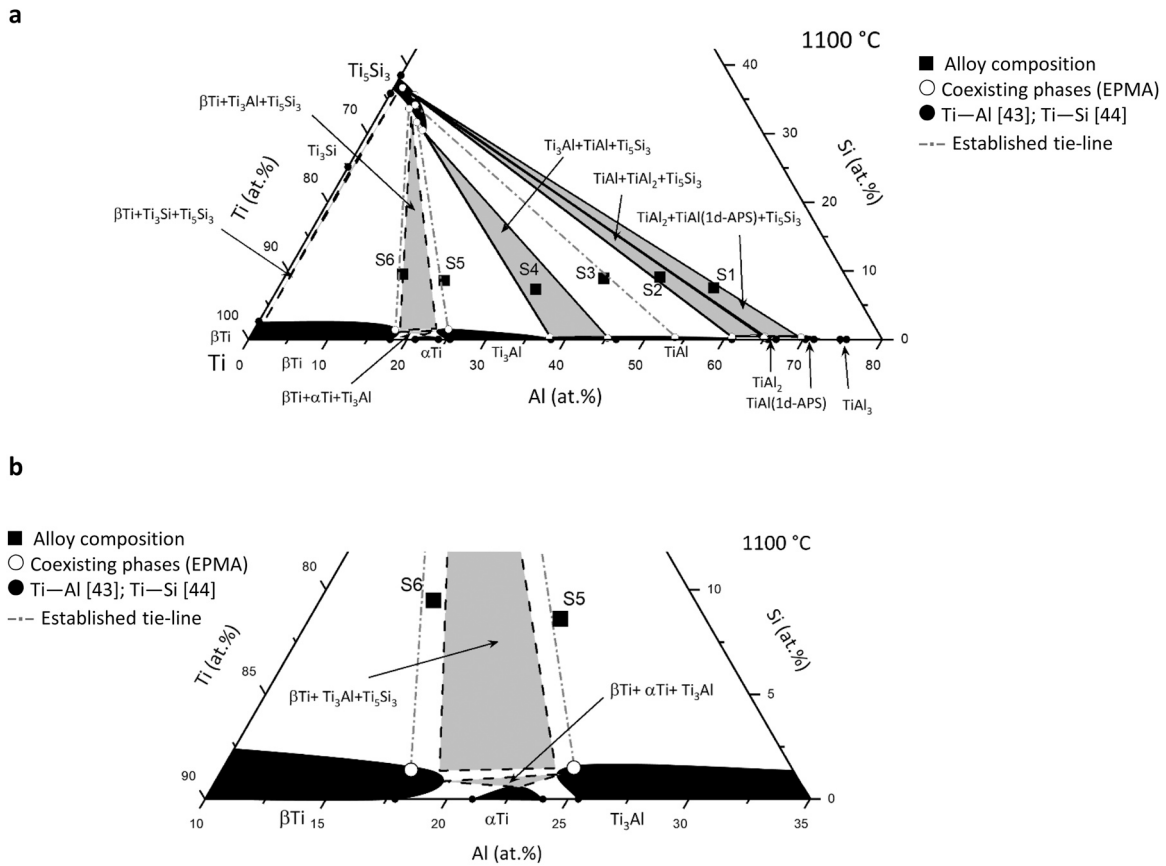
considered, phase equilibria in the more Al-rich part differ in [17] from present work (Fig. 2).

### 3.2. The partial isothermal section at 1100 °C

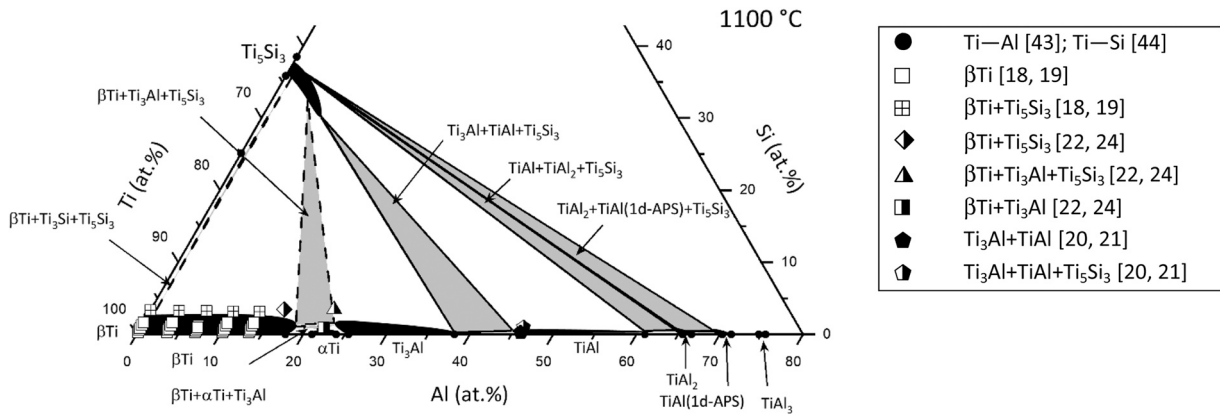
The partial isothermal section at 1100 °C is shown in Fig. 3a. At this temperature, alloys S1, S2, and S4 show three-phase equilibria (Table 3). Compared to the isothermal section at 1200 °C, Ti<sub>3</sub>Al is



**Fig. 2.** Partial Ti–Al–Si isothermal section at 1200 °C in comparison to experimental results from literature.



**Fig. 3.** a- Partial Ti-Al-Si isothermal section at 1100 °C. b- Enlarged part of the 1100 °C isotherm showing phase equilibria with  $\alpha$ Ti.



**Fig. 4.** Partial Ti—Al—Si isothermal section at 1100 °C with additional experimental results from literature.

present at 1100 °C and is in equilibrium with  $Ti_5Si_3$ , like  $\beta$ Ti, TiAl, and  $TiAl_2$ . No equilibrium between  $\alpha$ Ti and  $Ti_5Si_3$  is observed, in agreement with the DTA results, which show that  $\alpha$ Ti +  $Ti_5Si_3$  does not exist between 1095 and 1152 °C (see below). This finding is in agreement with Azevedo & Flower [22,24], who observed the three-phase equilibrium  $\beta$ Ti +  $Ti_3$ Al +  $Ti_5Si_3$  at 1100 °C. It may look strange, that the phase equilibrium  $\alpha$ Ti +  $Ti_5Si_3$  is observed at higher and lower temperatures, but not at 1100 °C. However, that at 1100 °C the equilibrium  $\alpha$ Ti +  $\beta$ Ti +  $Ti_3$ Al is observed instead (Fig. 3b) is in full agreement with the binary Ti—Al system, where no continuous phase field of  $\alpha$ Ti up to the melt exists. At 1100 °C previous data concentrated on the Ti corner [18–22,24] and Fig. 4 shows that these are in good agreement with the present ones.

### 3.3. The partial isothermal section at 1000 °C

For the determination of the phase equilibria at 1000 °C samples had initially been heat treated only for 100 h. This duration showed to be too short to reach equilibrium and therefore all alloys were annealed for 1000 h, from which the partial isothermal section in Fig. 5 was established. Microstructures and XRD analyses of the alloys heat-treated at 1000 °C/1000 h are shown in Figs. 6, 7. In alloys S1-S4 (Fig. 6) large, idiomorphic grains of  $Ti_5Si_3$  are observed. These are primary precipitates, which formed in the melt (Fig. 6b). As described above, no EPMA was performed on these primary grains, because they are still not in equilibrium after annealing for 1000 h, and hence measurements were only performed on small, spherical

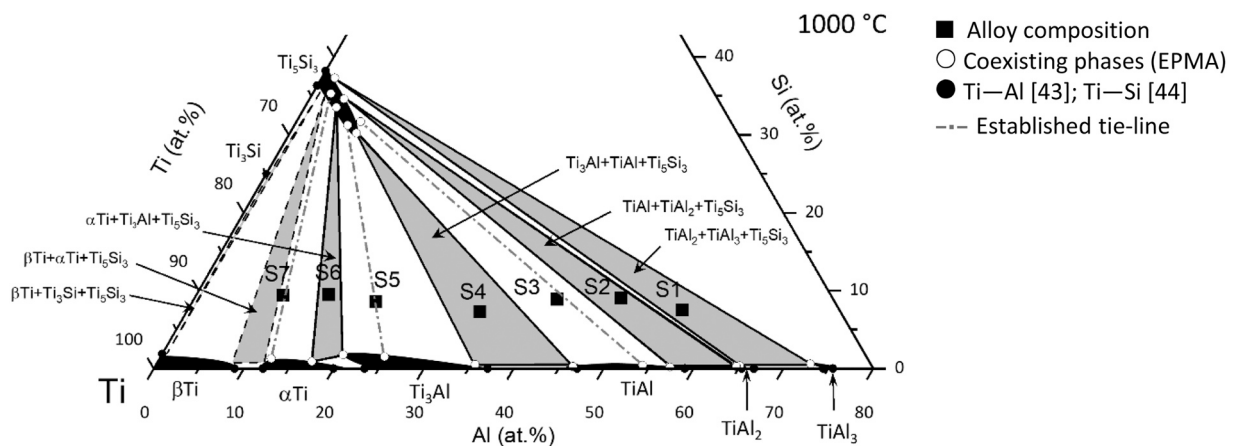


Fig. 5. Partial Ti–Al–Si isothermal section at 1000 °C.

Ti<sub>5</sub>Si<sub>3</sub> grains which are present in the alloys besides the large idiomorphic grains (Fig. 6b).

The partial isothermal section in Fig. 5 agrees qualitatively with the one determined by Liu et al. [27]. However, phase equilibria among the phases Ti<sub>5</sub>Si<sub>3</sub>, βTi, αTi, Ti<sub>3</sub>Al, and TiAl were not determined in [27] and were therefore shown by dashed lines. Liu et al. [27] reported a solid solubility of Al of 11 at% in Ti<sub>5</sub>Si<sub>3</sub>, which is only about 7 at% according to the present investigation. Additionally, the shape of the Ti<sub>5</sub>Si<sub>3</sub> single-phase field in [27] is different in that it stretches along a constant Ti:Si ratio, while the one shown in Fig. 5 is more inclined towards the Ti–Al side, indicating a more pronounced substitution of Si by Al than assumed in [27]. That the present finding is more likely is corroborated by the fact that the measured Al content in Ti<sub>5</sub>Si<sub>3</sub> at the three-phase equilibrium Ti<sub>5</sub>Si<sub>3</sub> + TiAl<sub>2</sub> + TiAl<sub>3</sub> was 2.5–3.9 at% in [27] (1.5 at% Al determined in here), while, due to the shape of their single-phase field, it is shown at 10 at% Al in their isothermal section.

The isothermal section established from diffusion couples by Gupta [26] differs considerably from the established partial isothermal section in Fig. 5. Gupta [26] found αTi, Ti<sub>3</sub>Al and TiAl in equilibrium with Ti<sub>3</sub>Si. There have been two other investigations of the Ti–Al–Si system at 1000 °C, both focussing on the Ti corner. As in the present investigation, they also found αTi, Ti<sub>3</sub>Al and TiAl in equilibrium with Ti<sub>5</sub>Si<sub>3</sub> instead of Ti<sub>3</sub>Si (Fig. 5) [15,16,22,24]. Additionally, Gupta observed Ti<sub>9</sub>Al<sub>23</sub>, which is no binary Ti–Al phase [39]. According to compositions reported in [26,60] it seems that this “phase” lies within the extended solid solubility range of Ti(Al,Si)<sub>3</sub>.

### 3.4. Partial isothermal sections at 900 °C and 800 °C

The partial isothermal sections at 900 °C (Fig. 8) and 800 °C (Fig. 10) show the same phase equilibria as at 1000 °C. Alloys S1, S2, S4, and S6 all lie within different three-phase fields from which the tie-triangles were determined. It is noted that in S1 annealed at 900 °C TiAl<sub>3</sub> was observed by EPMA and identified by XRD (Table 4), but that all particles were too small for quantitative EPMA.

For 900 °C phase equilibria are in qualitative agreement with previous investigations of the Ti corner at this temperature [15,16,22,24]. In the Ti/Al–Si diffusion couple analysed by Gupta at 900 °C, no Ti<sub>3</sub>Si was observed, while Ti<sub>9</sub>Al<sub>23</sub> was detected again [26]. More recently, complete isothermal sections were calculated for the temperature range 450–900 °C [31,61]. In Fig. 9 the calculated isothermal section for 900 °C by Li et al. [31] is compared to the present one. Calculated and experimentally determined phase equilibria are in qualitative agreement. As the calculation is based on a different description of the binary Ti–Al system and as except for βTi no solid solubility ranges for the third component, specifically not for Al in

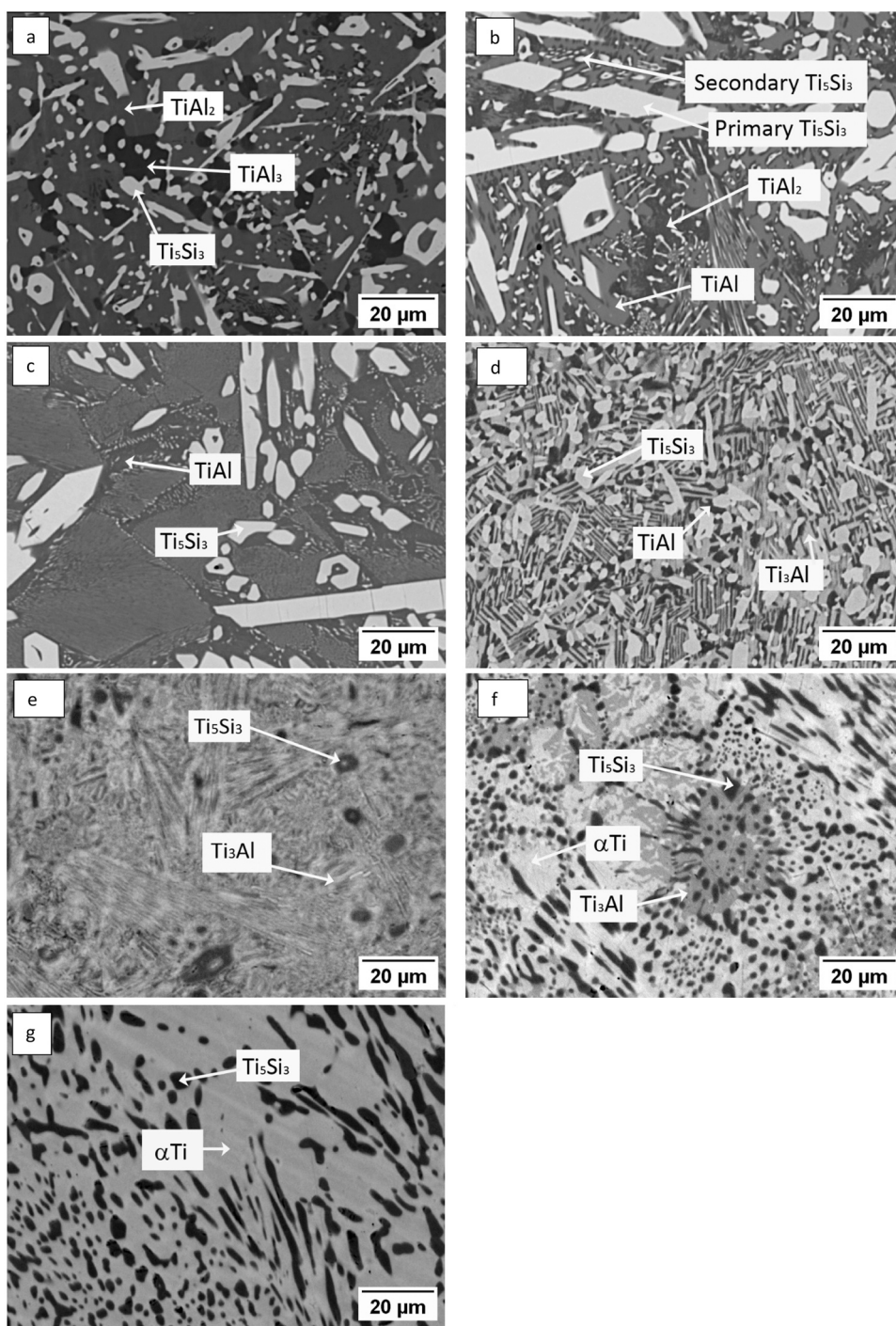
Ti<sub>5</sub>Si<sub>3</sub>, have been calculated, calculated and experimental determined phase equilibria are somewhat shifted against each other (Fig. 9). The most prominent difference is the extent of αTi + βTi + Ti<sub>3</sub>Si, which has not been determined in the present investigation, but which should be positioned much nearer to the Ti–Si side than shown in the calculation according to [19], who studied the respective composition range at 900 °C in much detail.

At 800 °C Ti<sub>3</sub>Si was again observed in a diffusion couple and therefore the existence of a three-phase field TiAl + Ti<sub>3</sub>Al + Ti<sub>3</sub>Si had been proposed [26]. According to the present investigation (Fig. 10), phase equilibria with Ti<sub>5</sub>Si<sub>3</sub> are observed instead. This is in accordance with the investigation of the Ti corner at 800 °C [15,16] where also αTi + Ti<sub>5</sub>Si<sub>3</sub> was observed, which rules out any phase equilibria of Ti<sub>3</sub>Si with more Al rich phases.

### 3.5. DTA analyses

DTA was performed on all alloys in the as-cast condition and, where results have been ambiguous, additionally on samples equilibrated at 900 °C. Table 5 summarizes observed temperatures, allocation to certain reactions, and references for invariant reactions. Temperatures given in Table 5 are evaluated from the first heating if not noted otherwise, but those, for which error limits are given, have also been observed in second heating and/or cooling cycles.

S1 showed melting at 1386 °C, in excellent agreement with 1391 °C [27] and 1380–1390 °C [15] observed for alloys of comparable composition. The temperature has been attributed to the invariant reaction  $L + \text{TiAl} \leftrightarrow \text{TiAl}_3 + \text{Ti}_5\text{Si}_3$  (U<sub>3</sub> in [27]). The strong signal at about 1100 °C is attributed to the reaction  $\text{TiAl} (1\text{d-APS}) + \text{Ti}_5\text{Si}_3 \leftrightarrow \text{TiAl}_2 + \text{TiAl}_3 + \text{Ti}_5\text{Si}_3$ . That the signal observed in the DTA is always stronger on cooling is in line that it stems from the eutectoid decomposition of TiAl (1d-APS). This reaction is listed in the reaction scheme in [15] as “U<sub>12</sub>”. No temperature for “U<sub>12</sub>” had yet been determined, but as indicated in [15], the temperature should be higher than 977 °C as in the binary system [43], presumably because TiAl<sub>3</sub> is the only binary Ti–Al phase which shows a substantial solid solubility for Si [17,27]. The present investigation now shows that indeed the temperature is about 120 K higher than in the binary system. The signal observed in S1 on heating of the equilibrated sample at about 1194 °C is associated with the transition from the three-phase field TiAl (1d-APS) + TiAl<sub>2</sub> + Ti<sub>5</sub>Si<sub>3</sub> to the two-phase field TiAl (1d-APS) + Ti<sub>5</sub>Si<sub>3</sub>, as the annealed sample consisted mainly out of TiAl<sub>2</sub>, in agreement with Fig. 8. The temperature is also in good agreement with the dissolution temperature of TiAl<sub>2</sub> in the binary system (1215 °C [43]), which should not be much lower in the ternary system, as the solid solubility for Si in TiAl<sub>2</sub> is very limited



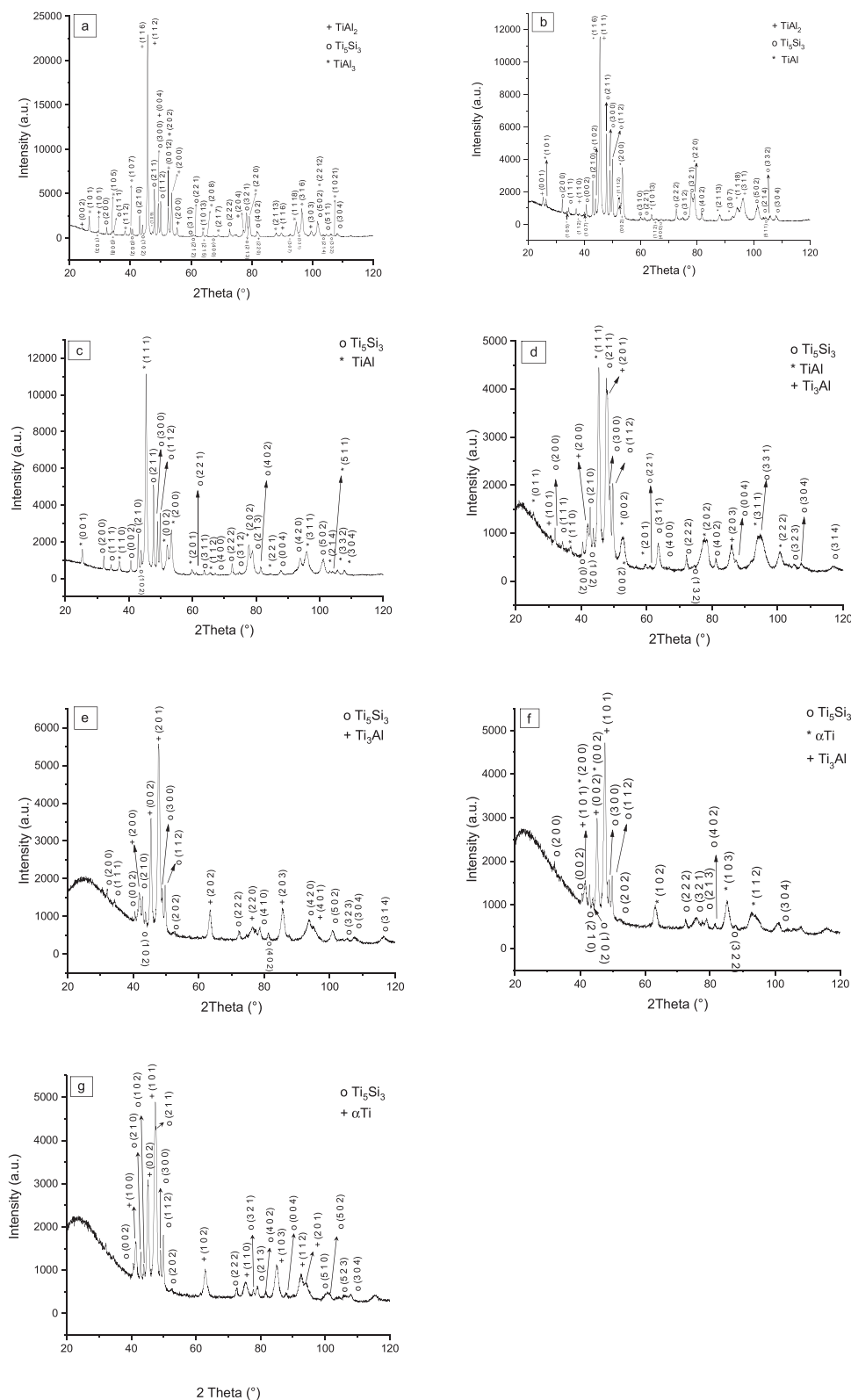
**Fig. 6.** Microstructures of the alloys a) S1; Ti-55Al-7.5Si (at%), b) S2; Ti-47.4Al-9.1Si, c) S3; Ti-40.4Al-8.9Si, d) S4; Ti-32.7Al-7.1Si, e) S5; Ti-20.4Al-8.6Si, f) S6; Ti-14.7Al-9.5Si, g) S7; Ti-9.7Al-9.6Si heat-treated 1000 °C/1000 h.

and actually 1216 °C have been observed for the stoichiometric ternary composition [32].

For S2 no signals were recorded during first heating (Table 5). A weak signal observed at 1143 °C during the second heating could indicate transition from  $\text{TiAl} + \text{TiAl}_2 + \text{Ti}_5\text{Si}_3$  to  $\text{TiAl} + \text{Ti}_5\text{Si}_3$ . No signals were observed for S3 up to 1400 °C. In S4 the eutectoid reaction  $\alpha\text{Ti} + \text{Ti}_5\text{Si}_3 \leftrightarrow \text{Ti}_3\text{Al} + \text{TiAl} + \text{Ti}_5\text{Si}_3$  is observed at 1110 °C, which is in excellent agreement with 1100 °C [27] and 1107 °C [15]. The two signals at 1325 °C and 1295 °C should be associated with the transition from  $\beta\text{Ti} + \text{Ti}_5\text{Si}_3$  to  $\alpha\text{Ti} + \text{Ti}_5\text{Si}_3$  on cooling.

In S5, the peritectoid formation of  $\text{Ti}_3\text{Al}$  on cooling is observed at 1152 °C, which was observed at 1158 °C in [27]. A signal observed at 1170 °C in an alloy of nearly the same composition may stem from the same reaction [27]. The signal in S6 at about 1095 °C is associated with the peritectoid formation of  $\alpha\text{Ti}$  and a signal observed at 1090 °C in [27] in an alloy of nearly identical composition should be related to the same reaction. The signals in S7 at about 1080 °C and about 1030 °C are associated with crossing the  $\alpha\text{Ti} + \beta\text{Ti}$  two-phase field, i.e. the formation of  $\alpha\text{Ti}$  and the dissolution of  $\beta\text{Ti}$  on cooling, respectively.





**Fig. 7.** XRD analyses of a) S1; Ti-55Al-7.5Si, b) S2; Ti-47.4Al-9.1Si, c) S3; Ti-40.4Al-8.9Si, d) S4; Ti-32.7Al-7.1Si, e) S5; Ti-20.4Al-8.6Si, f) S6; Ti-14.7Al-9.5Si, g) S7; Ti-9.7Al-9.6Si heat-treated 1000 °C/1000 h.

### 3.6. Vertical section at 9 at% Si

In order to check the consistency of the determined phase equilibria, a partial vertical section (Fig. 11) has been established from the intersections of the phase boundaries at 9 at% Si in Figs. 1, 3,

5, 8, 10 and the DTA results. It is noted that the actual Si content in the alloys deviates slightly from 9 at% Si (Table 1). Hence, some phase boundaries shown in Fig. 11 do not exactly match the temperatures determined by DTA (Table 5). Results from [15,16,27,62] for alloys with about 8 – 10 at% Si have been added for comparison and

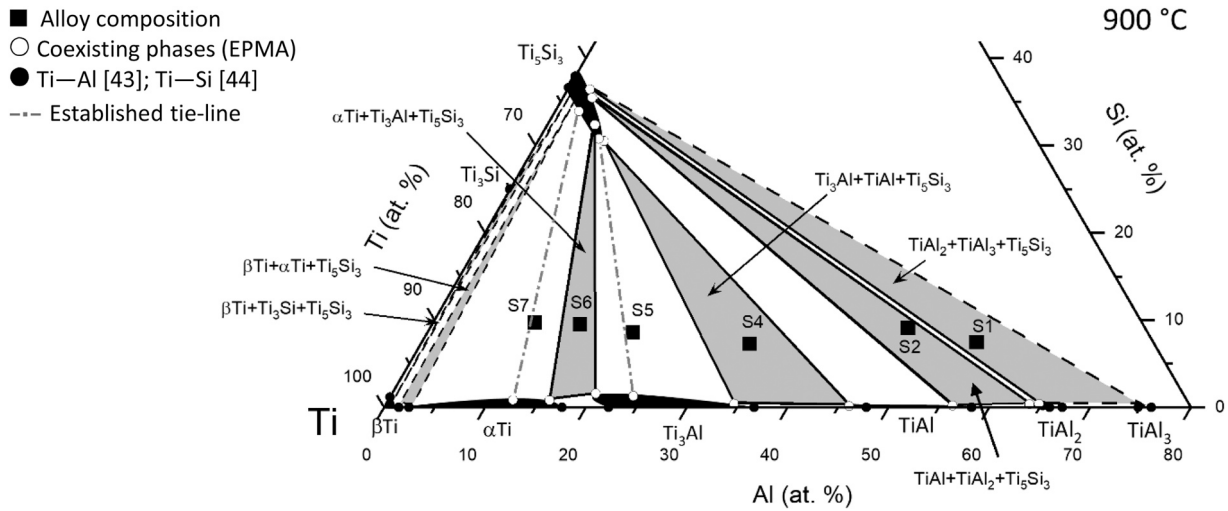


Fig. 8. Partial Ti–Al–Si isothermal section at 900 °C.

also to show continuation of phase boundaries up to the liquidus. As in the isothermal sections possible phase equilibria with  $Ti_3Si$  are indicated by dashed lines in Fig. 11.

Comparison of the vertical section and the actual phase content shows that only for one out of thirty-three samples there seems to be a discrepancy. According to Fig. 11, S4 should contain a minor amount of TiAl at 1200 °C, which could not be detected by EPMA or XRD. However, the composition of S4 is close to the  $\alpha Ti + Ti_5Si_3/\alpha Ti + TiAl + Ti_5Si_3$  phase boundary and as S4 is the alloy with the lowest Si content (7.1 at., Table 1), the shift with respect to the vertical section at 9 at% Si should account for this discrepancy.

The outline of the vertical section resembles that of the binary Ti–Al system. The same invariant reactions are observed except that  $Ti_5Si_3$  is additionally present in the ternary system. In Table 6 the determined temperatures of the invariant reactions are compared to those of the binary system. The peritectoid formation of  $Ti_3Al$  and of  $\alpha Ti$  occur at substantially lower temperatures than in the binary system, the eutectoid decomposition of TiAl (1d-APS) takes place at a much higher temperature in the ternary system, while the temperature of the eutectoid decomposition of  $\alpha Ti$  is little affected by the addition of Si.

Results from literature [15,16,27,47,62] have been added to the vertical section. It is noted that data taken from literature also do not always lie exactly on this vertical section, as many of the

investigated alloys contained 10 at% Si. However, nearly all of the results for equilibrated samples [15,16] are in agreement with the phase boundaries shown in Fig. 11.

Bulanova et al. [16] presented a partial vertical section at 10 at% Si for Al contents between 10 and 40 at%, which differs in two points from the present one. Besides showing phase equilibria with  $Ti_3Si$ , though this phase was not detected in any of their samples, they show a continuous phase field for  $\alpha Ti + Ti_5Si_3$ . Obviously, the continuous phase field was assumed in agreement with the shape of the  $\alpha Ti$  phase field in the then-accepted Ti–Al binary system. However, in order to fit with their DTA results, they had to draw S-shaped phase boundaries, which is thermodynamically improbable. The DTA results from [16] would fit with the vertical section shown in Fig. 9, however assuming different phase transitions in some of the alloys.

Data from [15,27,47] were used in Fig. 11 to show how phase boundaries may continue up to the liquidus. 1570 °C for the temperature of the invariant reaction  $L (+ Ti_5Si_3) \leftrightarrow \beta Ti (+ Ti_5Si_3)$  and 18 at% Al for the composition of L for the intersection of the eutectic line at 9 at% Si were adopted from [16]. This composition matches quite well with that calculated for a partial liquidus line (21 at% Al) [47] but is somewhat higher than 15 at% Al found in [27].

It is noted that phase boundaries extrapolated to lower temperatures are in good agreement with the isothermal section from Li et al. [30] at 700 °C.

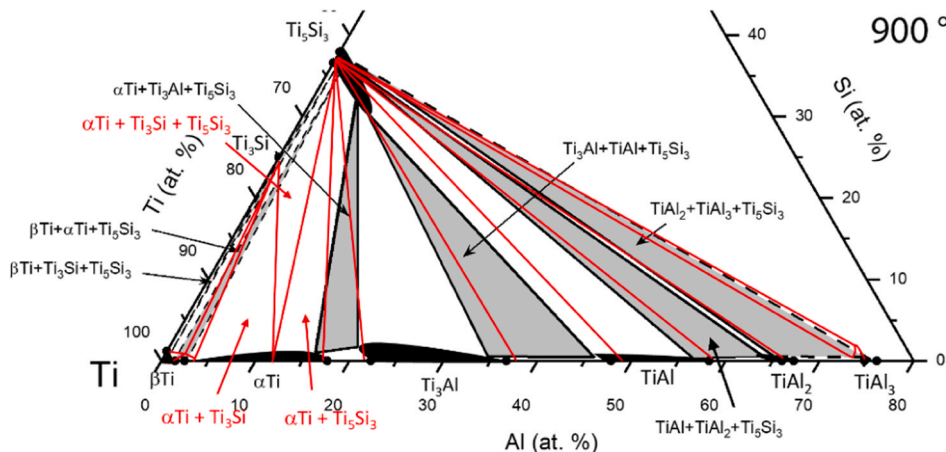
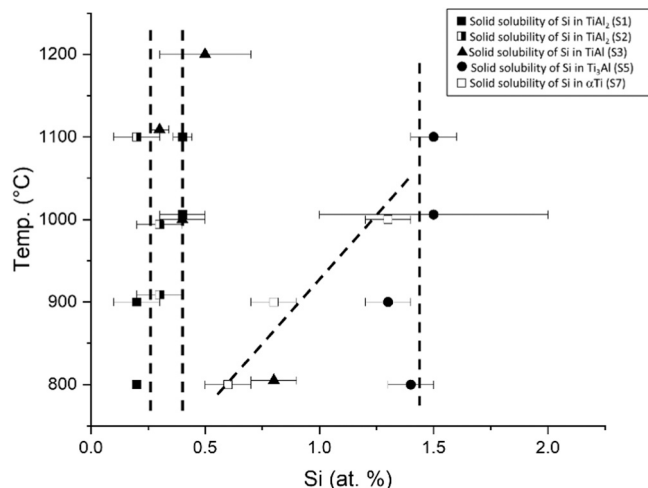


Fig. 9. Partial Ti–Al–Si isothermal section at 900 °C compared to the calculated one (in red) from [31].



**Table 6**  
Temperatures of invariant reactions in Ti–Al–Si compared to those in binary Ti–Al [39,43].

Reaction	Ti–Al–Si	Ti–Al [39,43]
$\beta\text{Ti} + \alpha\text{Ti} (+ \text{Ti}_5\text{Si}_3) \leftrightarrow \text{Ti}_3\text{Al} (+ \text{Ti}_5\text{Si}_3)$	1152 °C	1200 °C
$\alpha\text{Ti} (+ \text{Ti}_5\text{Si}_3) \leftrightarrow \text{Ti}_3\text{Al} + \text{TiAl} (+ \text{Ti}_5\text{Si}_3)$	1110 °C	1120 °C
$\text{TiAl}(\text{1d-APS}) (+ \text{Ti}_5\text{Si}_3) \leftrightarrow \text{TiAl}_2 + \text{TiAl}_3 (+ \text{Ti}_5\text{Si}_3)$	1100 °C	977 °C
$\beta\text{Ti} + \text{Ti}_3\text{Al} (+ \text{Ti}_5\text{Si}_3) \leftrightarrow \alpha\text{Ti} (+ \text{Ti}_5\text{Si}_3)$	1095 °C	1170 °C



**Fig. 12.** The solid solubility of Si in  $\alpha\text{Ti}$ ,  $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}$ , and  $\text{TiAl}_2$  in dependence on temperature in alloys S7, S5, S3, S2 and S1 respectively.

determined for  $\text{TiAl}$  in alloys S2 and S4. From the shape of the single-phase field in Figs. 1, 3, 5, 8, 10 it is evident that 0.5 at% Si should also correspond to the maximum solid solubility of Si in  $\text{TiAl}$ . This value agrees with data measured for  $\text{TiAl}$  in as-cast alloys [16] and in a directionally solidified alloy [63], but is considerably lower than found in most previous studies, where 1–4 at% Si at 550 °C [32], 0.8 at% Si at 700 °C [30], 2–3 at% Si at 700 °C [28] and at 1000 °C [27], 1 at% Si at 1200 °C [17], and 1–1.5 at% Si in diffusion couples annealed between 700 and 1000 °C [26] were reported. On the other hand, no Si was detected by TEM-EDS in  $\text{TiAl}$  in a two-phase  $\text{TiAl} + \text{Ti}_5\text{Si}_3$  alloy annealed at 1200 °C [59,64].

Data for S1 and S2 show that the solid solubility for Si in  $\text{TiAl}_2$  is only about 0.3 at%, independent of temperature. This value is much

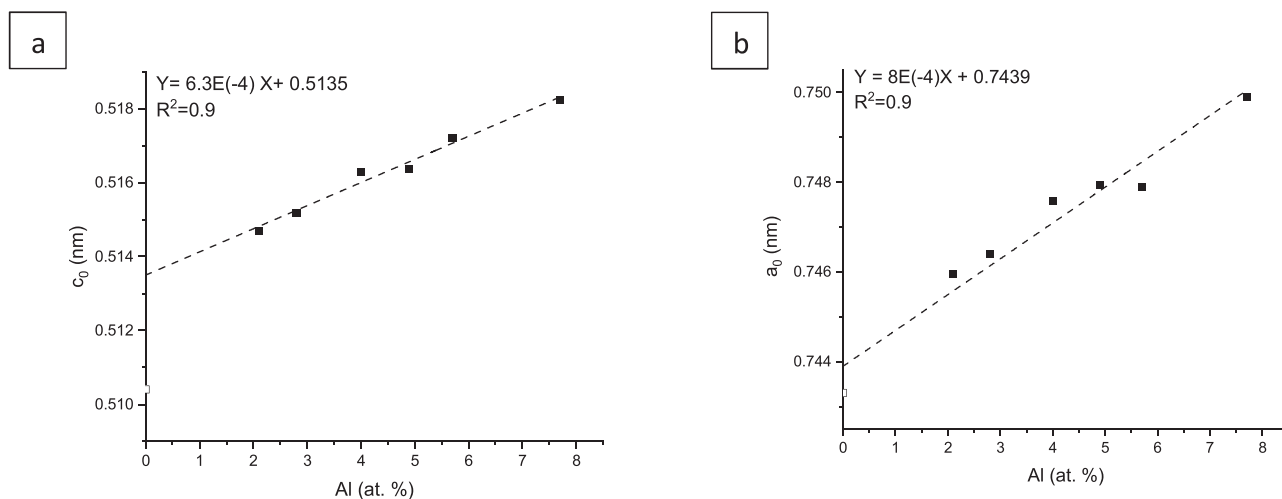
smaller than any of those measured before, i.e. 1.4 at% Si at 550 °C [32], 1.5 at 700 °C [30], 1.8 at% Si at 900 °C [26], and 0.7 at% Si at 1000 °C [27].  $\text{TiAl}_3$  is the only binary Ti–Al phase with a marked solid solubility for Si, which exceeds 10 at% in equilibrium with  $\text{TiSi}_2$  [15,17,25–27,30,62]. As no adequate alloy compositions have been studied, no additional information can be gained from the current investigation.

### 3.8. Solid solubility of Al in $\text{Ti}_5\text{Si}_3$

As detailed above, establishing the actual Al content of  $\text{Ti}_5\text{Si}_3$  is difficult because it is not possible to equilibrate large, primary  $\text{Ti}_5\text{Si}_3$  grains within reasonable annealing times. The established partial isothermal sections show that the maximum solid solubility for Al is always attained at the three-phase equilibrium  $\text{Ti}_5\text{Si}_3 + \alpha\text{Ti}$  or  $\text{Ti}_3\text{Al} + \text{TiAl}$  (Figs. 1, 3, 5, 8 & 10), which is observed in alloy S4. The data for S4 in Table 3 show a solid solubility of about 7 at% Al in  $\text{Ti}_5\text{Si}_3$  at all investigated temperatures. Though there is some scatter in the data, the solid solubility for Al does only little, if at all, change with temperature. The maximum solid solubility of about 7 at% Al corresponds to the value reported by Manesh & Flower [47] for “fine silicides” extracted from the eutectic in an as-cast alloy. A similar value for the maximum solid solubility has also been reported in the 1200 °C isotherm by Schob et al. [17], however for the equilibrium  $\beta\text{Ti} + \text{Ti}_3\text{Al}$  (“ $\text{Ti}_{3-2}\text{Al}$ ”) +  $\text{Ti}_5\text{Si}_3$ . Otherwise, mostly higher values have been measured, e.g., 10.9 at% Al for an alloy equilibrated at 1000 °C [27], 15–20 at% Al in samples prepared by self-propagating high-temperature synthesis (SHS) [35] or by ball milling [34,36]. However, for the latter case it has been shown that such high Al contents indicate metastable compositions of  $\text{Ti}_5\text{Si}_3$  [36]. Higher solid solubilities of either 9.2 [64] or 13.4 at% Al [59] measured by TEM-EDS in  $\text{Ti}_5\text{Si}_3$  after annealing for 12 h at 1200 °C are possibly due to a too short annealing time.

Significantly lower values for the maximum solid solubility of Al in  $\text{Ti}_5\text{Si}_3$  were shown in the 1000 °C isotherm by Gupta [26] (3 at% Al) and in the 700 °C isotherm by Raman & Schubert [28] (5 at% Al). In both cases the maximum solid solubility is shown for phase equilibria with  $\text{TiAl}_3$ . According to the partial isothermal sections shown in Figs. 1, 3, 5, 8, 10, such low Al contents are reasonable for  $\text{Ti}_5\text{Si}_3$  in equilibrium with  $\text{TiAl}_3$ , but do not correspond to the maximum solid solubility for Al, which is attained for  $\text{Ti}_5\text{Si}_3 + \text{Ti}_3\text{Al} + \text{TiAl}$  at these temperatures according to the present partial isothermal sections.

Zhang & Flower [65] showed that Al substantially increases the lattice constants of  $\text{Ti}_5\text{Si}_3$ , which was confirmed in [34,35], while



**Fig. 13.** a,b) Lattice constants of  $\text{Ti}_5\text{Si}_3$  in relation to Al content; samples have been quenched from 1200 °C. Filled symbols are from current work, and open symbols are lattice constants of  $\text{Ti}_5\text{Si}_3$  from binary Ti–Si [54].

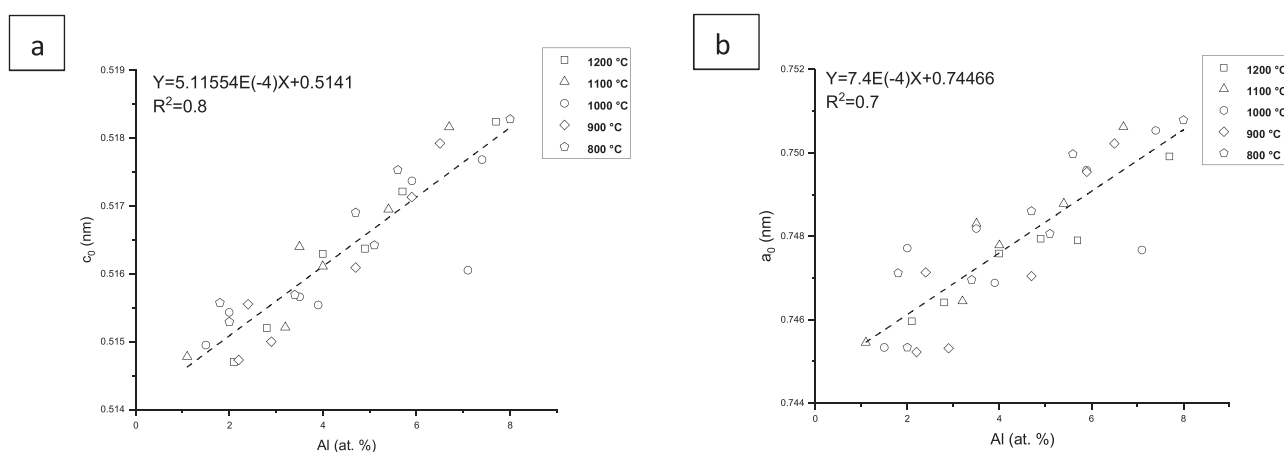


Fig. 14. a, b) Lattice constants of  $\text{Ti}_5\text{Si}_3$  in relation to Al content; samples have been quenched from 800° to 1200°C.

according to Zha et al. [35] the addition of Al has almost no effect on the lattice constants of  $\text{Ti}_5\text{Si}_3$  and Bulanova et al. [16] showed a graph, where  $a_0$  of  $\text{Ti}_5\text{Si}_3$  first decreases, then increases and then decreases again with increasing Al content. To solve this conflicting evidence, lattice constants measured in samples annealed at 1200 °C are plotted in Fig. 13 and all lattice constants are shown in Fig. 14. Both figures show a steady increase of the lattice constants with increasing Al content. For samples annealed at 1200 °C the increase is even linear (Fig. 13), while for other temperatures there is more scatter of the data (Fig. 14). Comparing the data for different temperatures in Fig. 14, there is no evident dependence between annealing temperature and lattice constants. It is noted that, though lattice constants of  $\text{Ti}_5\text{Si}_3$  show a strong dependence on Al content, they will also vary in dependence on Si content. However, data for  $\text{Ti}_5\text{Si}_3$  in S3 heat-treated at 1000 °C show the largest deviation in Fig. 14, which suggests that  $\text{Ti}_5\text{Si}_3$  should actually have a lower Al content than the measured value in Table 3. A lower Al content would indeed fit much better to those Al contents measured for  $\text{Ti}_5\text{Si}_3$  in S3 at all other temperatures.

The discrepancy in previous data is explained in that in [16,34,35] lattice constants were shown in dependence on the overall composition of the alloys and not on the actual Al content of  $\text{Ti}_5\text{Si}_3$ . The present results are therefore consistent with results by Kasraee et al. [34], who observed an increase of the lattice constants in “stoichiometric alloys” when they contained up to 7.5 at% Al, while no further increase was observed for higher Al contents. All samples in Zha et al. [35] were actually located in the three-phase field  $\text{TiAl}_3 + \text{Ti}_5\text{Si}_3 + \text{Ti}_5\text{Si}_4$ . Therefore it can be expected that the composition of  $\text{Ti}_5\text{Si}_3$  is the same in all samples, hence, the lattice constants do not change with increasing Al content. Lattice constants in Bulanova et al. [16] were taken from alloys annealed at about 1300 °C, in which  $\text{Ti}_5\text{Si}_3$  is in equilibrium with different phases. It is presumably therefore that lattice constants show a “sinus curve behaviour” in dependence on the Al content.

#### 4. Conclusion

Knowledge of the precise solid solubilities of Al in  $\text{Ti}_5\text{Si}_3$  and Si in the Ti–Al phases is a prerequisite for tailoring the microstructures and thereby the mechanical properties of TiAl-based alloys. From SEM, EPMA, XRD, TEM and DTA investigations, five partial isothermal sections between 800 and 1200 °C have been established.

No ternary phase was found and  $\text{Ti}_3\text{Si}$  was not detected in any of the alloys. The solid solubilities of Al in  $\text{Ti}_5\text{Si}_3$  and Si in TiAl,  $\text{TiAl}_2$  and  $\text{Ti}_3\text{Al}$  do not change in dependence on temperature. Lattice constants of  $\text{Ti}_5\text{Si}_3$  for all heat-treated samples were calculated and results show that both lattice constants increase with increasing Al content.

The partial vertical section of Si 9 at% shows that all established data are consistent. These data can now be employed to set up the next generation of advanced CALPHAD databases for the development of TiAl-based alloys with improved properties.

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#### CRediT authorship contribution statement

**Zahra Kahrobaee:** Data curation, Investigation, Formal analysis, Writing – original draft, Visualization, **Martin Palm:** Conceptualization, Validation, Writing – review and editing, Supervision, Project administration and funding acquisition.

#### Data availability

No data was used for the research described in the article.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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