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Phase Equilibria in the α-Ti-Al-Si Region of the Ti-Si-Al System

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An experimental investigation of the phase relations in the titanium (Ti)-aluminum (Al)-silicon (Si) system was undertaken by differential thermal analysis, x-ray diffraction, metallography, and microprobe analysis. The present measurements when combined with those from an earlier investigation at this laboratory provide data for 56 alloy compositions in the Ti-Al-Si system. The combined results allowed the construction of a solidus projection, a melting diagram including both solidus and liquidus, partial isothermal sections at 1270 °C and 1250 °C, three isopleths with a constant percentage of one or another component, and a reaction scheme.

1. Introduction

Industrial interest in multicomponent high-temperature alloys was the motivation for undertaking the present investigation of the phase relations in the titanium (Ti)-silicon (Si)-aluminum (Al) ternary system. Al increases the $\alpha \leftrightarrow \beta$ transformation temperature of Ti. Si improves high-temperature properties (i.e., strength, creep, and corrosion resistance) of both Ti alloys and Ti-Al alloys. Therefore, knowledge of the phase diagram of this ternary system is useful.

Despite the fact that the Ti-Si-Al system was studied in the past, the phase diagram in the whole concentration and temperature range has not previously been constructed. Most of the data available concern the Ti-corner of the system. Information on phase equilibria at other concentrations is scarce. In addition, the available data are often contradictory and do not correspond to the Ti-Al binary system that is accepted today.

A ternary compound (TC) in the vicinity of $TiSi_2$ with the structure of $ZrSi_2$ type has been reported by several previous investigations. In Nowotny and Huschka [1957Now] and Schob et al. [1962Sch] the $Ti(Si,Al)_2$ composition was ascribed to the phase. At 1250 °C, this phase was shown to correspond to the composition $TiSi_{1.7\text{-}1.4}Al_{0.3\text{-}0.6}$.

A TC was reported in Raman and Schubert [1965Ram] as Ti_2AlSi_3 (O phase). That report indicated that, after annealing at 1100 °C, an alloy 31Ti-50Si-19Al (in at.%) contained only the phase with the $ZrSi_2$ structure. In the as-cast state and after annealing at 700 °C, additional phases in the alloy were TiSi (FeB structure type) and Al, respectively. This shows that the O phase forms by peritectic reaction with participation of TiSi, and at 700 °C is in equilibrium with Al. At 16.5 at.% Al, compositions of $Ti(Al_xSi_{1-x})_2$ [1957Now, 1962Sch] and O phase [1965Ram] are identical. This implies that they are possibly the same phase resulting from an invariant equilibrium involving the phases L + TiSi + ~ + ($Ti(Al_xSi_{1-x})_2$ or O). According to Nowotny and Huschka [1957Now] and Schob et al. [1962Sch], the homogeneity region of the $Ti(Al_xSi_{1-x})_2$ phase is located along the isoconcentrate of Ti. However, other data [1965Ram] have indicated that the homogeneity range of the O phase follows an isoconcentrate of Si. In this respect, the data [1957Now, 1962Sch] seem to be preferable, because atomic size considerations favor the view that Al and Si atoms are more likely to substitute for each other than for Ti.

A suggestion was made by [1956Cot] that the high-temperature form of the $TiSi_2$ ($ZrSi_2$ type) is stabilized by Al additions. Then $Ti(Si,Al)_2$ might not be a TC, but a β-$TiSi_2$-based phase.

A $TiAlSi_2$ phase was reported by Kamei et al. [1968Kam] with the composition close to the above-mentioned compounds. According to Orynbekov et al. [1984Ory], this phase is in equilibrium with Al at 500 °C. The existence of all of the above phases was rejected by Zakharov et al. [1988Zak], and the compound $Ti_2Al_3Si_2$ has been proposed as having a homogeneity range within 26.3-29.7 at.% Si and 29.5-30.5 at.% Ti. One more TC U ($Ti_7Al_5Si_{12}$) was reported in Raman and Schubert [1965Ram] with the structure of $Zr_{1-}AlSi_{1+}$ [1963Sch]. All of the previous investigations show that the TC(s) coexist(s) with Si and/or Al. The existence of the $Ti_2Al_3Si_2$ compound [1988Zak] seems to be doubtful. As to the other phases, they probably form in a solid state. However, the question of the number of TCs, and of their compositions, crystal structures, and temperature stability is still open.

The Ti-Si-Al system is characterized by wide homogeneity regions of a few binary compounds. However, these homogeneity regions are not well-established, especially concerning Ti-Si-based compounds. Solidification of alloys along the Si-Al side of the ternary system was studied by Kamei et al. [1968Kam] and Zakharov et al. [1988Zak]. According to Kamei et al. [1968Kam], two invariant equilibria occur in this part of the system: peritectic L + $TiAl_3$ $\leftrightarrow$ $TiSi_2Al$ + Al; and eutectic L $\leftrightarrow$ $TiSi_2Al$ + Al + Si. The reaction temperatures were not given. Two peritectic equilibria were reported by [1988Zak]: L + $TiAl_3$ $\leftrightarrow$ $Ti_2Si_2Al_3$ + Al (579 °C, invariant point at 12.6 at.% Si and 0.11 at.%

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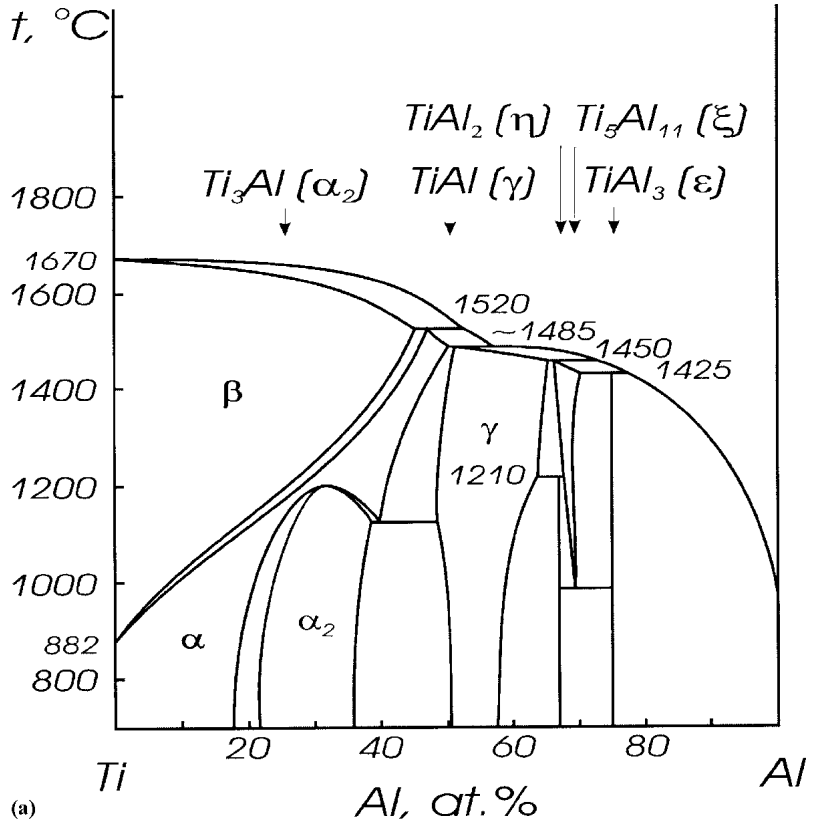


Fig. 1 The related binary systems: (**a**) Ti-Al [1996Tre]

Ti), and L + $Ti_2Si_2Al_3$ ↔ Al + Si. Results from Kamei et al. [1968Kam] and Zakharov et al. [1988Zak] show that the TC should melt congruently, which does not agree with to the information discussed above.

Available isothermal sections at 1200 °C [1962Sch], 700 °C [1965Ram], and 20 °C [1968Kam] seem to be doubtful, as they do not involve all the phases of the boundary binaries and show no equilibria with their participation. Besides, the homogeneity ranges of most of Ti-Al phases do not correspond to the accepted Ti-Al binary phase diagram.

Assessment of the information previous to 1993 on the Ti-Si-Al system is presented in Perrot [1993Per].

The goal of the present article is to present our experimental data on phase equilibria in the α-Ti-$TiAl_3$-TiSi region of the Ti-Si-Al system. During our experimental research, several alloys were studied to clarify the phase relations in the TiSi-$TiAl_3$-Al-Si region. The accepted Ti-Al and Ti-Si binaries are shown in the Fig. 1. The Ti-Al system (Fig. 1a) is from the assessment by Tretyachenko et al. [1996Tre]. The Ti-Si phase diagram (Fig. 1b) is from the thermodynamic evaluation of Seifert et al. [1996Sei], which is mainly based on the experimental data of Svechnikov et al. [1970Sve]. It was suggested in Zavodyanny et al. [1997Zav] that Ti_5Si_4 and TiSi silicides undergo polymorphous transformations at unknown temperatures above 800 °C. [1970Sve] observed the thermal effects at 1815 °C for the sample of Ti_5Si_4 composition, which might be either the temperature of allotropic transformation of HfO_2 (used as a crucible material), or the temperature of α ↔ β transformation of Ti_5Si_4. As to the TiSi compound, the question of polymorphism is still unclear.

2. Experimental Procedure

The purity of starting materials was identified to be as follows: Ti 99.85%; Si 99.999%; and Al 99.995%. The alloys were melted in an arc-melting furnace with a nonconsumable tungsten electrode on a water-cooled copper (Cu) hearth in an Ar atmosphere purified by the melting of Ti. The buttons were turned over and remelted three times to ensure homogeneity. The weight losses were no more than 1.0%, so a chemical analysis was not carried out. The weight of the buttons was about 10-15 g. The samples were placed into Mo containers and were then annealed at various temperatures in an Ar atmosphere purified with Zr chips.

The alloys were studied in as-cast and annealed states using DTA, x-ray diffraction, metallography, and EPMA examinations.

A DTA examination was performed under helium in a high-temperature DTA analyzer with a W/W-Re thermocouple and an Mo reference. The heating/cooling rate was ~30 °C/min. Al_2O_3 and Sc_2O_3 crucibles were used. The temperatures were taken from the heating curves, except in a few cases when they were taken at cooling. The accuracy of temperature measurements was estimated to be ±1%. Powder x-ray diffraction (XRD) was performed in Debye cameras (d = 57.3 mm) with CuKα-filtered radiation in an

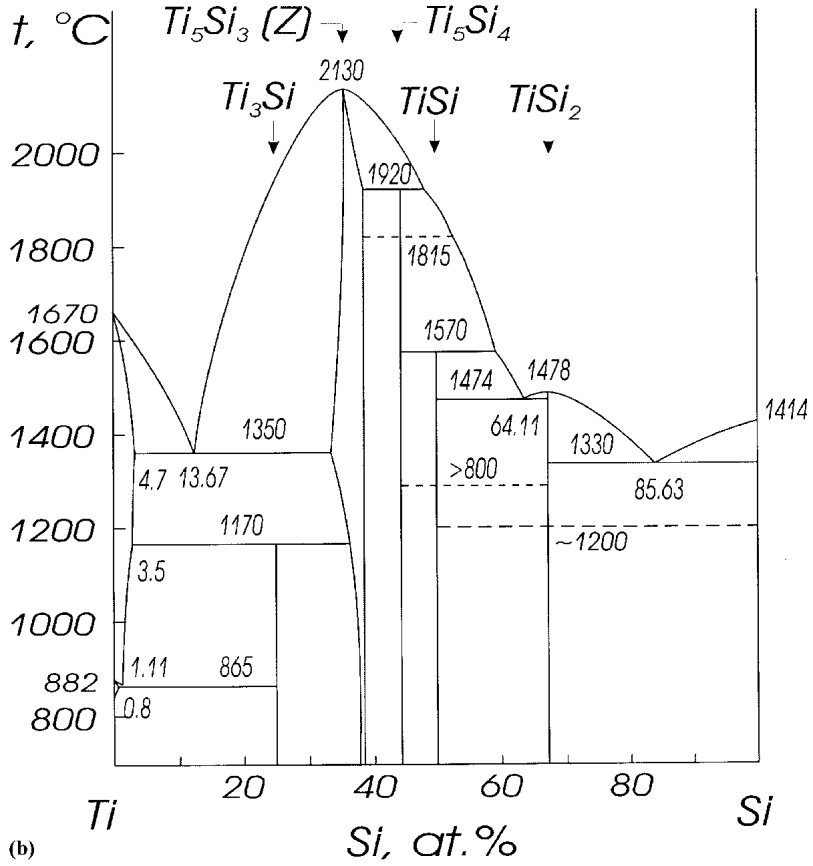


Fig. 1 cont. The related binary systems: (**b**) Ti-Si [1970Sve, 1996Sei, 1997Bul, 1997Zav]

URS-2.0 diffractometer (Nauchpribor, Orel, Russia) or with monochromatic CuKα- and CoKα-radiation in a DRON-UM diffractometer (Burevestnik, St. Petersburg, Russia). The lattice parameters were calculated by a least-squares method. The samples for the microstructure examination were polished with a water suspension of Cr_2O_3. A solution of HF:HNO_3:H_2O (1:2:3-5) was used for etching

EPMA was performed in a Superprobe-733 microanalyzer (JEOL, Japan). In the cases in which the grain size/beam spot ratio was greater than 10:1, the measured values were taken as the chemical compositions of corresponding phases. For small grains when the above ratio was not fulfilled, the experimental values were accepted as the chemical compositions of a mixture of coexisting phases. For two-phase samples, these values are always located in a tie-line passing through the alloy composition under examination. Thus, the direction of the tie-lines could be determined. In the cases in which the three-phase triangles are narrow with respect to one of the elements, this approach is useful in distinguishing different phase fields.

3. Results and Discussion

For convenience, the following designations are used: α and β for α-Ti-based and β-Ti-based solid solutions, respectively; α_2, γ, ξ, and ε for Ti_3Al, TiAl, Ti_5Al_{11} and $TiAl_3$-based phases, respectively; Z for a Ti_5Si_3-based phase; α5/4 and β5/4 for low-temperature and high-temperature modifications of Ti_5Si_4; α1/1 and β1/1 for low-temperature and high-temperature modifications of TiSi; and β1/2 for the high-temperature modification of $TiSi_2$. The β-Ti(Si,Al)$_2$ designation was used for TC or β1/2 phases in the cases when they could not be distinguished experimentally.

It should be noted in advance that we never observed the supposed high-temperature modification of the Ti_5Si_4 compound, nor the low-temperature allotropic forms of TiSi and $TiSi_2$. All of the x-ray patterns revealed Ti_5Si_4 with the Zr_5Si_4 structure type, corresponding to the low-temperature form. This possibly results from the fact that α ↔ β transformation of the compound occurs at high temperatures with the participation of the liquid, in analogy to the particular formation of the binary compound Ti_5Si_4 (Fig. 1b). For the TiSi and $TiSi_2$ compounds, only the high-temperature structures FeB and $ZrSi_2$, respectively, were observed. However, the appearance of the thermal effects at 940 °C and 860 °C for the alloy 33Ti-27Si-40Al allowed us to ascribe them to the α ↔ β transformation in TiSi. The observed $ZrSi_2$ structure might correspond either to the high-temperature form of the $TiSi_2$ compound or to the TC. We did not have enough results to distinguish the TC. Therefore, we opted to consider the formation of the TC from the liquid phase as the

Table 1 Phase Composition of the Ti-Si-Al Alloys

Sample Composition (at.%)	Heat Treatment	Phase Composition According to			
		X-ray	Metallography	EPMA	Totality of Data (a)
63Ti-5Si-32Al	As-cast	α_2 + Z	β* (b) + eutectic (β + Z)	…	β + Z
[1997Bul]	1300 °C, 40 h	α/α_2 + Z	…	…	(β + Z)/(α + β + Z)
	1300 °C, 40 h + 1150 °C, 40 h	α/α_2 + Z	…	…	α + α_2 + Z
60Ti-36Si-4Al	As-cast	Z + [ε] (c)	Z + RL (d)	…	Z + ε
56Ti-34Si-10Al	As-cast	Z + ε + α5/4	Z + RL	…	Z + ε + α5/4
	1300 °C, 33 h	…	…	…	Z + ε + α5/4
56Ti-38Si-6Al	As-cast	Z + α5/4 + [?]	Z + α5/4	Z + α5/4	Z + α5/4 + ε
[1997Bul]	1400 °C, 36 h	Z + α5/4	…	…	L + Z + α5/4
	1400 °C, 36 h + 1250 °C, 40 h	Z + α5/4 + [?]	…	…	Z + α5/4 + ε
	1250 °C, 40 h	Z + α5/4 + [?]	…	…	Z + α5/4 + ε
55Ti-5Si-40Al	As-cast	…	β* + [eutectic (β + Z)]	…	α + β + Z
[1997Bul]	1400 °C, 9 h	γ + Z	…	…	α + β + Z
	1300 °C, 40 h	[α_2] + γ + Z	…	…	α + γ + Z
	1300 °C, 40 h + 1150 °C, 33 h	γ + Z	…	…	α + γ + Z
	1300 °C, 40 h + 1150 °C, 33 h + 1090 °C, 45 h	[α_2] + γ + Z	…	…	α_2 + γ + Z
	1300 °C, 40 h + 1150 °C, 33 h + 1090 °C, 45 h + 1050 °C, 38 h	…	α_2 + γ + Z	…	α_2 + γ + Z
	1300 °C, 40 h + 1150 °C, 33 h + 1090 °C, 45 h + 1050 °C, 38 h + 950 °C, 36h	…	α_2 + γ + Z	…	α_2 + γ + Z
54Ti-2Si-44Al [1997Bul]	As-cast	…	β* + eutectic (β + Z)	…	α + β + Z
53Ti-3Si-44Al [1997Bul]	As-cast	γ + [Z]	β* + eutectic (β + Z)	…	α + β + Z
52Ti-4Si-44Al [1997Bul]	As-cast	γ + [Z]	β* + eutectic (β + Z)	…	α + Z
51Ti-5Si-44Al	As-cast	[α_2] + γ + Z	[Z] + eutectic (β + Z)	…	α + γ + Z
[1997Bul]	1400 °C, 9 h	γ + Z	…	…	α + γ + Z
	1300 °C, 38 h	γ + Z	…	…	α + γ + Z
	1300 °C, 38 h + 1250 °C, 37 h	γ + Z	…	…	α + γ + Z
50Ti-2Si-48Al	As-cast	γ + [Z]	β*	…	α + γ + Z
[1997Bul]	1400 °C, 9 h	γ + Z	…	…	α + γ + Z
	1300 °C, 35 h	…	…	…	α + γ + Z
50Ti-10Si-40Al	As-cast	[α_2] + γ + Z	Z + eutectic (γ + Z)	…	γ + Z
[1997Bul]	1300 °C, 38 h	γ + Z	…	…	γ + Z
50Ti-30Si-20Al	As-cast	…	Z + α5/4 + RL	…	Z + α5/4 + ε
	1300 °C, 33 h	…	…	…	Z + α5/4 + ε
50Ti-44Si-6Al	As-cast	…	Z + α5/4 + ε	ε + Z + α5/4	α5/4 + β1/1 + ε
	1400 °C, 36 h	Z + α5/4 + [?]	…	…	L + α5/4
	1400 °C, 36 h + 1090 °C, 45 h	Z + α5/4 + [?]	…	…	α5/4 + β1/1 + ε
	1090 °C, 45 h + 950 °C, 36 h	α5/4 + [?]	…	…	α5/4 + β1/1 + ε
49Ti-3Si-48Al	As-cast	[α_2] + γ + [Z]	α* (e) + eutectic (α + Z)	…	α + γ + Z
[1997Bul]	1300 °C, 35 h	…	…	…	α + γ + Z
48Ti-4Si-8Al [1997Bul]	As-cast	γ + Z	[Z] + [eutectic (α + Z)] + eutectic (α + γ + Z)	…	α + γ + Z
	1400 °C, 9 h	γ + Z	…	…	α + γ + Z
47Ti-5Si-48Al	As-cast	…	[Z] + eutectic (γ + Z)	…	γ + Z
[1997Bul]	1400 °C, 9 h	…	…	…	γ + Z
	1300 °C, 35 h	…	…	…	γ + Z
45Ti-4Si-51Al	As-cast	γ + Z	γ + eutectic (γ + Z)	…	γ + Z
[1997Bul]	1300 °C, 35 h	…	γ + Z	…	γ + Z
44Ti-2Si-54Al	As-cast	γ + Z	γ + eutectic (γ + Z)	…	γ + Z
[1997Bul]	1270 °C, 32 h	…	…	…	γ + Z

(continued)

Table 1 Phase Composition of the Ti-Si-Al Alloys (continued)

Sample Composition (at.%)	Heat Treatment	Phase Composition According to			
		X-ray	Metallography	EPMA	Totality of Data (a)
42Ti-26Si-32Al	As-cast	ε + Z + α5/4	Z + ε + RL	…	Z + ε + α5/4
41Ti-5Si-54Al	As-cast	γ + Z	γ + eutectic (γ + Z)	…	γ + Z
[1997Bul]	1270 °C, 32 h	…	…		γ + Z
40Ti-20Si-40Al	As-cast	ε + Z	Z + ε + RL	…	Z + ε + α5/4
	1250 °C, 36 h	…	…	…	ε + Z + α5/4
38Ti-2Si-60Al	As-cast	γ + Z	γ + eutectic (γ + Z)	γ	γ + Z
	1270 °C, 25 h	…	…	…	γ + Z
37Ti-23Si-40Al	As-cast	Z + ε + 5/4	Z + ε + RL	…	ε + α5/4
35Ti-5Si-60Al	As-cast	γ + ξ + ε + Z	γ + eutectic (γ + Z)	γ + ξ + ε + Z	ξ + Z
	1270 °C, 25 h	ξ + Z	…	…	ξ + Z
33.5Ti-3.5Si-63Al	As-cast	ξ + [γ] + [Z]	γ + eutectic (γ + Z)	…	ξ + Z
33Ti-27Si-40Al	As-cast	α5/4 + ε + Al + ?	Z + ? + RL	…	ε + β1/1 + β-Ti(Si,Al)$_2$
33Ti-37Si-30Al	As-cast	β-Ti(Si,Al)$_2$ + β1/1 + Al + (?)	Z + α5/4 + RL	…	ε + β-Ti(Si,Al)$_2$
33Ti-47Si-20Al	As-cast	β1/1 + β-Ti(Si,Al)$_2$ + Al + Si + (?)	β-Ti(Si,Al)$_2$ + RL	β1/1 + β-Ti(Si,Al)$_2$ + Al	ε + β-Ti(Si,Al)$_2$ + Si
32Ti-2Si-66Al	As-cast	γ + ξ + Z	ξ + eutectic (ξ + Z)	ξ	ξ + Z
	1270 °C, 25 h	…	…	…	ξ + Z
32Ti-20Si-48Al	As-cast	Z + α5/4 + ε	Z + ε + RL	…	ε + α5/4
31Ti-39Si-30Al	As-cast	β1/2 + β1/1 + Al + [Z] + [α5/4]	Z + α5/4 + ? + RL	Z + α5/4 + β1/1 + Al + [Si]	ε + β-Ti(Si,Al)$_2$ + Si
30Ti-10Si-60Al	As-cast	…	Z + eutectic (ε + Z)	…	ε + α5/4 + Z
	1250 °C, 36 h	…	…	ε + Z	ε + α5/4 + Z
30Ti-22Si-48Al	As-cast	α5/4 + ε + Al	Z + ε + ? + RL	…	ε + β1/1 + β-Ti(Si,Al)$_2$
29Ti-5Si-66Al	As-cast	…	ε + eutectic (ε + Z)	ε + ξ	ε + Z
	1270 °C, 25 h	…	…	…	ε + Z
29Ti-17Si-54Al	As-cast	α5/4 + ε + ?	Z + α5/4 + ε + RL	…	ε + α5/4
29Ti-31Si-40Al	As-cast	β-Ti(Si,Al)$_2$ + β1/1 + Al + ?	Z + α5/4 + ε + RL	…	ε + β-Ti(Si,Al)$_2$
27.5Ti-3.5Si-69Al	As-cast	…	ε + eutectic (ε + Z)	…	ε + Z
27Ti-25Si-48Al	As-cast	α5/4 + ε + Al	Z + α5/4 + ε + RL	…	ε + β-Ti(Si,Al)$_2$ + Si
26Ti-1Si-73Al	As-cast	ε + (?)	ε + eutectic (ξ + ε)	…	ξ + ε
26Ti-2Si-72Al	As-cast	ε + (?)	ε + eutectic (ε + Z)	…	ε + Z
	1270 °C, 25 h	…	…	…	ε + Z
26Ti-5Si-69Al	As-cast	…	ε + eutectic (ε + Z)	…	ε + Z
	1300 °C, 33 h	…	…	…	ε + Z
26Ti-8Si-66Al	As-cast	ε + (?)	Z + eutectic (ε + Z)	…	ε + α5/4
26Ti-10Si-64Al	As-cast	…	Z + eutectic (ε + Z)	…	ε + α5/4
26Ti-14Si-60Al	As-cast	ε + α5/4 + Al + (Z)	Z + α5/4 + ε + RL	…	ε + β1/1
26Ti-17Si-57Al	As-cast	ε + α5/4 + Al	Z + α5/4 + ε + RL	…	ε + β-Ti(Si,Al)$_2$
26Ti-20Si-54Al	As-cast	ε + α5/4 + Al	Z + α5/4 + ε + RL	…	ε + β-Ti(Si,Al)$_2$ + Si
25Ti-3Si-72Al	As-cast	ε + Al	ε + RL	…	ε
25Ti-9Si-66Al	As-cast	ε + Al	Z + ε + RL	…	ε
25Ti-15Si-60Al	As-cast	ε + α5/4 + Al + (?)	Z + α5/4 + ε + RL	…	ε + β-Ti(Si,Al)$_2$ + Si
25Ti-16Si-59Al	As-cast	ε + α5/4 + Al	Z + α5/4 + ε + RL	…	ε + β-Ti(Si,Al)$_2$ + Si
24Ti-1Si-75Al	As-cast	…	ε + RL	…	ε + Al
23Ti-5Si-72Al	As-cast	…	ε + RL	…	ε + Al
20Ti-2Si-78Al	As-cast	…	ε + RL	…	ε + Al
17Ti-5Si-78Al	As-cast	…	ε + RL	…	ε + Al
8Ti-2Si-90Al	As-cast	…	ε + RL	…	ε + Al
5Ti-5Si-90Al	As-cast	ε + Al + ?	ε + RL	ε + Al	ε + Al + Si

(a) Phase composition of as-cast samples corresponds to the solidus surface.
(b) β*, transformed primary β-phase
(c) In [ ] small amount (traces) of phase is shown.
(d) RL, remnant liquid
(e) α*, transformed at cooling α-phase

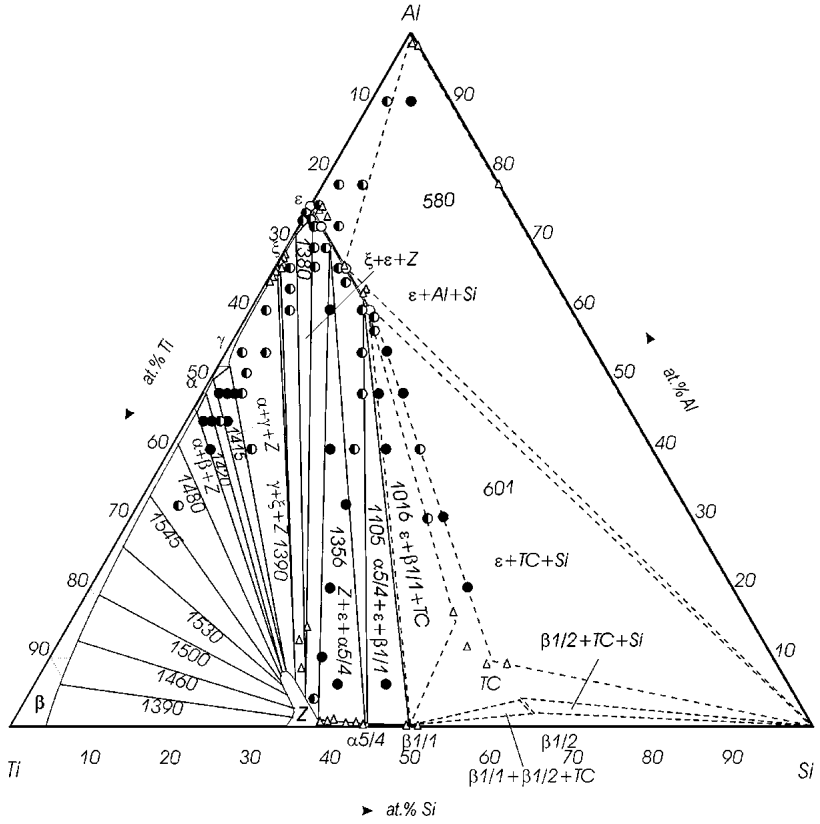


Fig. 2 The solidus surface of the Ti-Si-Al system according to the results of this investigation and our previous data [1997Bul]: (○) single-phase sample; (◐) two-phase sample; (●) three-phase sample; and (△) EPMA results

more complex variant. Meanwhile, we do not rule out the possibility that this phase is the high-temperature form of $TiSi_2$.

Phase compositions of the alloys studied are summarized in Table 1. The solidus projection resulted from this investigation and our previous data [1997Bul] for the Ti-corner of the system is shown in Fig. 2. The homogeneity ranges of the phases were established mainly from the EPMA results (Table 2). It should be noted that the EPMA results obtained for the cast alloys were attributed to the solidus temperatures as they were observed in the Ti-corner of the system [1997Bul]. The solubility of Si in the Ti-Al-based binary phase or of Al in the Ti-Si-based binary phase was found to be essentially independent of temperature. The maximum solubility of Si in the γ- and ξ-phases was established to be about 0.5 and <0.5 at.%, respectively. $TiAl_3$ dissolves up to 15 at.% Si due to substitution of Al for Si that was evidenced by decreasing of the lattice parameters of the ε-phase versus the Si content. This result is in good agreement with the value of 15 at.% reported in Schob et al. [1962Sch]. This is also in reasonable agreement with the value of 20 at.% reported in Schubert et al. [1963Sch].

According to our previous data [1997Bul], the maximum solubility of Al in the Z phase is about 8 at.%. The peculiarity of the atom substitution along the Ti-rich boundary was discussed in Bulanova et al. [1997Bul]. The Al solubility in the Ti_5Si_4 and TiSi phases is about 0.5 at.%. The result for TiSi does not agree with data reported by Schubert et al. [1963Sch] (~9 at.%) and Kamei et al. [1968Kam] (~12 at.%). The maximum Al solubility in the TC or β1/2 was found to be about 16 at.%. The homogeneity range shows that Al mainly substitutes for Si.

According to the present results, phase equilibria at the solidus temperatures in the concentration region under investigation involve phases γ, ξ, ε, Z, β5/4, α5/4, β1/1, TC (if it forms), β1/2, Si, and Al. These phases interact to form the following three-phase fields: Z + γ + ξ; Z + ξ + ε; Z + ε + α5/4; Z + α5/4 + β5/4; ε + α5/4 + β1/1; ε + β1/1 + β-Ti(Si,Al)$_2$; ε + β-Ti(Si,Al)$_2$ + Si; and ε + Si + Al. If a TC forms from the liquid, the additional three-phase regions β1/1 + TC + β1/2 and TC + β1/2 + Si should occur.

The existence of the ε + β-Ti(Si,Al)$_2$ + Si and ε + Si + Al three-phase regions at the solidus temperatures does not agree with results of the studies of Kamei et al. [1968Kam] and Zakharov et al. [1988Zak], in which the three-phase regions ε + TC + Al and TC + Si + Al are shown. Our results are based on EPMA and x-ray diffraction data for the as-cast alloy 5Ti-5Si-90Al. Both methods definitely revealed ε and Al phases. The x-ray pattern contained additional reflections that could not be indexed. This showed the three-phase nature of the alloy. The ε-phase in the alloy contained 8.6 at.% Si. The phase relations shown in the solidus surface (Fig. 2) suggest that the third phase could not be a TC. It could be Si or an additional unknown phase.

Table 2 Results of EPMA of Ti-Si-Al Alloys

Sample (at.%)			Identification of the Measurement	EPMA Results (at.%)		
Ti	Si	Al		Ti	Si	Al
As-cast						
56	38	6	Z	61.05	38.36	0.59
50	44	6	α5/4	56.24	43.14	0.60
			α5/4	56.19	43.22	0.59
			ε	24.51	12.80	62.69
			ε	24.24	12.95	62.81
			ε	24.14	13.20	62.63
38	2	60	γ	35.42	0.54	64.04
			γ	33.89	0.53	65.58
			γ	34.96	0.51	64.52
			γ	33.44	0.67	65.89
35	5	60	ξ	33.00	0.83	66.18
			ξ	32.57	0.79	66.64
			ξ	32.61	0.84	66.55
			Z	62.41	35.14	2.46
33	47	20	β-Ti(Si,Al)$_2$	36.10	55.10	8.80
			β-Ti(Si,Al)$_2$	33.53	57.47	8.99
			β1/1	50.54	49.38	0.04
			β1/1	48.87	51.06	0.06
32	2	66	ξ	32.04	0.54	67.42
			ξ	32.13	0.42	67.45
			ξ	32.45	0.47	67.08
			ξ	31.22	0.55	68.24
			ξ	31.64	0.48	67.88
31	39	30	β-Ti(Si,Al)$_2$	36.30	47.13	16.58
			β-Ti(Si,Al)$_2$	37.31	51.26	11.43
			Al	0.30	1.84	97.87
29	5	66	ξ	31.22	1.62	67.16
			ε	23.52	2.80	73.68
			ε	24.01	1.67	74.32
			ε	23.28	1.71	75.01
5	5	90	ε	24.95	8.61	66.44
			ε	24.60	8.72	66.67
			Al	0.37	1.82	97.82
			Al	0.20	1.06	98.73
1270 °C						
35	5	60	ξ	32.96	0.45	66.59
			ξ	32.50	0.46	67.04
			ξ	32.88	0.48	66.64
			ξ	32.41	0.49	67.10
			Z	61.01	36.49	2.50
			Z	61.52	36.14	2.34
29	5	66	ε	26.88	2.31	70.81
			ε	26.07	1.24	72.69
			Z	60.08	36.82	3.10
1250 °C						
40	20	40	ε	24.81	3.81	71.38
			ε	24.98	3.67	71.34
			ε	25.03	3.78	71.19
			ε	24.82	3.78	71.40
			ε	24.69	3.83	71.48
30	10	60	ε	25.35	3.58	71.07
			ε	25.33	3.52	71.15
			Z	60.28	37.99	1.73
			Z	60.37	37.91	1.72

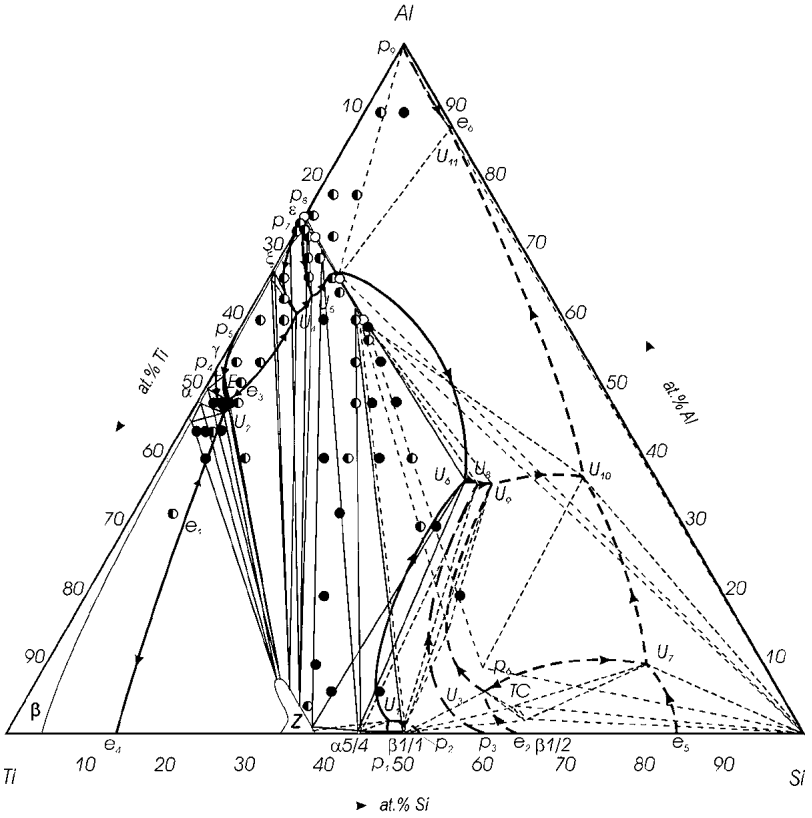


Fig. 3 The melting diagram (solidus + liquidus) of the Ti-Si-Al system according to results of this investigation and our previous data [1997Bul]: (○) single-phase sample; (◐) two-phase sample; and (●) three-phase sample

The melting diagram (solidus plus liquidus) of the Ti-Si-Al system is shown in Fig. 3. In the studied region, the liquidus surface is characterized by the fields of primary crystallization of γ, ξ, ε, Z, β5/4, α5/4, β1/1, Si, Al, and β-Ti(Si,Al)$_2$ or β1/2. These are separated from each other by the following monovariant curves showing the composition of liquids involved in the reaction:

γ: L + α ↔ γ (p_5E), L ↔ γ + Z (Ee_3U_4), L + γ + ξ (p_7U_4, the equilibrium shifts from peritectic L + γ ↔ ξ to eutectic L ↔ γ + ξ);

ξ: L + γ + ξ (p_7U_4), L ↔ ξ + Z (U_4U_5), L + ξ + ε (p_8U_5, the equilibrium shifts from peritectic L + ξ ↔ ε to eutectic L ↔ ξ + ε);

ε: L + ξ + ε (p_8U_5), L + ε + Z (U_5U_6, the equilibrium modifies from eutectic L ↔ ε + Z to peritectic L + Z ↔ ε), L ↔ ε + α5/4 (U_6U_8), L ↔ ε + β1/1 (U_8U_9), L ↔ ε + β-Ti(Si,Al)$_2$ (U_9U_{10}), L ↔ ε + Si ($U_{10}U_{11}$), L + ε ↔ Al (p_9U_{11});

Z: L ↔ β + Z ($e_4e_1U_2$), L ↔ α + Z (U_2E), L ↔ γ + Z (Ee_3U_4), L ↔ ξ + Z (U_4U_5), L + ε + Z (U_5U_6), L + Z + α5/4 (U_1U_6, equilibrium changes character from peritectic L + Z ↔ α5/4 to eutectic L ↔ Z + α5/4), L + Z ↔ β5/4 (p_1U_1);

β5/4: L + Z ↔ β5/4 (p_1U_1), L + Z + α5/4 (U_1U_6), L + β5/4 + α5/4 (p_2U_1, the mode of the reaction is unknown);

α5/4 L + β5/4 + α5/4 (p_2U_1), L ↔ ε + α5/4 (U_6U_8), L + α5/4 + β1/1 (p_3U_8, equilibrium changes character from peritectic L + α5/4 ↔ β1/1 to eutectic L ↔ α5/4 + β1/1);

β1/1: L + α5/4 + β1/1 (p_3U_8), L ↔ ε + β1/1 (U_8U_9), possibly L + β1/1 + TC (U_3U_9, equilibrium changes character from eutectic L ↔ β1/1 + TC to peritectic L + TC ↔ β1/1), L ↔ β1/1 + β1/2 (e_2U_3);

β1/2: L ↔ β1/1 + β1/2 (e_2U_3), possibly L + β1/2 ↔ TC ($U_3p_6U_7$), L ↔ β1/2 + Si (e_5U_7);

TC: L + β1/1 + TC (U_3U_9), L ↔ TC + Al (U_9U_{10}), L ↔ TC + Si (U_7U_{10}), L ↔ β1/2 + Si (e_5U_7), L + β1/2 ↔ TC ($U_3p_6U_7$);

Si: L ↔ β1/2 + Si (e_5U_7), possibly L ↔ TC + Si (U_7U_{10}), L ↔ ε + Si ($U_{10}U_{11}$), L ↔ Si + Al ($U_{11}e_6$);

Al: L + ε ↔ Al (p_9U_{11}), L ↔ Si + Al ($U_{11}e_6$).

The isopleths that show isoconcentrates for Si, Ti, and Al are shown in Fig. 4-6. Tables 3 and 4 list the temperatures of phase transformations. The character of equilibria at solidification, as well as a location of invariant points and monovariant curves, were determined from an examination of the microstructures of as-cast samples.

The alloys 44Ti-2Si-54Al, 41Ti-5Si-54Al, 38Ti-2Si-60Al, 35Ti-5Si-60Al, and 33.5Ti-3.5Si-63Al are located in the field of γ-phase primary crystallization. The microstruc-

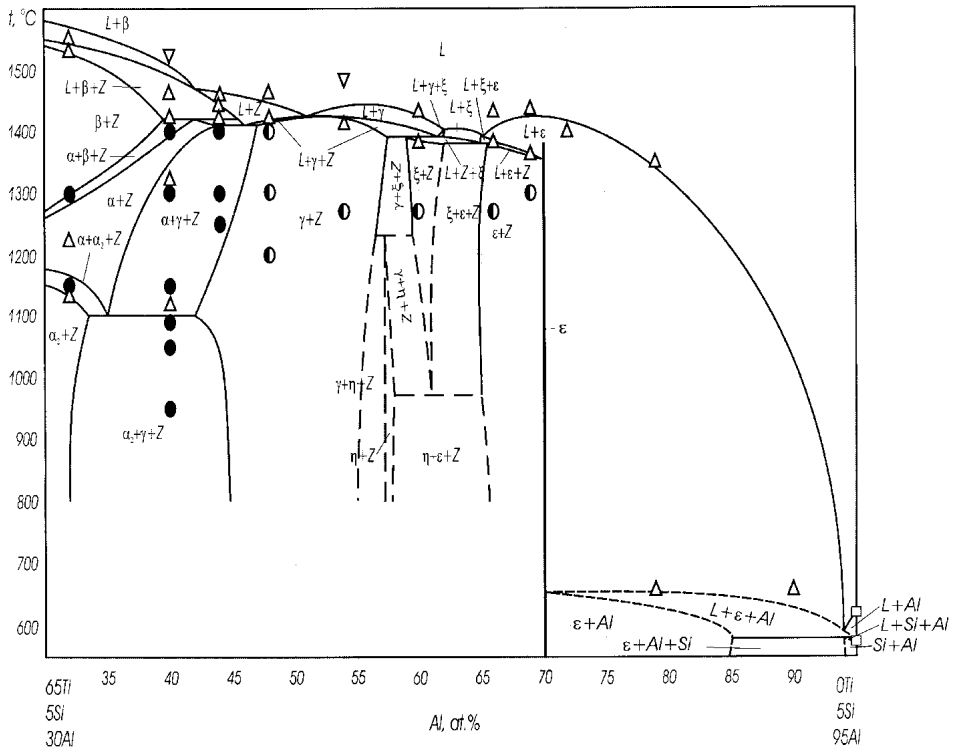


Fig. 4 Isopleth at 5 at.% Si of the Ti-Si-Al system: (◐) two-phase sample; (●) three-phase sample; and (△) DTA results

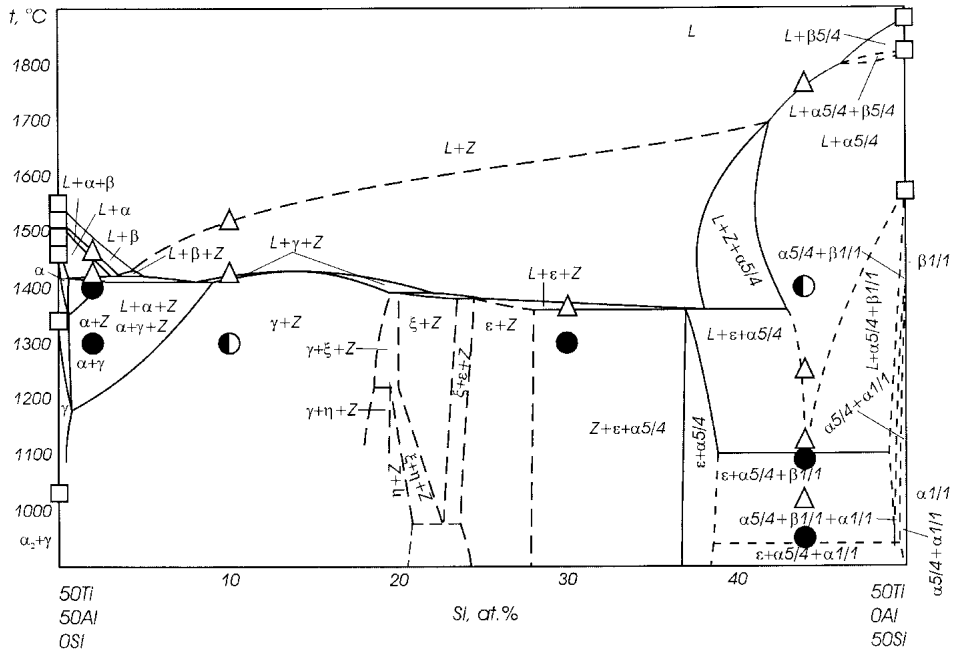


Fig. 5 Isopleth at 50 at.% Ti of the Ti-Si-Al system: (◐) two-phase sample; (●) three-phase sample; and (△) DTA results

ture of the last alloy shows the presence of Z phase in the eutectic mixture. So, this eutectic mixture is of an L ↔ γ + Z nature (Ee_3U_4). This is possible if the eutectic curve extends to compositions ≥ ~60 at.% Al.

Location of the second monovariant curve corresponding to the reaction L + γ ↔ ξ coming into the invariant point U_4 (p_7U_4; Fig. 3) was determined from a comparison of the microstructures of the samples 44Ti-2Si-54Al, 38Ti-2Si-

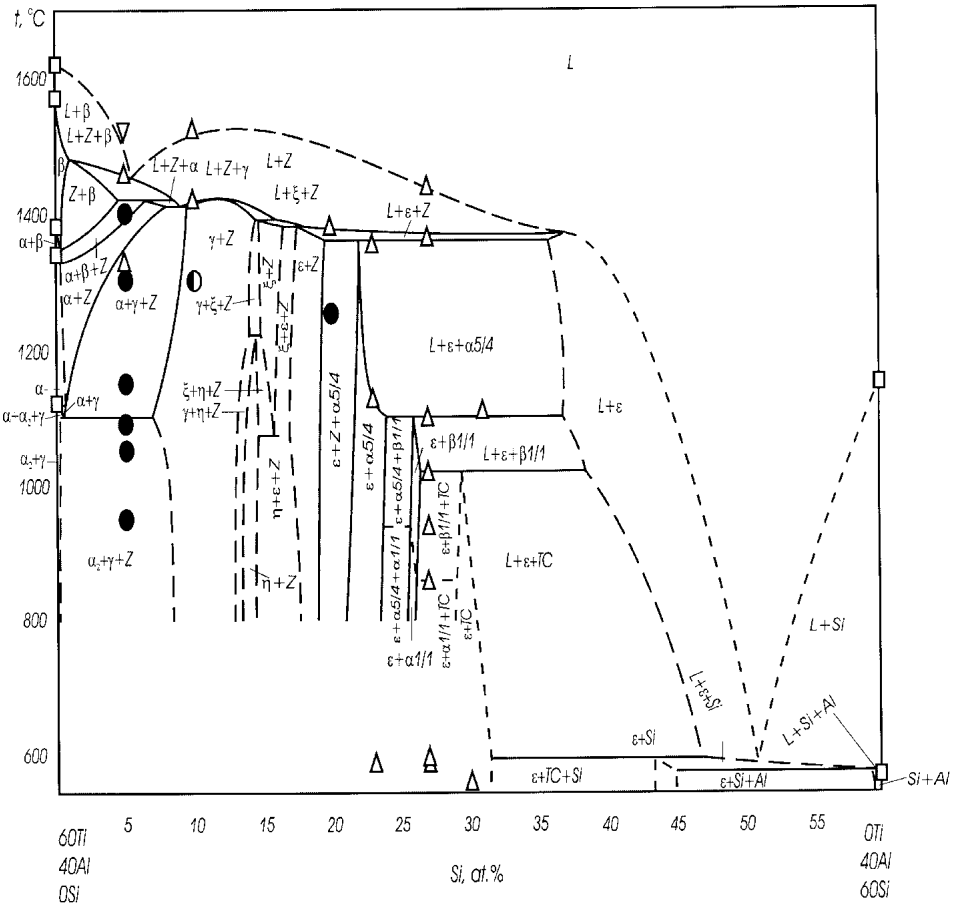


Fig. 6 Isopleth at 40 at.% Al of the Ti-Si-Al system: (◐) two-phase sample; (●) three-phase sample; and (△) DTA results

60Al, and 32Ti-2Si-66Al. The primary phase in the alloy 32Ti-2Si-66Al has a striped appearance. This can be due to solid-state transformations of the primary phase, in contrast to the first two samples. Among the phases of the Ti-Al system in the concentration interval of interest, only Ti_5Al_{11} undergoes decomposition in the solid state. Thus, the conclusion was made that the primary phase in the alloy 32Ti-2Si-66Al is ξ-phase rather than γ-phase, which was observed in the alloys 44Ti-2Si-54Al and 38Ti-2Si-60Al. The eutectic morphology in these three alloys looks rather similar. The typical feature is the presence of the Z phase in the eutectic composition. Then, in the alloy 32Ti-2Si-66Al after the primary solidification of the ξ-phase, the eutectic reaction L ↔ ξ + Z (U_4U_5) takes place. Thus, the monovariant curve corresponding to the peritectic reaction L + γ ↔ ξ (p_7U_4), comes out of the composition 28Ti-72Al (p_7), passes between the alloys 33.5Ti-3.5Si-63Al and 32Ti-2Si-66Al, and meets the monovariant curve corresponding to the eutectic reaction L ↔ γ + Z (Ee_3U_4) at the composition ~33.5Ti-6.5Si-60Al (invariant point U_2). The outgoing monovariant reaction is L ↔ ξ + Z (U_4U_5). The invariant equilibrium can be written then as L + γ ↔ ξ + Z. This results in the γ + ξ + Z field at the solidus surface, which is very narrow owing to an insignificant difference in compositions (no more than 1 at.%) of γ- and ξ-phases coexisting in this three-phase region. The temperature of the invariant equilibrium was determined to be ~1390 °C.

The fields of the primary crystallization of the ξ- and ε-phases are separated by the monovariant liquid curve p_8U_5 of the reaction in a L + ε + ξ volume, which changes from peritectic L + ξ ↔ ε to eutectic L ↔ ξ + ε after intersecting the boundary of the homogeneity range of the ε-phase. In the alloys 29Ti-5Si-66Al, 27.5Ti-3.5Si-69Al, and 26Ti-2Si-72Al, the primary phase is ε, while the Z phase is eutectic constituent, so the nature of the eutectic mixture in these alloys results from the eutectic L ↔ ε + Z reaction.

No ternary eutectic mixture was observed for the alloys in this concentration field, so an equilibrium of L + ξ + ε + Z can be assumed to be of peritectic type L + ξ ↔ ε + Z. Then, the composition of invariant point U_5 should be located outside the three-phase field ξ + ε + Z in the solidus surface. This is possible when the ε-corner of the ξ + ε + Z triangle is located at a low Si content. Accordingly, the position of the invariant point U_5 was accepted at ~30Ti-6Si-64Al. The above equilibrium takes place at ~1380 °C. Location of the ε-corner of the three-phase field ξ + ε + Z at the solidus surface was determined to be at ~0.5 at.% Si on the basis of the lattice parameters of the ε-phase (Table 5).

Table 3 Solidification Temperatures the Ti-Si-Al Samples Measured for As-Cast Alloys

	Liquidus		Solidus		Tie-lines Surface	
Alloy	***T*** **(°C) (a)**	**Primary Phase**	***T*** **(°C)**	**Phase Region**	***T*** **(°C)**	**Phase Boundary**
60Ti-36Si-4Al	[1960]	Z	1365	Z + ε	…	…
56Ti-34Si-10Al	[1780]	Z	1370	Z + ε + α5/4	…	…
56Ti-38Si-6Al	>1790 (b) [1860]	Z	1360	Z + ε + α5/4	…	…
54Ti-2Si-44Al	1490 (c) [1520]	β	1430 (c)	α + β + Z	1465	L + β/L + β + Z
53Ti-3Si-44Al	1465 (c)	β	1420 (c)	α + β + Z	1385	L + β/L + β + Z
50Ti-10Si-40Al	1480 (c) [1520]	Z	1415 (c)	γ + Z	…	…
50Ti-30Si-20Al	[1620]	Z	1355	Z + ε + α5/4	…	…
50Ti-44Si-6Al	1760	α5/4	1115	α5/4 + ε + β1/1	…	…
44Ti-2Si-54Al	1460	γ	1410	γ + Z	…	…
42Ti-26Si-32Al	1500	Z	1355	Z + ε + α5/4	…	…
40Ti-20Si-40Al	[1490]	Z	1355	Z + ε + α5/4	1385	L + Z/L + Z + ε
38Ti-2Si-60Al	1450	γ	1395	γ + Z	…	…
37Ti-23Si-40Al	[1470]	Z	1130	ε + α5/4	…	…
35Ti-5Si-60Al	1430	γ	1380	ξ + Z	…	…
33Ti-27Si-40Al	1435	Z	1020	β1/1 + ε + β-Ti(Si,Al)$_2$	…	…
33Ti-37Si-30Al	1410	Z	1015	ε + β-Ti(Si,Al)$_2$	…	…
33Ti-47Si-20Al	1245	TC	595	ε + Si + β-Ti(Si,Al)$_2$	…	…
32Ti-2Si-66Al	[1400]	ξ	1390	ξ + Z	…	…
32Ti-20Si-48Al	[1410]	Z	1115	ε + α5/4	…	…
31Ti-39Si-30Al	1390	α5/4	605	ε + Si + β-Ti(Si,Al)$_2$	…	…
30Ti-10Si-60Al	1390	Z	1350	Z + ε + α5/4	…	…
30Ti-22Si-48Al	1445↓ (d) [1400]	Z	1015	β1/1 + ε + β-Ti(Si,Al)$_2$	…	…
29Ti-5Si-66Al	1420	ε	1380	ε + Z	…	…
29Ti-17Si-54Al	1395	Z	1215	ε + α5/4	…	…
27.5Ti-3.5Si-69Al	1460	ε	[1380]	ε + Z	1410	L + ε/L + ξ + ε
27Ti-73Al	1440	γ	1395	ξ + ε	…	…
27Ti-25Si-48Al	1400↓	Z	595	ε + Si + β-Ti(Si,Al)$_2$	…	
26Ti-74Al	1435	ξ	1390	ξ + ε	…	
26Ti-1Si-73Al	1415	…	1375	ξ + ε	…	…
26Ti-2Si-72Al	1420	ε	1385	Z + ε	…	…
26Ti-5Si-69Al	1435	ε	1365	Z + ε	…	…
26Ti-8Si-66Al	[1380]	Z	1295	ε + α5/4	…	…
26Ti-10Si-64Al	[1380]	Z	1300	ε + α5/4	…	…
26Ti-14Si-60Al	[1380]	Z	…	ε + β1/1	1380	L + Z/L + ε + Z
26Ti-17Si-57Al	[1390]	Z	…	ε + β-Ti(Si,Al)$_2$	1390	L + Z/L + ε + Z
26Ti-20Si-54Al	1380↓	Z	595	ε + Si + β-Ti(Si,Al)$_2$	…	…
25Ti-75Al	1450	ξ	640	ε + Al	…	…
25Ti-3Si-72Al	1415	ε	…	ε	(640) (e)	L + ε + Al/ε + Al
25Ti-9Si-66Al	…	Z	1280	ε	…	…
25Ti-15Si-60Al	1385	Z	600	ε	…	…
25Ti-16Si-59Al	1385	Z	600	ε + Si + β-Ti(Si,Al)$_2$	1385	L + Z/L + ε + Z
24Ti-1Si-75Al	1445	ε	…	ε + Al	…	…
23Ti-5Si-72Al	1400	ε	…	ε + Al	…	…
20Ti-2Si-78Al	1415	ε	…	ε + Al	…	…
17Ti-5Si-78Al	1350	ε	…	ε + Al	660	L + ε/L + ε + Al
8Ti-2Si-90Al	…	ε	…	ε + Al	660	L + ε/L + ε + Al
5Ti-5Si-90Al	…	ε	…	ε + Al + Si	660	L + ε/L + ε + Al

(a) In [ ] our estimation of the temperature is given based on the totality of experimental data.
(b) After heating up to this temperature the sample was not melted.
(c) Data from Bulanova et al. [1997Bul]
(d) ↓, the temperature taken at cooling
(e) Effect results from nonequilibrium liquid

Table 4 Temperatures of Invariant Equilibria of the Ti-Si-Al System Measured for As-Cast Samples

	T (°C) (a)					
Alloy	**L + ξ ↔ ε + Z**	**L + Z ↔ ε + α5/4**	**L + α5/4 ↔ ε + β1/1**	**L + β1/1 ↔ ε + TC**	**L + TC ↔ ε + Si**	**L + ε ↔ Al + Si**
56Ti-34Si-10Al	…	1370	…	…	…	…
56Ti-38Si-6Al	…	1360	…	…	…	…
50Ti-30Si-20Al	…	1355	…	…	…	…
50Ti-44Si-6Al	…	…	1115	(1025) (b)	(600)	…
42Ti-26Si-32Al	…	1355	…	…	…	…
40Ti-20Si-40Al	…	1355	…	…	…	…
37Ti-23Si-40Al	…	1345	…	…	(590)	…
35Ti-5Si-60Al	1380	…	…	…	…	…
33Ti-27Si-40Al (a)	…	1350	1100	1020	(605)	(585)
33Ti-37Si-30Al	…	…	1120	1015	(600)	…
33Ti-47Si-20Al	…	…	…	…	595	…
32Ti-20Si-48Al	…	1320	(1095)	…	(600)	(580)
31Ti-39Si-30Al	…	…	…	1015	605	…
30Ti-10Si-60Al	…	1350	…	…	…	…
30Ti-22Si-48Al	…	…	1090	1015	(600)	(580)
29Ti-5Si-66Al	1380	…	…	…	…	…
29Ti-17Si-54Al	…	…	1090	…	(595)	(580)
29Ti-31Si-40Al	…	…	1110	…	…	(570)
27Ti-25Si-48Al	…	…	1125	1035	595	…
26Ti-2Si-72Al	1385	…	…	…	…	…
26Ti-8Si-66Al	…	1365	…	…	…	…
26Ti-10Si-64Al	…	1345	…	…	…	…
26Ti-14Si-60Al	…	…	(1105)	…	(605)	(590)
26Ti-17Si-57Al	…	…	1095	…	(600)	(580)
26Ti-20Si-54Al	…	…	1090	1010	595	(575)
25Ti-9Si-66Al	…	1350	…	…	(615)	(580)
25Ti-15Si-60Al	…	…	1095	…	600	(580)
25Ti-16Si-59Al	…	…	1095	1015	600	(580)
Average	1380	1356 ± 8	1105 ± 15	1016 ± 5	601 ± 5	580 ± 2

(a) Effects at 840 and 760 °C were ascribed to α5/4 + β1/1 ↔ ε + α1/1 (due to nonequilibrium solidification) and ε + β1/1 ↔ α1/1 + TC.
(b) In ( ) effects resulted from nonequilibrium crystallization of as-cast samples are shown.

The monovariant reaction L ↔ ε + Z (U_5U_6) also changes its character from eutectic to peritectic L + Z ↔ ε when intersecting the boundary of the homoheneity region of the ε-phase. Thus, ε-phase melts congruently at an Si content of ~0.5-8.5 at.%, and incongruently at 0-0.5 and 8.5-15 at.% Si. The intersection of the monovariant liquid curve L + Z + ε (U_5U_6) with the ε-phase boundary occurs in the vicinity of the composition 25Ti-8.5Si-66.5Al, which is determined from the microstructure of the alloy 25Ti-9Si-66Al, where the primary phase is Z, in a very small amount. The last phase is also primary Z in the alloys 33Ti-37Si-30Al, 30Ti-10Si-60Al, 29Ti-31Si-40Al, 27Ti-25Si-48Al, 26Ti-14Si-60Al, 26Ti-17Si-57Al, 26Ti-20Si-54Al, 25Ti-15Si-60Al, and 25Ti-16Si-59Al. So, the field of its primary crystallization is very wide.

In the samples 50Ti-44Si-6Al and 31Ti-39Si-30Al, the primary phase is α5/4. The comparison of the alloys 33Ti-37Si-30Al and 31Ti-39Si-30Al revealed different kinds of the primary phases, as follows: Z in the first one; and α5/4 in the second. So, the monovariant liquid curve corresponding to the equilibrium L + Z + α5/4 (U_1U_6) passes between the compositions of these two alloys, and passes near the composition of the alloy 50Ti-44Si-6Al on the side of higher Ti concentration. The equilibrium changes from peritectic to eutectic L ↔ Z + α5/4 in the vicinity of the first alloy. The curve then decreases into the invariant point U_6 of the equilibrium L + Z ↔ ε + α5/4. The temperature of this equilibrium was determined to be 1356 °C. The composition of the invariant point U_6 was estimated to be located at 24Ti-39Si-37Al. The coordinates of invariant equilibrium L + Z + α5/4 + β5/4 were not determined, while the nature of the primary phase in the alloy 50Ti-44Si-6Al allowed us to assume the composition of the invariant point U_1 at ~51Ti-47Si-2Al.

In the alloy 33Ti-47Si-20Al, the primary phase has the structure of a $ZrSi_2$ type and melts congruently. This might be either TC or β1/2. Then two additional curves of monovariant equilibria should be located between the compositions of the above phase and the curve U_1U_6. These seem to be L + α5/4 + β1/1 (p_3U_8 changes from peritectic L + α5/4 ↔ β1/1 to eutectic L ↔ α5/4 + β1/1) and L + β1/1 + β-Ti(Si,Al)$_2$ (p_3U_8 changes from eutectic L ↔ β1/1 + β-

Table 5 The Crystal Structure of Ti-Si-Al Phases

Phase	Crystal Structure	Lattice Periods, Å	Remarks	Refs.
γ, TiAl	AuCu, tP4-P4/mmm	a = 4.0155 – 3.976		[1983Rog]
		c = 4.0625 – 4.049		
		a = 4.005, c = 4.070	50Ti-50Al	[1985Vil]
		a = 4.000(1), c = 4.075(1)	50Ti-50Al, 1200 °C + 1000 °C	[1995Bra]
		a = 3.994(1), c = 4.080(1)	47.5Ti-52.5Al, 1200 °C + 1000 °C	[1995Bra]
		a = 3.989(1), c = 4.081(1)	45Ti-55Al, 1200 °C + 1000 °C	[1995Bra]
		a = 3.984(1), c = 4.079(1)	42.5Ti-57.5Al, 1200 °C + 1000 °C	[1995Bra]
		a = 3.983(1), c = 4.074(1)	40Ti-60Al, 1200 °C + 1000 °C	[1995Bra]
		a = 3.9869, c = 4.0539	Al-rich boundary	[1990Sch]
		a = 3.991 ± 0.002	44Ti-2Si-54Al, as-cast	This work
		c = 4.048 ± 0.004		
		a = 4.006 ± 0.004	41Ti-5Si-54Al, as-cast	This work
		c = 4.073 ± 0.005		
		a = 3.976 ± 0.007	38Ti-2Si-60Al, as-cast	This work
		c = 4.04 ± 0.01		
		a = 3.989 ± 0.003	35Ti-5Si-60Al, as-cast	This work
		c = 4.052 ± 0.004		
		a = 3.980 ± 0.006	32Ti-2Si-66Al, as-cast	This work
		c = 4.08 ± 0.01		
ξ Ti_5Al_{11}	$ZrAl_3$, tI16	a = 3.9230, c = 16.5349		[1990Sch]
		a = 3.917, c = 16.524		[1990Sti]
		a = 3.920 ± 0.002	27Ti-73Al, as-cast	This work
		c = 16.54 ± 0.01		
		a = 3.900 ± 0.002	26Ti-74Al, as-cast	This work
		c = 16.55 ± 0.01		
		a = 3.926 ± 0.001	35Ti-5Si-60Al, as-cast	This work
		c = 16.553 ± 0.005		
		a = 3.916 ± 0.002	35Ti-5Si-60Al, 1270 °C	This work
		c = 16.58 ± 0.01		
		a = 3.924 ± 0.001	33.5Ti-3.5Si-63Al, as-cast	This work
		c = 16.552 ± 0.006		
		a = 3.927 ± 0.002	32Ti-2Si-66Al, as-cast	This work
		c = 16.542 ± 0.007		
ε, $TiAl_3$	$TiAl_3$, tI8-I4/mmm	a = 3.8488, c = 8.5982		[1990Sch]
		a = 3.85, c = 8.596		[1990Sti]
		a = 3.857 ± 0.001	27Ti-73Al, as-cast	This work
		c = 8.593 ± 0.004		
		a = 3.856 ± 0.001	26Ti-74Al, as-cast	This work
		c = 8.589 ± 0.003		
		a = 3.852 ± 0.001	25Ti-75Al, as-cast	This work
		c = 8.595 ± 0.004		
		a = 3.842 ± 0.001	60Ti-36Si-4Al, as-cast	This work
		c = 8.525 ± 0.001		
		a = 3.836 ± 0.003	56Ti-34Si-10Al, as-cast	This work
		c = 8.60 ± 0.01		
		a = 3.823 ± 0.003	50Ti-30Si-20Al, as-cast	This work
		c = 8.58 ± 0.01		
		a = 3.823 ± 0.004	42Ti-26Si-32Al, as-cast	This work
		c = 8.59 ± 0.01		
		a = 3.837 ± 0.005	40Ti-20Si-40Al, as-cast	This work
		c = 8.59 ± 0.01		
		a = 3.806 ± 0.002	37Ti-23Si-40Al, as-cast	This work
		c = 8.576 ± 0.005		
		a = 3.796 ± 0.002	33Ti-27Si-40Al, as-cast	This work
		c = 8.553 ± 0.007		

(continued)

Table 5 The Crystal Structure of Ti-Si-Al Phases (continued)

Phase	Crystal Structure	Lattice Periods, Å	Remarks	Refs.
		a = 3.802 ± 0.001 c = 8.571 ± 0.004	32Ti-20Si-48Al, as-cast	This work
		a = 3.833 ± 0.003 c = 8.606 ± 0.009	30Ti-10Si-60Al, as-cast	This work
		a = 3.805 ± 0.003 c = 8.55 ± 0.01	30Ti-22Si-48Al, as-cast	This work
		a = 3.840 ± 0.002 c = 8.579 ± 0.005	29Ti-5Si-66Al, as-cast	This work
		a = 3.844 ± 0.002 c = 8.596 ± 0.005	29Ti-5Si-66Al, 1270 °C	This work
		a = 3.812 ± 0.002 c = 8.567 ± 0.009	29Ti-17Si-54Al, as-cast	This work
		a = 3.850 ± 0.001 c = 8.572 ± 0.005	27.5Ti-3.5Si-69Al, as-cast	This work
		a = 3.851 ± 0.001 c = 8.587 ± 0.004	26Ti-1Si-73Al, as-cast	This work
		a = 3.844 ± 0.001 c = 8.589 ± 0.003	26Ti-2Si-72Al, as-cast	This work
		a = 3.833 ± 0.002 c = 8.592 ± 0.004	26Ti-5Si-69Al, as-cast	This work
		a = 3.822 ± 0.001 c = 8.579 ± 0.004	26Ti-8Si-66Al, as-cast	This work
		a = 3.813 ± 0.001 c = 8.584 ± 0.003	26Ti-10Si-64Al, as-cast	This work
		a = 3.801 ± 0.001 c = 8.564 ± 0.003	26Ti-17Si-57Al, as-cast	This work
		a = 3.804 ± 0.002 c = 8.581 ± 0.009	26Ti-20Si-54Al, as-cast	This work
		a = 3.839 ± 0.002 c = 8.598 ± 0.004	25Ti-3Si-72Al, as-cast	This work
		a = 3.819 ± 0.001 c = 8.586 ± 0.002	25Ti-9Si-66Al, as-cast	This work
		a = 3.801 ± 0.002 c = 8.577 ± 0.007	25Ti-15Si-60Al, as-cast	This work
		a = 3.808 ± 0.001 c = 8.578 ± 0.003	25Ti-16Si-59Al, as-cast	This work
		a = 3.844 ± 0.001 c = 8.598 ± 0.003	24Ti-1Si-75Al, as-cast	This work
		a = 3.828 ± 0.001 c = 8.595 ± 0.002	23Ti-5Si-72Al, as-cast	This work
		a = 3.842 ± 0.001 c = 8.605 ± 0.003	20Ti-2Si-78Al, as-cast	This work
		a = 3.831 ± 0.002 c = 8.596 ± 0.003	17Ti-5Si-78Al, as-cast	This work
		a = 3.814 ± 0.004 c = 8.596 ± 0.003	5Ti-5Si-90Al, as-cast	This work
Z, Ti_5Si_3	Mn_5Si_3, hP16-$P6_3$/mcm	a = 7.465, c = 5.162		[1961Mir]
		a = 7.429, c = 5.139		[1985Vil]
		a = 7.431(6), c = 5.135(5)		[1970Sve]
		a = 7.4565, c = 5.1495		[1997Zav]
		a = 7.456 ± 0.002 c = 5.157 ± 0.002	62.5Ti-37.5Si, as-cast	[1997Bul]
		a = 7.466 ± 0.006 c = 5.16 ± 0.01	86.5Ti-13.5Si, 1250 °C	[1997Bul]
		a = 7.462, c = 5.150	80Ti-20Si, 1300 °C	[1999Tre]

(continued)

Table 5 The Crystal Structure of Ti-Si-Al Phases (continued)

Phase	Crystal Structure	Lattice Periods, Å	Remarks	Refs.
		a = 7.469 ± 0.007	60Ti-36Si-4Al, as-cast	This work
		c = 5.170 ± 0.008		
		a = 7.474 ± 0.001	56Ti-34Si-10Al, as-cast	This work
		c = 5.169 ± 0.001		
		a = 7.478 ± 0.002	56Ti-38Si-6Al, as-cast	This work
		c = 5.179 ± 0.002		
		a = 7.468 ± 0.002	56Ti-38Si-6Al, 1400 °C	This work
		c = 5.168 ± 0.002		
		a = 7.461 ± 0.002	56Ti-38Si-6Al, 1250 °C	This work
		c = 5.162 ± 0.002		
		a = 7.452 ± 0.002	56Ti-38Si-6Al, 1400 °C + 1250 °C	This work
		c = 5.160 ± 0.002		
		a = 7.471 ± 0.004	50Ti-30Si-20Al, as-cast	This work
		c = 5.178 ± 0.004		
		a = 7.430 ± 0.005	44Ti-2Si-54Al, as-cast	This work
		c = 5.208 ± 0.008		
		a = 7.472 ± 0.002	42Ti-26Si-32Al, as-cast	This work
		c = 5.165 ± 0.002		
		a = 7.517 ± 0.004	41Ti-5Si-54Al, as-cast	This work
		c = 5.202 ± 0.004		
		a = 7.471 ± 0.003	40Ti-20Si-40Al, as-cast	This work
		c = 5.168 ± 0.004		
		a = 7.465 ± 0.004	37Ti-23Si-40Al, as-cast	This work
		c = 5.170 ± 0.004		
		a = 7.452 ± 0.007	35Ti-5Si-60Al, as-cast	This work
		c = 5.148 ± 0.008		
		a = 7.450 ± 0.005	35Ti-5Si-60Al, 1270 °C	This work
		c = 5.152 ± 0.007		
		a = 7.460 ± 0.008	33.5Ti-3.5Si-63Al, as-cast	This work
		c = 5.173 ± 0.008		
		a = 7.46 ± 0.01	30Ti-10Si-60Al, as-cast	This work
		c = 5.17 ± 0.01		
		a = 7.48 ± 0.01	29Ti-5Si-66Al, as-cast	This work
		c = 5.148 ± 0.007		
		a = 7.451 ± 0.007	29Ti-5Si-66Al, 1270 °C	
		c = 5.166 ± 0.005		
		a = 7.45 ± 0.01	27.5Ti-3.5Si-69Al, as-cast	This work
		c = 5.18 ± 0.01		
		a = 7.458 ± 0.005	26Ti-5Si-69Al, as-cast	This work
		c = 5.159 ± 0.005		
β5/4, β-Ti_5Si_4	Sm_5Ge_4, oP36-Pnma	a = 6.506, b = 12.690,		[1969Nic, 1997Zav]
		c = 6.645		
α5/4, α-Ti_5Si_4	Zr_5Si_4, tP36-$P4_12_12$	a = 7.133, c = 12.977		[1970Sve]
		a = 6.702, c = 12.165		[1997Zav]
		a = 6.723 ± 0.007	56Ti-38Si-6Al, 1400 °C	This work
		c = 12.16 ± 0.01		
		a = 6.690 ± 0.004	56Ti-38Si-6Al, 1400 °C + 1250 °C	This work
		c = 12.12 ± 0.01		
		a = 6.709 ± 0.006	56Ti-38Si-6Al, 1250 °C	This work
		c = 12.15 ± 0.01		
		a = 6.706 ± 0.002	50Ti-44Si-6Al, 1400 °C	This work
		c = 12.180 ± 0.007		
		a = 6.702 ± 0.002	50Ti-44Si-6Al, 1400 °C + 1090 °C	This work
		c = 12.174 ± 0.008		
		a = 6.717 ± 0.004	50Ti-44Si-6Al, 1090 °C + 950 °C	This work

(continued)

Table 5 The Crystal Structure of Ti-Si-Al Phases (continued)

Phase	Crystal Structure	Lattice Periods, Å	Remarks	Refs.
		c = 12.19 ± 0.01		
		a = 6.702 ± 0.007	33Ti-27Si-40Al, as-cast	This work
		c = 12.20 ± 0.01		
		a = 6.707 ± 0.004	32Ti-20Si-48Al, as-cast	This work
		c = 12.138 ± 0.008		
		a = 6.703 ± 0.005	30Ti-22Si-48Al, as-cast	This work
		c = 12.19 ± 0.01		
		a = 6.709 ± 0.003	29Ti-17Si-54Al, as-cast	This work
		c = 12.162 ± 0.006		
		a = 6.695 ± 0.005	27Ti-25Si-48Al, as-cast	This work
		c = 12.19 ± 0.01		
		a = 6.699 ± 0.004	26Ti-14Si-60Al, as-cast	This work
		c = 12.23 ± 0.01		
		a = 6.693 ± 0.006	26Ti-17Si-57Al, as-cast	This work
		c = 12.21 ± 0.01		
		a = 6.709 ± 0.007	26Ti-20Si-54Al, as-cast	This work
		c = 12.19 ± 0.01		
		a = 6.697 ± 0.005	25Ti-15Si-60Al, as-cast	This work
		c = 12.19 ± 0.01		
β1/1, β-TiSi	FeB, oP8-Pnma	a = 6.551, b = 3.633(3), c = 4.983(5)		[1970Sve]
		a = 6.5381, b = 3.6390, c = 5.0010		[1997Zav]
		a = 6.606 ± 0.009	33Ti-47Si-20Al, as-cast	This work
		b = 3.619 ± 0.005		
		c = 5.007 ± 0.009		
		a = 6.57 ± 0.01	33Ti-37Si-30Al, as-cast	This work
		b = 3.628 ± 0.005		
		c = 5.01 ± 0.01		
		a = 6.56 ± 0.01	31Ti-39Si-30Al, as-cast	This work
		b = 3.632 ± 0.008		
		c = 5.00 ± 0.01		
		a = 6.592 ± 0.007	29Ti-31Si-40Al, as-cast	This work
		b = 3.636 ± 0.003		
		c = 4.980 ± 0.004		
α1/1, α-TiSi	Orthorhombic	a = 18.747, b = 7.081, c = 3.596		[1997Zav]
β1/2, β-$TiSi_2$	$ZrSi_2$, oC12-Cmcm	a = 3.62, b = 13.76, c = 3.60		[1991Che]
α1/2, α-$TiSi_2$	$TiSi_2$, oF24-Fddd	a = 8.236, b = 4.773, c = 8.523		[1939Lav, Mas2]
		a = 8.257(7), b = 4.802(4) c = 8.557(7)		[1970Sve]
		a = 8.254, b = 4.783, c = 8.523		[1973Bon]
		a = 8.253, b = 4.783, c = 8.540		[1986Mur, 1991Che]
		a = 8.25, b = 4.78, c = 8.50		[1995Jin]
		a = 8.265, b = 4.789, c = 8.549		[1997Zav]
$TiSi_{1.7\text{-}1.4}$ $Al_{0.3\text{-}0.6}$	$ZrSi_2$ oc12, Cmcm		1250 °C	[1957Now, 1962Sch]
$Ti(Al_xSi_{1-x})_2$	$ZrSi_2$, oc12, Cmcm	a = 3.590-3.618, b = 13.517, c = 3.520-3.618	1200 °C	[1961Bru]
O, Ti_2AlSi_3	$ZrSi_2$, oc12, Cmcm	a = 3.635, b = 14.19, c = 3.613	25Ti-7Al-68Si, 700 °C (O + 30Si + 10Al)	[1965Ram]
	$ZrSi_2$, tc12, Cmcm	a = 3.60, b = 13.53, c = 3.60	31Ti-19Al-50Si, 1100 °C (single-phase)	[1965Ram]
U, $Ti_7Al_5Si_{12}$	$Zr_{1-x}AlSi_{1+x}$, t.24, $I4_1/amd$	a = 3.576, c = 27.15	27Ti-20Al-53Si, 700 °C (U + 5Si + 5Al)	[1965Ram, 1963Sch]
		a = 3.645, c, = 28.65	25Ti-7Al-68Si, 1100 °C (U + 20Si + ?)	]1965Ram]
$TiAlSi_2$				[1968Kam]
$Ti_2Al_3Si_2$				[1988Zak]

(continued)

$Ti(Si,Al)_2$ to peritectic L + β-$Ti(Si,Al)_2$ ↔ β1/1). The last comes into invariant point U_9. We did not have any sample within the field of the primary crystallization of β1/1 phase, so our results are insufficient to determine exact location of the curve p_3U_8.

The shape of the last two monovariant curves indicates that the invariant equilibrium L + α5/4 + β1/1 + β-$Ti(Si,Al)_2$ might occur in this concentration interval, rather than the equilibria proposed. In this case, the three-phase field α5/4 + β1/1 + β-$Ti(Si,Al)_2$ should exist at the solidus temperature. Then, β1/1 cannot coexist with the ε-phase, as was observed experimentally (see above). The solidus temperature corresponding to the three-phase field α5/4 + β1/1 + ε was determined to be 1105 °C. Thus, this is the temperature of the invariant equilibrium L + α5/4 ↔ β1/1 + ε (invariant point U_8).

The solidus temperature of the three-phase field β1/1 + ε + β-$Ti(Si,Al)_2$ was determined to be 1016 °C, corresponding to the invariant equilibrium L + β1/1 ↔ β-$Ti(Si,Al)_2$ + ε (invariant point U_9).

As can be seen from Table 4, there are few additional sets of temperatures observed for a number of alloys that should be attributed to other invariant equilibria (at 601 ± 5 °C and 580 ± 5 °C). These are related to equilibria in the Al-corner of the system as composition of the remnant liquid phase moves toward this direction for solidification of the alloys. It should be noted that the temperature 580 °C is close to the temperature of the binary eutectic L ↔ Al + Si (577 °C) and

Table 5 The Crystal Structure of Ti-Si-Al Phases (continued)

Phase	Crystal Structure	Lattice Periods, Å	Remarks	Refs.
β1/2 or TC	$ZrSi_2$, oc12, Cmcm	a = 3.616 ± 0.002 b = 13.49 ± 0.01 c = 3.604 ± 0.008	33Ti-37Si-30Al, as-cast	This work
		a = 3.598 ± 0.004 b = 13.54 ± 0.01 c = 3.506 ± 0.007	33Ti-47Si-20Al, as-cast	This work
		a = 3.616 ± 0.006 b = 13.30 ± 0.02 c = 3.559 ± 0.008	31Ti-39Si-30Al, as-cast	This work
		a = 3.594 ± 0.002 b = 13.611 ± 0.006 c = 3.416 ± 0.007	29Ti-31Si-40Al, as-cast	This work

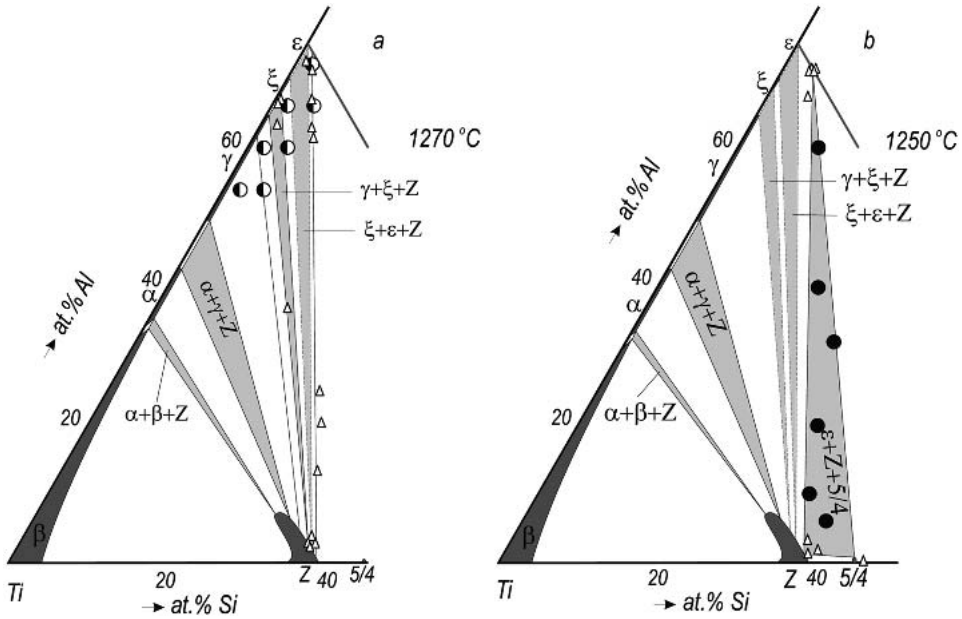


Fig. 7 Partial isothermal sections at 1270 °C (**a**) and 1250 °C (**b**) of the Ti-Si-Al system in the α-Ti-$TiAl_3$-TiSi field: (◐) two-phase sample; (●) three-phase sample; and (△) EPMA results

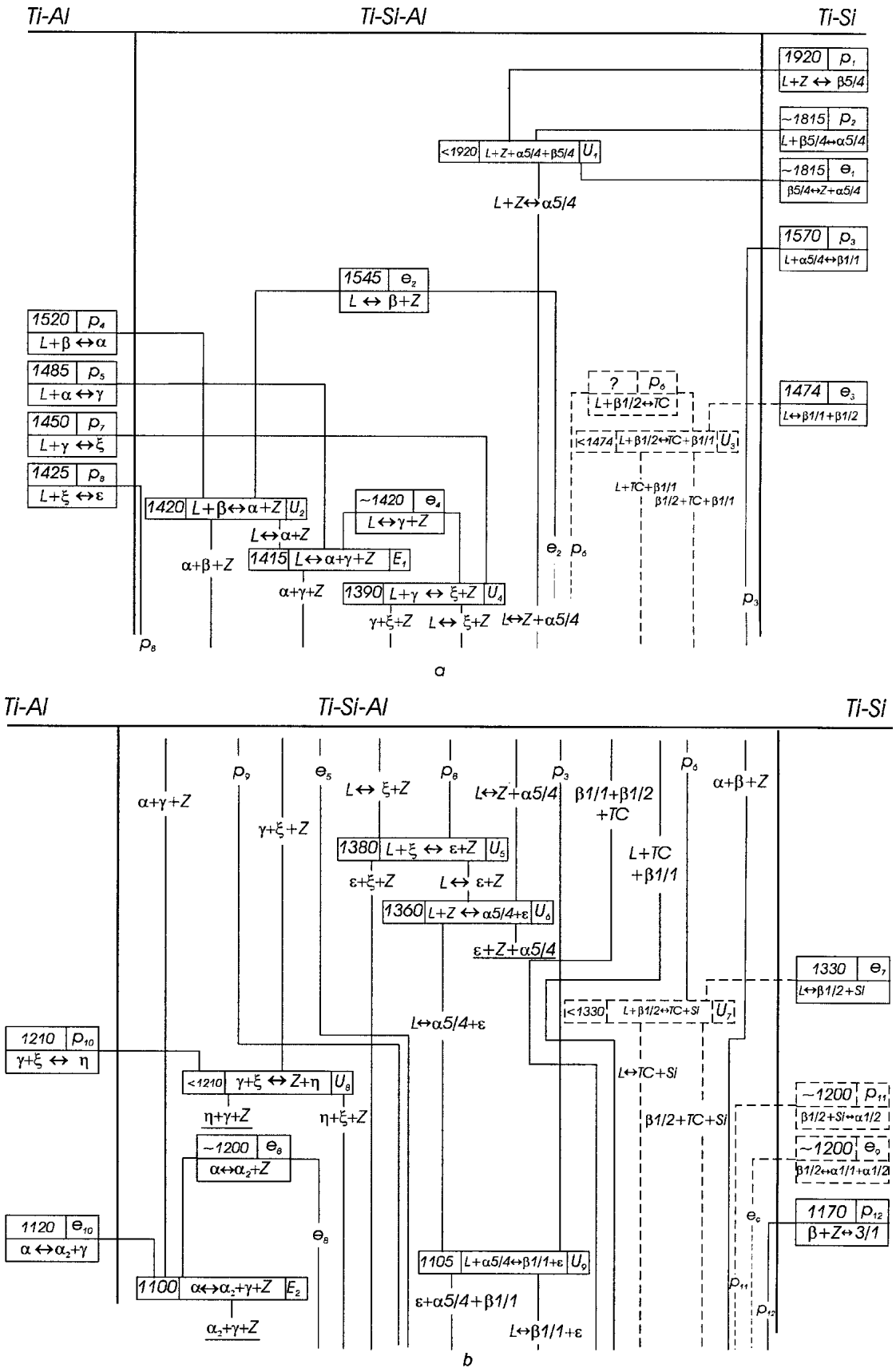
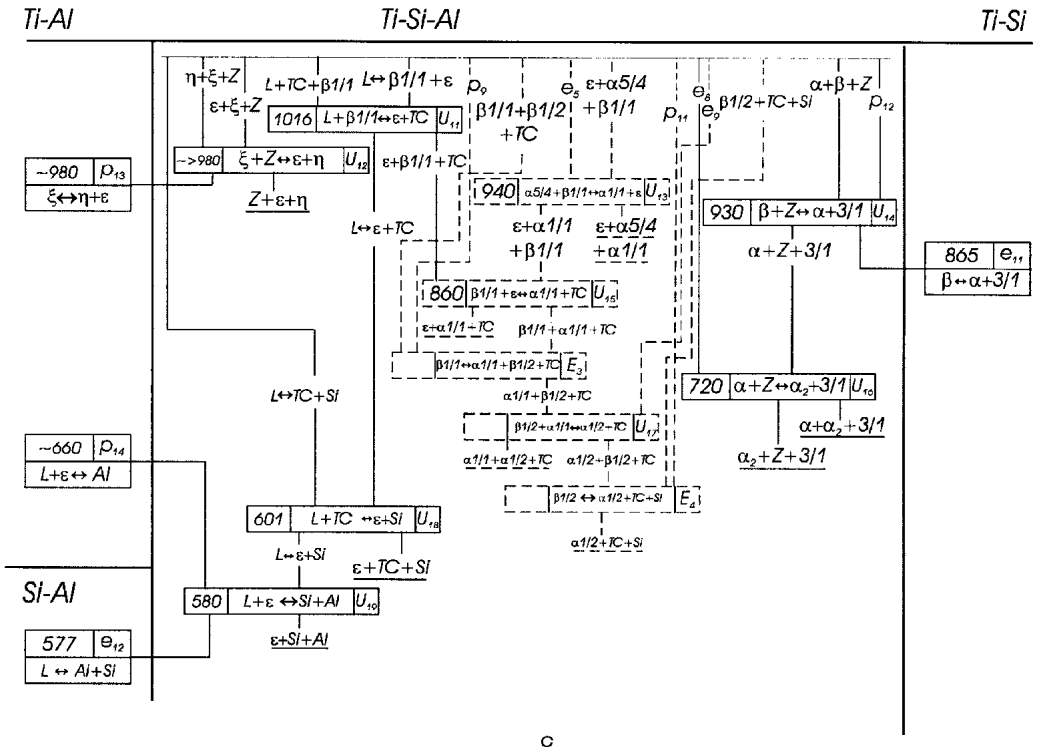


Fig. 8 Reaction scheme in the Ti-Si-Al system according to the results of this work: **(a)** $T > 1390$ °C; **(b)** 1100 °C < T < 1390 °C



c

Fig. 8 cont. Reaction scheme in the Ti-Si-Al system according to the results of this work: (**c**) $T < 1100$ °C

seems to correspond to the invariant equilibrium L + ε ↔ Si + Al (invariant point U_{11}). The temperature 601 °C then corresponds to the equilibrium L + TC ↔ ε + Si (invariant point U_{10}). So, the solidification process seems to finish with crystallization of the above binary eutectic, passing via invariant peritectic processes at 601 °C and 580 °C. This conclusion is quite compatible with the results of Zakharov et al. [1988Zak], although this is inconsistent with the conclusion of the study by Kamei et al. [1968Kam], in which the ternary eutectic is reported to be near the binary eutectic Al + Si.

The broad concentration regions on the Al-Si side of the system was not specially studied by us except for a very few Al-rich alloys. Nevertheless, the above results allow the reasonable estimate shown in the Fig. 3. This region needs additional thorough examination.

Thus, the character and coordinates of invariant four-phase equilibria with the participation of the liquid in the Ti-Si-Al system can be summarized as follows:

U_1:	L + Z + α5/4 + β5/4	~51Ti-47Si-2Al, temperature unknown;
U_2:	L + β ↔ α + Z	~49Ti-4Si-47Al, 1420 °C [1997Bul];
E:	L ↔ α + γ + Z	~48Ti-4Si-48Al, 1415 °C [1997Bul];
U_3:	L + β1/2 ↔ β1/1 + TC	composition and temperature unknown;
U_4:	L + γ ↔ ξ + Z	~33Ti-6Si-61Al, 1390 °C;
U_5:	L + ξ ↔ ε + Z	~30Ti-6.5Si-63.5Al, 1380 °C;
U_6:	L + Z ↔ ε + α5/4	~21Ti-37Si-42Al, 1356 °C;
U_7:	L + β1/2 ↔ TC + Si	composition and temperature unknown;
U_8:	L + α5/4 ↔ ε + β1/1	composition unknown, 1105 °C;
U_9:	L + β1/1 ↔ ε + TC	composition unknown, 1016 °C;
U_{10}:	L + TC ↔ ε + Si	composition unknown, 601 °C;
U_{11}:	L + ε ↔ Si + Al	composition unknown, 580 °C.

Some non-interpreted temperatures are shown in the isopleths (Fig. 4-6). Most of them, however, result from the as-cast and, thus, nonequilibrium state of the samples. The thermal effects at 940 °C and 860 °C (Fig. 6) were ascribed to α1/1↔β1/1-transformation.

Partial isothermal sections of the Ti-Si-Al system at 1270°C and 1250°C are shown in Fig. 7. Isothermal sections in the region α-Ti-$TiAl_3$-Ti_5Si_4 are similar to the solidus surface, and in the concentration region studied are characterized by three-phase triangles Z + γ + ξ, Z + ξ + ε, and Z + ε + α5/4. Compositions of Z and 5/4 phases of the region Z + ε + 5/4 at the temperature 1250 °C coincide with those at the solidus temperature (1356 °C). The ε-composition slowly shifts toward a lower Si concentration as the temperature decreases.

The lattice parameters of the Ti-Si-Al phases are sum-

marized in Table 5. The partial of reaction scheme resulting from this investigation is shown in Fig. 8.

4. Conclusions

Phase equilibria in the α-Ti-Al-Si region of the Ti-Si-Al system were studied by the methods of DTA, XRD, metallography, and EPMA. Results are given as a solidus projection, a melting diagram (solidus + liquidus), partial isothermal sections at 1270 °C and 1250 °C, three isopleths (at 5 at.% Si, 40 at.% Al, and 50 at.% Ti), and a reaction scheme. Experimental results are insufficient to make a decision concerning the existence of a TC reported in the vicinity of Ti disilicide. Two variants of equilibria are probable, either the coexistence of the TC with $TiSi_2$ or the existence of the $TiSi_2$ with a wide homogeneity range for the high-temperature modification. The equilibria at the solidus temperatures are characterized by an existence of the following three-phase fields: Ti_5Si_3 + α-Ti_5Si_4 + β-Ti_5Si_4 (1356 < t < ~1815 °C); γ + ξ + Ti_5Si_3 (1390 °C); ξ + ε + Ti_5Si_3 (1380 °C); ε + Ti_5Si_3 + α-Ti_5Si_4 (1356 °C); ε + α-Ti_5Si_4 + β-TiSi (1105 °C); ε + β-TiSi + β-$Ti(Si,Al)_2$ (1016 °C); ε + β-$Ti(Si,Al)_2$ + Si (601 °C); and ε + Si + Al (580 °C). In the case of the existence of the TC, two additional three-phase regions should be present: β-TiSi + β-$TiSi_2$ + TC; and β-$TiSi_2$ + TC + Si. The above fields result from the following invariant equilibria: L + Ti_5Si_3 + α-Ti_5Si_4 + β-Ti_5Si_4 (invariant point U_1: ~51Ti-47Si-2Al); L + γ ↔ ξ + Ti_5Si_3 (invariant point U_4: ~33.5Ti-6.5Si-60Al); L + ξ ↔ ε + Ti_5Si_3 (invariant point U_5: ~30Ti-6Si-64Al); L + Ti_5Si_3 ↔ ε + α-Ti_5Si_4 (invariant point U_6: ~21Ti-37Si-42Al); L + α-Ti_5Si_4 ↔ ε + β-TiSi (invariant point U_8: ~23Ti-41Si-36Al); L + β-TiSi ↔ ε + β-$Ti(Si,Al)_2$ (invariant point U_9: ~23Ti-43Si-34Al); L + β-$Ti(Si,Al)_2$ ↔ ε + Si (invariant point U_{10}); and L + ε ↔ + Si + Al (invariant point U_{11}). In the case of the existence of the TC compound, additional invariant equilibria L + β-$TiSi_2$ ↔ β-TiSi + TC (invariant point U_3) and L + β-$TiSi_2$ ↔ TC + Si (invariant point U_7) take place.

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